



## Research paper

# Fabrication of a selective mercury sensor based on the adsorption of cold vapor of mercury on carbon nanotubes: Determination of mercury in industrial wastewater

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## ARTICLE INFO

## Article history:

Received 28 May 2009

Received in revised form 24 August 2009

Accepted 27 August 2009

Available online 1 September 2009

## Keywords:

Carbon nanotubes

Mercury sensor

Cold vapor

Impedance

Wastewater

## ABSTRACT

A new sensor for the determination of mercury at  $\mu\text{g ml}^{-1}$  levels is proposed based on the adsorption of mercury vapor on single-walled carbon nanotubes (SWCNTs). The changes in the impedance of SWCNTs were monitored upon adsorption of mercury vapor. The adsorption behaviour of mercury on SWCNTs was compared with that on multi-walled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs). Cold vapor of mercury was generated at 65 °C using Sn(II) solution as a reducing agent. The limit of detection was 0.64  $\mu\text{g ml}^{-1}$  for Hg(II) species. The calibration curve for Hg(II) was linear from 1.0 to 30.0  $\mu\text{g ml}^{-1}$ . The relative standard deviation (RSD) of eight replicate analyses of 15  $\mu\text{g ml}^{-1}$  of Hg(II) was 2.7%. The results showed no interfering effects from many foreign species and hydride forming elements. The system was successfully applied to the determination of the mercury content of different types of wastewater samples.

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## 1. Introduction

During the last decade, there has been a great interest in the determination of mercury species. Mercury is a toxic element with low vapor pressure. Inhaling air containing mercury vapor causes deposition of this element onto the brain matrix through the blood cycle. This may cause some mental disabilities [1–3]. Wastewater is one of the most important sources of mercury. Long-term exposure to even very low levels of mercury in water is dangerous for the human health [4,5].

Several spectrometric and electrochemical methods are available for mercury determination. Different species can be separated by high-performance liquid chromatography [6–9]. The detection is performed by inductively coupled plasma (ICP) optical emission spectrometry [10,11], ICP mass spectrometry [11–14] or cold vapor atomic absorption spectroscopy (CVAAS) [15–19]. Electrochemical methods for mercury determination are usually based on the formation of the complex with appropriate ligands [20–22]. But in spectrometric methods, short analysis time, high sensitivity and selectivity of CVAAS, have caused this technique to be adopted as the method of choice for mercury determination.

Mercury has a large tendency for surface adsorption on the carbon substrates [23–28]. Compared to amorphous carbon, CNTs have some properties such as high aspect ratio (surface to the volume ratio), low density, low resistance, and high surface area for the adsorption of different species such as hydrogen [29–31]. Therefore, CNTs can be used as an appropriate sensing device for the determination of mercury based on the adsorption property of CNTs.

Many batch methods have been introduced in which Sn(II) has been used for generation of elemental mercury. Various types of gas–liquid separators [32–34] achieve the separation of mercury vapor from the liquid in continuous flow systems. The mercury vapor is transferred to the detection system by an inert gas. To achieve higher precision and accuracy as well as to decrease the analysis time, flow methods are used [35,36]. Various multi-channel segmented or continuous flow methods have been investigated. Flow methods are more suitable for large number of samples. Steady state signal is obtained when mercury vapors are circulated through the detection system.

During the last decades, mercury pollutant of the environment by mining activities [37], fuel gases from combustion sources [38], chemical trades such as battery, gauges, relays, switches, and manometer manufacturings [39], and industrial water samples such as water used in crude oil refining process [40], has resulted in worldwide contamination of large areas of industrial wastewater [40] and led to elevated atmospheric

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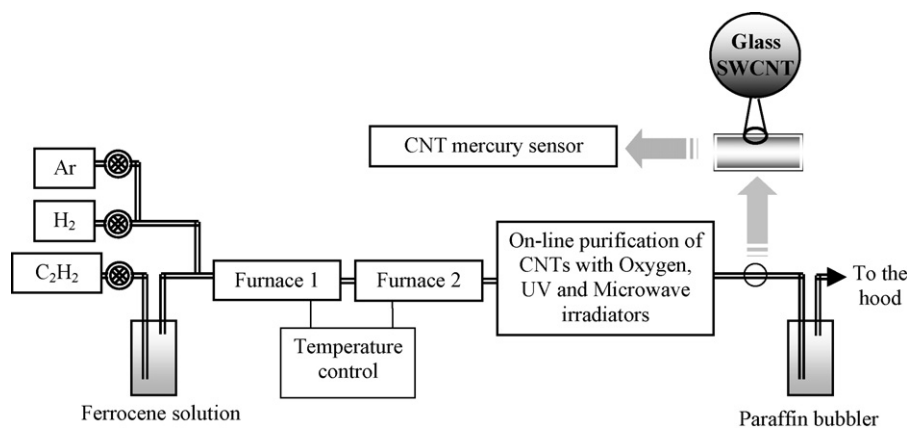


Fig. 1. Schematic diagram of the apparatus for synthesis, online purification, and direct coating of SWCNT bundles on the inner wall of glass tubing.

mercury levels [41]. Mercury-contaminated industrial wastewaters in many forms are presented at various U.S. Department of Energy (DOE) sites [42]. The amounts of mercury in these wastewaters sometimes attain several  $\mu\text{g ml}^{-1}$  levels [37–42]. This problem has led the Environmental Protection Agency (EPA) to require suitable methods for direct monitoring and rapid removal of mercury in the industrial wastewater samples [42,43].

On the other hand, because of the high sensitivity and improved detection limit of the current methods such as CVAAS and electrochemical techniques, direct determination of mercury at  $\mu\text{g ml}^{-1}$  levels is considered as a challenge [14]. Therefore, for determination of mercury in industrial wastewater, introduction of a rapid, low cost and direct monitoring system is essential.

In this work, a novel mercury sensor is introduced for rapid determination of mercury content in various types of industrial wastewater solutions, using highly purified single-walled carbon nanotubes (SWCNTs) synthesized with chemical vapor deposition (CVD) method. The sensor was used for reproducible determination of mercury at  $\mu\text{g ml}^{-1}$  levels based on recording the changes in the electrical impedance of SWCNTs upon physical adsorption of mercury vapors on SWCNTs.

## 2. Experimental

### 2.1. Reagents and solutions

Tin (Sn(II)) stock solution (0.01 M) was prepared by weighting 0.2256 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Fluka, Barcelona, Spain) and transferring to a 50 ml Erlenmeyer flask and addition of about 20 ml of distilled water. To completely dissolve Sn(II) salt, the solution was heated to about 60 °C and shaken vigorously for about 20 min and then, was left to cool to room temperature. Finally, the solution was transferred to a 100 ml volumetric flask and diluted to the mark with distilled water. The Hg(II) stock solution ( $1000 \mu\text{g ml}^{-1}$ ) was prepared by dissolving 0.1354 g of  $\text{HgCl}_2$  (99.9995%, Fluka, Barcelona, Spain) in distilled water in a 100 ml volumetric flask. Then, 1.0 ml of 0.1 M hydrochloric acid (36% purity percent, Pannaca) was added and diluted to the mark with distilled water. The fresh standard mercury solutions were prepared daily by successive dilution of Hg(II) solution.

A solution of 0.01 M sodium borohydride (Merck) was prepared by dissolving an appropriate amount of  $\text{NaBH}_4$  in distilled water. Standard solution of each interfering ion was prepared from analytical grade reagents.

To study the interference effects, individual stock solutions of some water soluble materials (Merck) including Fe(II), Fe(III), Ni(II), Cu(II), Zn(II), Cr(III), As(III), Sb(III), Se(IV), and Pb(II) were prepared in distilled water.

Gases including pure argon (99.998%) and oxygen–argon (8% O<sub>2</sub> in Ar) were purchased from “Parsbaloon Company, Iran”. Hydrogen (99.9998%) was procured from “Linde, Germany”. The carbon nanostructures including: SWCNTs (10–30 nm i.d., 99.80% pure), multi-walled carbon nanotubes (MWCNTs) (40–60 nm i.d., 99.80% pure), and carbon nanofibers (CNFs) (250–400 nm i.d., 99.80% pure) were synthesized at temperatures around 1300 °C at an inert atmosphere of argon using acetylene gas (Parsbaloon Company, Iran) as a source of carbon and ferrocene (Merck, Darmstadt, Germany) as a source of catalyst. The synthesized carbon nanostructures were then treated by on-line purification, end-opening and slow oxidation using oxygen.

### 2.2. Instrumentation

#### 2.2.1. Mercury sensor

The sensor was fabricated by coating the SWCNT bundles on the inner wall of a glass tube (3-cm long) by CVD method and on-line purification. The setup of the system is shown in Fig. 1. The production and purification line was a quartz tubing (1 cm diameter) with a total length of about 4 m. The quartz tube passed through three furnaces, an ultraviolet (UV) irradiator, and a microwave oven. Several vibrators and magnets were also attached to the line as shown in Fig. 1. The synthesized CNT bundles were regularly coated on the inner wall of a glass tube during their flow towards the end parts of CVD production line by argon as shown in Fig. 1. The preferential growth of different forms of CNTs, under controlled conditions was then successfully used for fabrication of mercury sensor. For this purpose, a CNT tubing with 3 cm length was cut and then two wires were attached to the two ends of this tubing which serve as connections to measure the resistance. This was used as mercury sensor. The detection system of the fabricated mercury sensor was based on recording the change in electrical impedance of SWCNTs upon adsorption of the generated mercury vapors.

#### 2.2.2. Procedure for synthesis and on-line purification of carbon nanostructures

Acetylene, as the source of carbon, was bubbled through a solution of ferrocene and thiophene in benzene, mixed with hydrogen and argon, and introduced to the line. The flow of all gases was automatically controlled by solenoid valves. The whole system was also controlled via computer software written in Visual Basic. The

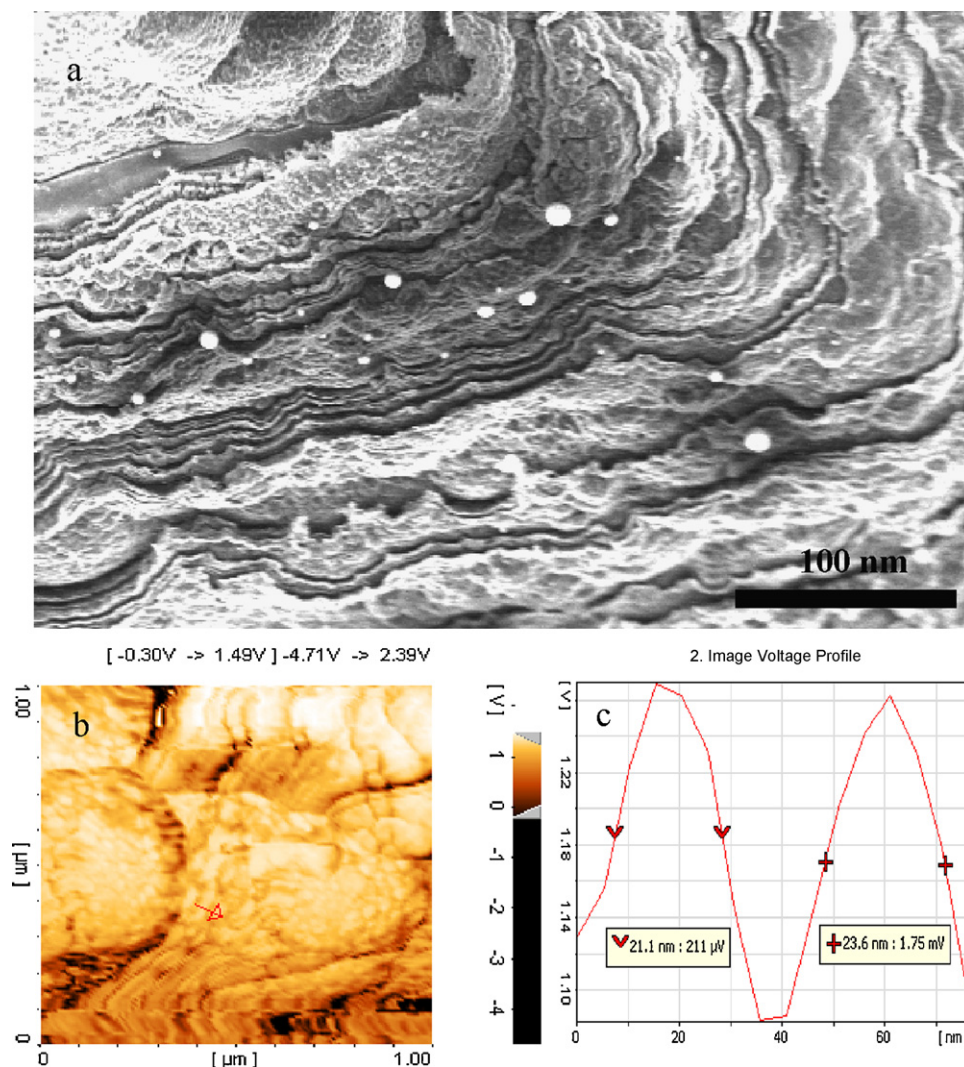


Fig. 2. Characterization of CNT mercury sensor. Images of (a) SEM, (b) AFM and (c) voltage profile of deposited SWCNTs in the fabrication of CNT mercury sensor.

software was able to control all parameters such as the temperature of the furnaces, the solenoid valves, the UV irradiator and all parameters of the microwave oven.

### 2.2.3. Instrumentation for characterization of carbon nanostructures

The synthesized CNTs were characterized using some electron microscopic techniques such as scanning electron microscopy (SEM, XL-30 FEG SEM, Philips, 20 KV), transmission electron microscopy, atomic force microscopy (AFM, DME-SPM, version 2.0.0.9), and also using some thermal and spectroscopic methods such as thermogravimetric analysis, FT-IR and Raman spectrometers, and patterned X-ray diffraction. The morphology of the SWCNT bundles coated on the inner wall of the glass tube are exhibited according to the SEM, AFM and voltage profile images shown in Fig. 2a–c, respectively.

### 2.2.4. Apparatus for mercury determination

The mercury measuring principle used here was based on (1) formation of mercury vapors under optimized conditions via reduction of Hg(II) by Sn(II), (2) separation of mercury vapors from aqueous solution using ultrasonic and nitrogen as carrier gas, (3) circulation of mercury vapors through the SWCNTs using a circulation pump, (4) physical adsorption of mercury on SWCNTs, and

monitoring the changes in the electrical resistance of SWCNTs during the adsorption process.

The setup of the system used to generate and detect the mercury vapors is shown in Fig. 3. It consists of a straight 15-cm glass tube (i.d. 1.8 cm) as the reaction cell that was fixed on an ultrasonic vibrator. The reaction cell was heated using a furnace around it. The temperature of the cell was controlled using a Ni–Cr thermocouple and a laboratory designed electronic circuit.

The reaction cell was connected to a glass-T-connector. The end part of the T-connector was connected to the injection port and a septum for the introduction of the mercury sample by a syringe. The side-arm of the glass-T was connected to CNT mercury sensor. A small hole was also drilled in the T-connector and a piece of Teflon tubing was inserted into the reaction cell through this hole. This tubing was used for the introduction of the carrier gas. Two valves (three-way) were also positioned at both sides of the CNT mercury sensor. The valves were connected to each other through a circulation pump. In order to collect the mercury vapors, a flask containing 0.5 M nitric acid was also placed at the end of the line. The residual mercury exhausts were then directed towards the hood through silicone tubing.

To measure the resistance, the sensor was placed in the feedback circuit of an operational amplifier. The output signal was digitized by an analog to digital converter (ADC). The output of the

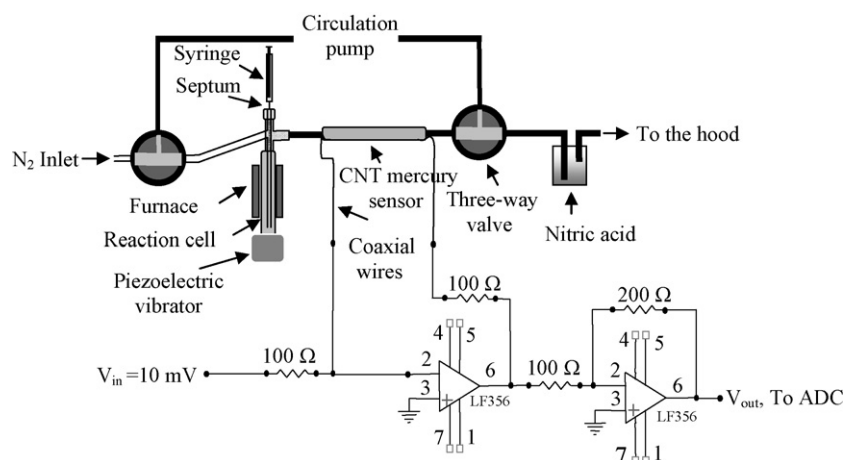


Fig. 3. Schematic diagram of the apparatus for mercury determination.

converter was transferred to a computer. The data were analyzed and plotted by a program written in visual basic.

#### 2.2.5. Procedure for mercury determination

To the reaction cell was added 5.0 ml of 1.0 mM  $\text{SnCl}_2$  and the cell was heated to  $65^\circ\text{C}$ . Nitrogen flow rate was  $2.0\text{ ml min}^{-1}$ . The rotational speed of the circulation pump was set to around  $200 \pm 2\text{ rpm}$ . After about 5 min, the system was changed to a closed circuit by proper positioning of the three-way valves shown in Fig. 3. Then 1.0 ml of Hg(II) sample solution was introduced by a syringe through a septum. After about 20 s from the introduction of Hg(II) sample, the mode of the valves was changed to get a steady state signal.

After each mercury analysis, in order to desorb the mercury vapors, the CNT sensor was heated to about  $100^\circ\text{C}$  while purging nitrogen with  $20\text{ ml min}^{-1}$  flow rate for about 15 min, under a hood.

#### 2.3. Real sample pretreatment and preservation

To detect the mercury contents of industrial wastewater solutions, the samples were preserved by acidification with nitric acid to pH 2 or lower immediately at the time of collection [43].

For mercury determination, 5.0 ml of each type of wastewater was transferred to a 10 ml volumetric flask. Then 1.0 ml of potassium permanganate (0.01 M) was added to eliminate the possible interferences of sulfide and chloride [43]. Care must be taken to assure that free chlorine is absent before mercury is reduced and swept into the detection system [43]. This may also be accomplished using an excess of hydroxylamine sulfate reagents (2 ml) [43]. The solution was then diluted to the mark. The quantities of Hg(II) in wastewater samples were then determined by standard addition method. The real samples were finally analyzed as suggested by the recommended procedure.

### 3. Results and discussion

#### 3.1. Optimization of the operating parameters

Several parameters were optimized to attain the highest sensitivity for mercury determination. The parameters having influence on the sensitivity of the formation of cold vapor of mercury are: the type of CNTs used in the sensor, the thickness of coated CNTs, length of the CNT coated glass sensor, concentration of Sn(II), the reaction temperature, the effects of circulation pump and ultrasonic vibrator.

Different forms of the synthesized carbon nanomaterials such as SWCNTs, MWCNTs and CNFs were tested to attain the maximum efficiency in the CNT mercury sensor. The results showed that, the mercury sensor based on the SWCNT bundles had more active surface area for the adsorption of mercury vapor. Also, the sensor had lower background resistance, more improved detection limit and higher saturation limit that made it suitable for the quantitative analysis of mercury. The results are reported in Table 1.

The temperature of the reaction cell was adjusted to attain the maximum sensitivity. The maximum sensitivity was observed from  $60^\circ\text{C}$ . At temperatures above  $70^\circ\text{C}$ , a decrease in sensitivity was observed due to the formation of large amounts of water vapor. Thus,  $65^\circ\text{C}$  was selected as the optimum temperature. Higher temperatures were avoided in order to prevent the adsorption of water vapor onto the CNT sensor.

The effect of the nitrogen flow rate for purging the reagents in order to carry the mercury vapors was investigated. At nitrogen flow rates above  $2.5\text{ ml min}^{-1}$ , large amounts of water aerosols were transferred towards the CNT mercury sensor and were adsorbed onto the CNTs. This affects the sensitivity and reproducibility of the sensor. The optimum nitrogen flow rate was  $2.0\text{ ml min}^{-1}$  for Hg(II) determination. At higher nitrogen flow rates, the mercury vapors have less chance of deposition on CNTs, causing loss of precision.

Table 1

Comparison between the effects of different forms of carbon nanomaterials in fabrication of mercury sensor.<sup>a</sup>

Substrate <sup>b</sup>	$V_{\text{background}}^c$ (V)	$V_{\text{out}}^d$ (V)	Detection limit ( $\mu\text{g ml}^{-1}$ )	Saturation limit ( $\mu\text{g ml}^{-1}$ )
SWCNTs	0.0082	0.1911	0.64	95
MWCNTs	0.0132	0.1851	0.72	80
CNFs	0.0197	0.1809	0.79	50

<sup>a</sup> The lengths of all mercury sensors were 3.0 cm.

<sup>b</sup> Equal amounts of carbon nanomaterials were used for fabrication of different forms of mercury sensor.

<sup>c</sup> The output voltage of the electronic circuit before introduction of mercury.

<sup>d</sup> The output voltage of the electronic circuit after injection of  $15\text{ }\mu\text{g ml}^{-1}$  of Hg(II).

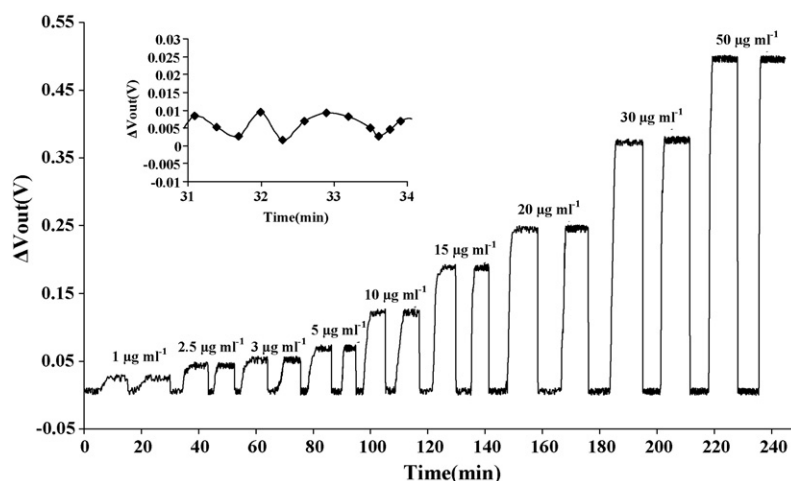


Fig. 4. Trace of Hg(II) standard solutions from 1.0 to 30.0  $\mu\text{g ml}^{-1}$ , and the steady baseline signal (inset).

To have CNT mercury sensor with maximum mechanical stability of coated CNTs on the inner wall of the glass tube against the flow of nitrogen and mercury vapors, the thickness of CNT sensor was optimized. The thickness of the CNTs is usually controlled by controlling the duration time of the deposition of highly purified activated CNTs inside the glass tubing in the CVD instrumentation system. In this study, the maximum thickness for SWCNTs was around 230  $\mu\text{m}$ . This was estimated according to the active surface area of the SWCNTs. The results reveal that, at thicknesses smaller than  $\sim 200 \mu\text{m}$ , the capacity of the coated SWCNTs were so small, that noisy signals were obtained due to the rapid saturation of SWCNTs from mercury vapor. Also, at thicknesses higher than  $\sim 250 \mu\text{m}$ , the SWCNT bundles were not well coated on the inner wall of the glass tubing. Also, accumulation of high-density metallic CNTs in the sensor led to loss of sensitivity.

To attain maximum sensitivity, the length of CNT sensor was optimized. The optimum length was 3.0 cm. At lengths lower than 2.8 cm, the signals were low, probably due to the rapid saturation of CNTs from mercury vapors. At lengths longer than 3.1 cm, the impedance of the CNT mercury sensor was so high that loss of sensitivity occurred.

Sodium borohydride and tin chloride are considered as the best reductants for cold vapor production of mercury [44]. In this study, both  $\text{NaBH}_4$  and  $\text{SnCl}_2$  had similar effects in the formation of elemental mercury and thus,  $\text{SnCl}_2$  was used as the reductant. Different concentrations of  $\text{SnCl}_2$  were tested. 1.0 mM of  $\text{SnCl}_2$  was selected as the optimum concentration of Sn(II) needed. For about 5.0 ml of 1.0 mM Sn(II), three injections of 1.0 ml mercury solution are possible. However, if a high precision is demanded, it is recommended to use fresh reducing agent for each injection.

To achieve more sensitivity as well as to reduce the analysis time, the solution was sonicated during the formation of mercury vapors. Ultrasonic radiation has kinetic effect on the formation of elemental mercury during the reduction of Hg(II) with Sn(II) solution [45]. It also affects the gas–liquid separation of mercury [46]. There is also no doubt that the container materials inside the reaction cell can affect the elemental mercury species loss by different adsorption mechanisms [47]. Therefore, ultrasonic treatment of the mercury sample container prior to the determination of total Hg is likely to increase the recovery [47].

To adsorb maximum amounts of mercury species on the CNT mercury sensor and to attain the highest sensitive signal, a circulation pump was used to circulate the mercury vapors. A more sensitive steady state signal was obtained when a circulation pump was used. In this experiment, the circulation was performed for about 20 min after injection of each mercury sample.

At least 10 successive injections of mercury samples can be done on a single CNT mercury sensor. However, after each mercury injection, it is better to desorb the adsorbed mercury from the CNT mercury sensor. Heating the sensor to about 100  $^\circ\text{C}$ , while purging with a nitrogen flow rate of 20  $\text{ml min}^{-1}$  for about 15 min, removes the elemental mercury from CNT mercury sensor. The results revealed that, the CNT mercury sensor was stable after at least one-year use for mercury determination.

### 3.2. Analytical figures of merit

In the electronic circuit, the CNT sensor was used as the feedback of an operational amplifier as shown in Fig. 3. To follow the changes in the resistance of the CNT mercury sensor ( $R_{\text{CNT}}$ ), a regulated DC voltage (10.0 mV) as input voltage ( $V_{\text{in}}$ ) was applied. The output voltage of the preamplifier was then electronically amplified using a second operational amplifier. The output voltage ( $V_{\text{out}}$ ) of the electronic circuit is related to  $R_{\text{CNT}}$  [48]. Therefore, the changes in  $R_{\text{CNT}}$  are calculated according to the gains of the operational amplifier used in electronic circuit of the CNT mercury sensor [48].

The calibration curve for Hg(II) solutions was linear from 1.0 to 30  $\mu\text{g ml}^{-1}$ . The trace of signals for different concentrations of Hg(II) standard solutions is illustrated in Fig. 4. Good reproducibility (2.7% relative standard deviation, RSD) was obtained for eight replicate analyses of 15  $\mu\text{g ml}^{-1}$  of Hg(II). The regression equation and the correlation coefficient are illustrated in Table 2. Volume of mercury sample injected for each analysis was 1.0 ml.

The detection limit was defined as the concentration of mercury giving a signal equal to triple value of the standard deviation of the blank plus blank signal. The trace of blank signal is shown in Fig. 4(inset). The limit of detection was found as 0.64  $\mu\text{g ml}^{-1}$  (0.64  $\mu\text{g}$  of mercury per 1.0 ml of real sample).

The CNT sensor for gas sensing is evaluated by sensitivity and response time [49]. Sensitivity is defined by the percentage of the maximum change in the output response of the CNT mercury sensor for a solution with a fixed concentration of mercury according to

**Table 2**  
Analytical figures of merit for mercury determination.

Linear range ( $\mu\text{g ml}^{-1}$ )	Regression equation <sup>a</sup>	Correlation coefficient ( <i>R</i> )
1.0–30.0	$V = 1.15E - 2 \times C + 0.0085$	0.9994

<sup>a</sup> *V* is the output response of the operational amplifiers and *C* is the mercury concentration ( $\mu\text{g ml}^{-1}$ ).

the following equation:

$$\text{Sensitivity} = \frac{V_{\text{out}} - V_0}{V_0} \times 100\% \quad (1)$$

where  $V_0$  is the response of the CNT mercury sensor exposed to nitrogen only and  $V_{\text{out}}$  represents the highest response after exposure to a gas containing mercury vapor [50]. Also, the sensitivity of the CNT mercury sensor depended on the density of SWCNTs (i.e. the thickness of SWCNT film). The device with thicker SWCNT film shows lower sensitivity. It has been reported that, the morphology of the SWCNTs also significantly affects the performance of the resulting sensor. It has been reported [50] that, the sensors fabricated with high-density SWCNT network, exhibited much lower sensitivities than the sensors fabricated with moderate-density SWCNT network.

The response time of the sensor,  $\tau$ , is defined as the time required for the sensor to attain  $e^{-1}$  (i.e.  $\sim 36.8\%$ ) of the maximum output response change after the CNT mercury sensor is exposed to a given gas [50]. In this study, two different response times were observed for the fabricated CNT mercury sensor for low and high concentrations of mercury (Fig. 5a). The CNT mercury sensor had also short response times. The response time ( $1/\tau$ ), which was proportional to the adsorption rate, had a linear correlation to the concentration of mercury (Fig. 5b).

### 3.3. Interferences

The procedures reported so far for mercury determination using CVAAS technique, have shown interferences from diverse species that influence the determination of mercury to various degrees [44]. Interference effects of metal ions may occur by a number of mechanisms, including consumption of reducing agent, and/or formation of metals with a zero oxidation state. The interfering effects of different metals were investigated. Several metal ions are reduced by Sn(II). In this experiment, the concentration of Sn(II) is high enough to compensate for consumption by some metal ions. The results show that, 1000 fold excess of Fe(II), Fe(III), Ni(II), Cu(II), Zn(II), Cr(III) and 500 folds of hydride forming elements such as As(III), Sb(III), Se(IV) and Pb(II) had no interfering effect in the analysis of  $15.0 \mu\text{g ml}^{-1}$  of mercury solution. This is due to the lack of generation of hydride species, especially in the presence of Sn(II). Also excess amounts of volatile organic species such as toluene had no interfering effect on mercury determination. Therefore, selectivity, simplicity, portability and very low cost make this sensor suitable for facile determination of the mercury content of industrial wastewater samples.

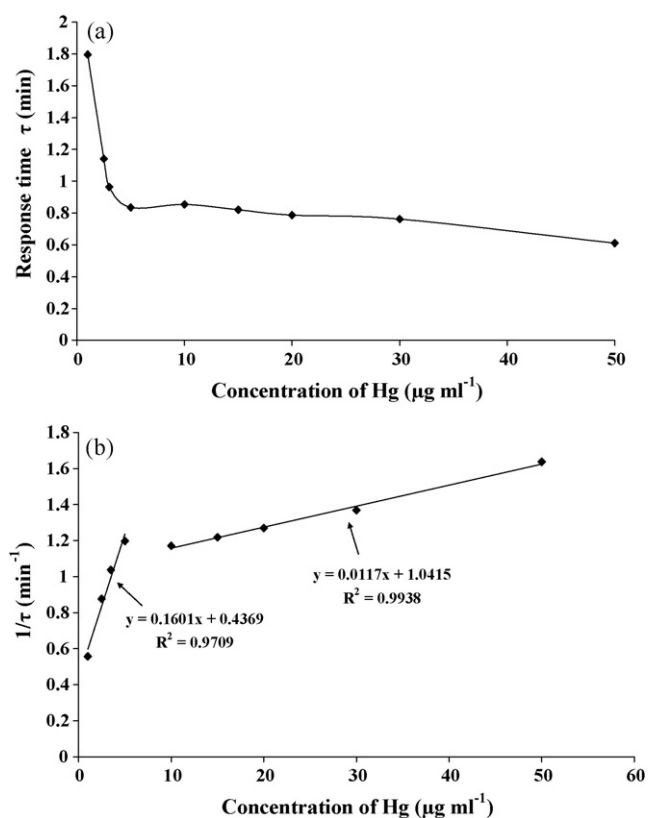


Fig. 5. Evaluation of the performance of the CNT mercury sensor. Plots (a and b): response times as a function of the mercury concentration.

### 3.4. Real sample analysis

The reliability of the method was evaluated by determining mercury content of different kinds of industrial wastewater samples. Standard addition method was used to fix the matrix effect of the standard solution with real samples via addition of the same volume of different concentrations of Hg(II) standard solution to the fixed volumes of wastewater samples and finally equal dilution for the solutions. To validate the proposed analytical approach, a recovery test was performed. Known amounts of Hg(II) were spiked into different samples and the percentage recovery of each species was calculated. The analysis showed very satisfactory results (Table 3).

**Table 3**  
Recovery of spiked mercury in industrial wastewater samples.

Real sample <sup>a</sup>	Mercury added ( $\mu\text{g ml}^{-1}$ )	Mercury found ( $\mu\text{g ml}^{-1}$ )	Recovery (%)
Wastewater 1 (petroleum industry)	0	3.74	98.7
	15.00	18.55	
Wastewater 2 (Cr electroplating)	0	5.18	99.3
	15.00	20.07	
Wastewater 3 (crude oil refining)	0	2.51	99.7
	15.00	17.46	
Wastewater 4 (paper industry before air treatment)	0	9.49	100.2
	15.00	24.52	
Wastewater 4 (paper industry after air treatment)	0	1.83	99.9
	15.00	16.81	
Wastewater 5 (resin industry)	0	3.09	100.1
	15.00	18.11	

<sup>a</sup> The sources of industrial wastewater were reported in parenthesis.

**Table 4**

Comparisons between the proposed method and cold vapor atomic absorption spectrometry for mercury determination.

Parameters	Proposed method	Cold vapor atomic absorption spectrometry
Instrumental components needed	Heated cell, two valves, connectors, circulation pump, ultrasonic vibrator	Gas-liquid separator, several valves, mixing chamber, multi-channel peristaltic pump [44,49]
Volume of mercury sample injected	1.0 ml	Few ml [51]
Interferences	No interference	Cu(II), Co(II), Ni(II) [44]

#### 4. Conclusions

Table 4 shows a comparison between the proposed method and CVAAS method. This table shows the advantages such as simplicity and freedom from interferences for the fabricated CNT mercury sensor. Although, the sensitivity of the proposed method is lower than that of CVAAS technique, considering the high selectivity of the method, simplicity of the setup and low consumption of the reagents and samples, the present method is beneficial.

#### Acknowledgements

The authors wish to acknowledge the support of this work by the office of Fars governor, Iran, the Third World Academy of Sciences, Iran Chapter (TAWASAC) and Shiraz University Research Council.

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