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Original Article

Optimization of a Novel Setup for an On-Line Study of Elemental Mercury Adsorption by Cold-Vapor Atomic Absorption Spectrometry

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ARTICLE INFORMATION

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ABSTRACT

Background: The objective of this work was developing a simple and stable time-based on-line setup for assessing the potential of mercury (Hg) vapor adsorption of the commercial sorbents used in air sampling and control operation followed by cold vapor atomic absorption spectrometry (CVAAS).

Methods: A special designed separation chamber was used where reduction of the injected Hg (II) solution took place. Purge gas passes through this chamber resulting to a prompt release of mercury vapor, purging into the adsorbent that regulated at the desired adsorption temperature. After sorbent saturation, in order to study the adsorption parameters of sorbents (activated carbon and bone char) such as breakthrough time (BTT), and adsorptive capacity, mercury gas stream was passed through the sorbents, directly transport to the CVAAS.

Results: Preliminary experiments concerning the reductant solution showed that $SnCl_2$ offers higher stability than $NaBH_4$. Around the loading range 0.125-2.5 ml min^{-1} of 100 µg l^{-1} Hg(II) solution, a linear calibration curve with the equation peak area=0.134; loading flow=-0.017 and a correlation coefficient r=0.996 was obtained, and the detection limit was improved up to c_L=1µg l^{-1}. The relative standard deviation of five measurements of lowest flow loading of Hg (II) was RSD=2.8%. The significant differences were observed in the breakthrough time and mercury adsorptive capacity between activated carbon and bone char (*P*=0.010).

Conclusion: This novel setup is suitable for an on-line study of elemental mercury adsorption, determination of breakthrough time and adsorption capacity, and because of its stable performance during all experiments; it can be applied to the time based studies.

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Introduction

Mercury and its compounds are recognized as potentially hazardous materials and are rated as the main category of environmental and occupational pollutants. Global emissions of mercury to the atmosphere have increased 3 times during the recently century year, due to primarily anthropogenic releases, associated with fossil fuel burning and waste incineration[1,2]. Mercury exists in several physical states and chemical forms depending on temperature and pressure. Because of its propensity to undergo biological interaction, mercury generally undergoes complex and difficult-to-predict changes in its concentration levels and chemical forms. As point of physical view, mercury species in the air, in the form of gaseous are more than particulate components. Mercury has been grouped into three categories: (1) elemental mercury; (2) inorganic mercury; and, (3) organic mercury[3,4].

Adsorption in solid materials is a process that offers great potential for achieving high quality air, with respect to mercury emissions, because of the most of existing air pollution control technologies, such as electrostatic precipitators and bag houses, cannot remove effectively the gas phase mercury emissions, except for the particle-bound mercury atoms[5-7].

Cold vapor atomic absorption spectrometry (CVAAS) is recognized as a routine procedure for mercury determination in various fields, due to the advantages of efficient matrix separation, high analyte transport efficiency, high selectivity, simple instrumentation and ease of automation[8]. There are two different ways for

producing constant mercury vapor concentration in a gas stream: Application of permeable membranes and evaporating the liquid mercury, while each method has its advantages and limitations. Continuous flow (CF) or flow injection (FI) and recently sequential injection (SI) systems can overcome the existing draw backs because they offer automated handling of sample, improved precision, drastic diminishing of reagents and sample consumption and increased sampling frequency[9-13].

Although mercury in metallic form has a considerable vapor pressure (0.0016 mbar at 20 °C corresponding to a concentration of ca. 14 mgm^{-3} in air), always needs to be separated efficiently from the liquid phase, in order to ensure that Hg^0 is transferred to the atomic absorption cell and consequently to improve the sensitivity. This is achieved by the gas–liquid separator device. Generally, there are three approaches for the separation of the gaseous phase: (a) hydrostatic (U-type), (b) with forced outlet, (c) micro porous poly-tetra-fluoro-ethylene (PTFE) membrane. In batch CVAAS methods, the Gas Liquid Separator (GLS) is employed also as reaction chamber for mercury reduction. On the other hand, various GLS configurations for on-line systems have been presented in the literature, in order to increase peak height of the transient signal[14,-15].

The objective of this work was developing a simple and stable time-based on-line setup for assessing the potential of mercury vapor adsorption of the commercial sorbents used in air sampling and control operation followed by CVAAS. The proposed setup involves a new separation chamber, which in parallel operates as reactor. This was tested by activated carbon and bone char in order to determine the breakthrough and total capacity of this sorbent.

Methods

Reagents

Ultrapure water (TKA; Smart 2 Pure; Germany) was used. All chemicals including $HgCl_2$, $SnCl_2 \cdot 2H_2O$, $NaBH_4$, NaOH, 65%w/w HNO_3, and 37%w/w HCl were analytical-reagent grade provided from Merck, Darmstadt, Germany. Argon (Ar) and N_2 gases were research grade and supplied from Roham, Tehran, Iran which used as the purge gas. A stock solution (1000 mg l^{-1}) of Hg (II) was prepared by dissolution of mercury chloride salt. The mercury stock solution was stored at 4°C prior to use. Working standard solutions of Hg (II) were prepared by appropriate stepwise dilution of stock standard solution in 0.5 mol l^{-1} HNO_3 to the required levels just before use. The reducing agents ($SnCl_2$ in 0.6 mol l^{-1} HCl or $NaBH_4$ in 0.1 mol l^{-1} NaOH) was prepared fresh daily. The reductant solutions were purified from possible traces of elemental mercury by 30 min degassing with argon prior to use.

Instrumentation

An atomic absorption spectrometer model Analyst 700 Perkin Elmer (Precisely) equipped with quartz cell. An Hg hollow cathode lamp (Lumina™ Perkin Elmer) was used as the radiation source. Peak absorbance of the transient signal was chosen for quantification. Instrumental parameters were set up as follows: lamp intensity: 6 mA; wavelength: 253.7 nm; spectral band pass: 0.7 nm; quartz cell temperature: 25 °C; and measurement mode: peak height.

The proposed setup was consisted of two peristaltic pumps (JMS model SP-510 and JAZ-1800) and adjustable valves. The whole system was controlled via WinLab32™ software. A silicon tube (4.9 mm i.d.) was used for separation chamber and CVAAS connection, in order to keep the dead volume of the system at minimum level and thus the vapor dispersion at lower level. Ar gas was used for the mercury vapor release from liquid mixture. The separation chamber was constructed of a cylindrical polyethylene container (164.3 mm length, 72.7 mm i.d.) and the push-fit connections made of poly-tetra-fluoro-ethylene. The channels in upper cell managed two tubes (4.9 mm i.d.) made of silicon, one tube for the inlet purge gas and another for outlet mixture (Hg^0 + Ar). The channels in lower cell managed two parallel outlets, one for $HgCl_2$ solution and the other for reducing agent. The above system is shown schematically in Figure 1.
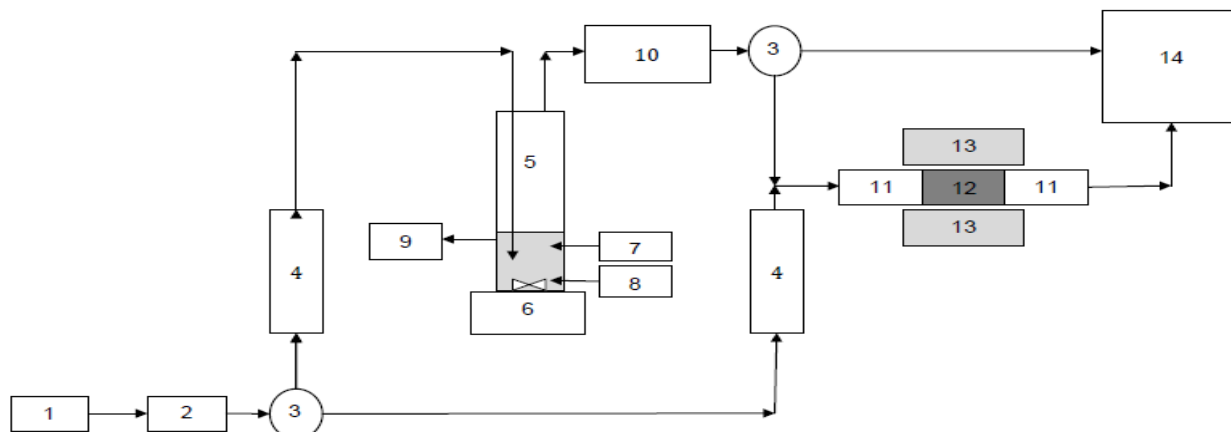
Figure 1: The schematic of a novel setup used for testing the elemental mercury adsorption. (1) Purge gas, (2) Dryer (3) Adjusted valve (4) Flow meter (5) Separation chamber (6) Stirrer (7) Hg (II) peristaltic pump (8) Reductant peristaltic pump (9) Waste (10) Temperature controller (11) Quartz tube (12) Sorbent (13) Oven (14) CVAAS

Procedure

Mercury vapor generation; the proposed mercury vapor generator unit was based on reduction of Hg (II)solution and bubbling purge gas through on it (Figure 1). The efficiency of mercury reduction and discharging of it was checked by pumping the Hg (II) and reducing agents ($SnCl_2$ or $NaBH_4$) into the separation chamber for long and short period. $HgCl_2$ solution and reducing agent were loaded sequentially to the container by activating peristaltic pumps. The reduction of Hg (II) causes mercury drift that it provides a well detectable mercury concentration in the gas stream. The reducing agent and $HgCl_2$ solution continuously stirred by using a magnetic stirrer in order to assure better mixing and sufficient reduction time. Ar passes through separation chamber resulting to a prompt release and transportation of mercury vapor to the CVAAS (Figure 1). The peak height of the absorbance signal that was proportional to mercury vapor concentration in the solution was used for all measurements. Each instance repeated three times in all cases, and repeatability was shown with relative standard deviation (RSD %).

Mercury adsorption experiments were conducted by two type sorbents, activated carbon made of coconut charcoal and bone char. The mass and mesh of sorbents were 150 mg and 20/40, respectively. The reactor adsorber was a quartz tube (185.6 mm in length with an outer diameter of 7.9 mm and inner diameter of 4.9 mm) that held in a vertical position. The variety of adsorption units was described with more details by Skodras et al.[16]. Quartz has good chemical resistance and is inert to elemental mercury. A furnace equipped with temperature controller was employed to keep the adsorbent reactor bed at a desired temperature. When the thermal stability was provided, the pure Ar was directed to the empty reactor. Then the mercury vapor generator unit that was considered to generate the desired mercury concentration was placed in line. At the same time, the reactor outlet was absorbed into the absorbent that was set the desired adsorption temperature, and then determined the Hg^0 concentration by CVAAS (Figure 1). In order to study of adsorption parameters such as breakthrough time (BTT), and adsorptive capacity, the experiment was performed by using of 100 µg l^{-1} Hg (II) solution in both loading flow 1.25 and 2.5 ml min^{-1}. The purge gas stream and the adsorption temperature were adjusted at 200 ml min^{-1} and 50 °C respectively.

It should be noted that the mercury vapor released from the reaction vessel discharge of the lab by the efficient ventilation system and wastes disposal after finishing the experiment managed in an appropriate and approved waste disposal facility.

Results

Optimization of proposed system parameters

The optimization of the system parameters was preceded under the above procedure (Figure 1), using of Hg (II) standard solution in the concentration range on 10-1000 µg l^{-1} and loading flow rate in the range on 0.1-5 ml min^{-1} respectively. The results were indicated that the flow rate and concentrations of mercury influenced the peak height. The optimization of system performance data are presented in Table 1. A linear calibration curve was obtained in the concentration on 100 µg l^{-1} and the loading range of 0.125-2.5 ml min^{-1} of Hg (II) with the equation p=0.134L-0.017 (p, peak area; L, loading flow) and a correlation coefficient r=0.996, and the detection limit up to c_L= 1µg l^{-1} was improved (Figure 2). The relative standard deviation of five measurements of the lowest loading of Hg (II) was RSD=2.8%.

Table 1: The optimization of setup performance data

Setup performance data	Optimized value
Hg (II) conc. (µg l^{-1})	100
Hg (II) loading (ml min^{-1})	0.125-2.5
Reducing agent ($SnCl_2$) conc.	2.5% m/v in HCl
$SnCl_2$ loading (ml min^{-1})	0.025-0.125
Purge gas (Ar) flow rate (ml min^{-1})	200
Regression equation ([HgII] in µg l^{-1})	p=0.134L-0.017 L=Hg(II) loading flow
Correlation coefficient	r=0.996
LOD (µg l^{-1})	cL=1
Precision (R.S.D., n = 5; (0.125 µg l^{-1}) (%)	2.8

The effect of reducing agent concentration on the generation of mercury vapor was studied from 1 to5% (w/v). The results clearly indicated that as the reducing agent concentration increased; signal intensity of mercury significantly increased and reached to a maximum when the $SnCl_2$ and $NaBH_4$ concentrations were 2.5% and 1% respectively (Figure 3). Furthermore, the effect of the reducing agent flow rate on the mercury vapor generation was also tested from 0.01 to 5 ml min^{-1} keeping the concentration of the reducing agents at above values. That is, considering the sensitivity and the consumption of Hg (II) solution, the $SnCl_2$ and $NaBH_4$ flow rates were optimized in the ranges of 0.025–0.125 and 0.01–0.1 ml min^{-1} respectively keeping mercury concentration and flow rate at 100 µg l^{-1} and 1 ml min^{-1}. The results from preliminary experiments concerning the reducing agent showed that $SnCl_2$ offers higher stability than $NaBH_4$. When 1% $NaBH_4$ was used it was observed that reproducibility reduced, despite the signal intensity increased. In addition, the peak height of mercury decreased when $NaBH_4$ concentration was increased further to 3%. Thus, $SnCl_2$ solution 2.5% (W/V) was selected as adaptable concentration of the reductant in all the subsequent experiments. In all cases, the solution was prepared in basic media (HCl 0.6 mol l^{-1}), in order to stabilize this reagent. The optimal concentration and flow rate ranges of mercury and $SnCl_2$ solutions were used throughout.
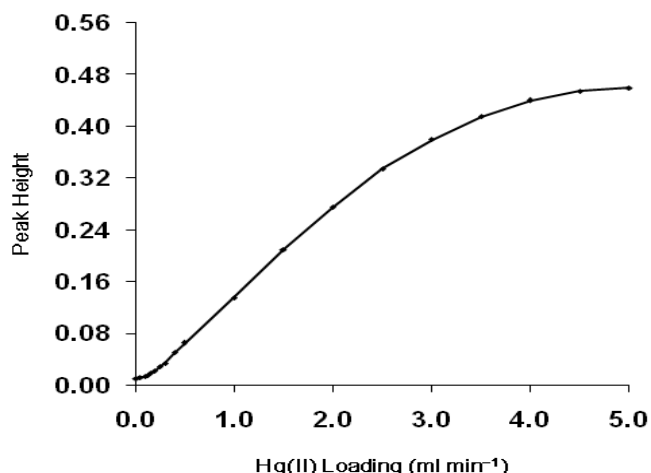
Figure 2: Calibration curve of Hg vapor production and loading range of Hg (II); 100 µg l⁻¹Hg(II)initial concentration, 200 ml min⁻¹ Ar flow rate
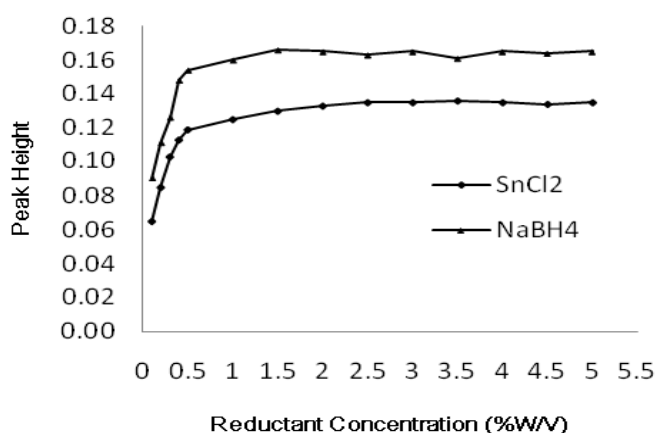
Figure 3: Effect of reducing agents concentration on peak area; 100 µg l⁻¹Hg (II) initial concentration, 1ml min⁻¹ Hg (II)flow rate

To check the influence of purge gas type and flow rate on peak height was tested within the range of 100-600 ml min⁻¹keeping the concentration and flow rate of Hg (II) and SnCl₂ solution at optimized values. The obtained results were shown that the peak height was increased by increasing of the flow rate, up to 200 ml min⁻¹ and over this value, it would be decreased. In addition, by increasing the purge gas flow rate higher than 400 ml min⁻¹the peak height was significantly decreased. Thus for all subsequent experiments 200 ml min⁻¹argon flow rate was used.

The results indicate a significant relationship between the stirring of separation chamber and peak height (P=0.010), this relationship especially was more when the air was used as purge gas. The relationship between type of purge gas (Ar, N₂ or Air) and the peak height at the optimized experimental conditions was not significant. Furthermore, at these conditions, the relationship between quartz cell types (open or closed) and the peak height was not significant.

Using of novel setup for the determination of mercury adsorption

This experiment was performed by using initial concentration at 100 µg l⁻¹ in both loading flow 1.25 and 2.5 ml min⁻¹. The mercury breakthrough curves, during 90 min adsorption experiment were determined by using of continuous collected data. Then the total adsorptive capacity of sorbents was calculated by comparison of the shapes and the bases of these curves. As shown in Table 2in above loading flows, the obtained breakpoints from activated carbon were 45 and 12 min and from bone char were 6 and 1 min. As observed in Figure 4, the breakthrough curves of activated carbon followed a much more efficient profile than in bone char. Thus, for activated carbon, the mercury adsorbed quantity was higher than bone char. The significant differences were observed in the breakthrough time and mercury adsorptive capacity between activated carbon and bone char (P=0.010).

Table 2: Compression of breakpoints from activated carbon and bone char

Sorbent	Breakpoint (min)	Hg⁰ adsorptive capacity at breakpoint (ng/mg)	Total breakthrough (min)	Hg⁰ adsorptive capacity (ng/mg)
With 1.25 (ml min⁻¹) Hg⁰flow rate				
Activated carbon	40	33.3	87	72.5
Bone char	6	5.0	37	30.8
With 2.5 (ml min⁻¹) Hg⁰flow rate				
Activated carbon	12	20.0	44	73.3
Bone char	1	1.7	26	43.3

90 min adsorption experiment, 100 µg l⁻¹Hg(II)initial concentration, 50⁰C adsorption temperature, 200 ml min⁻¹ Ar flow rate.

Discussion

The simultaneous investigation of loading flow rate and concentration of Hg (II) solution, the type and loading flow rate of reducing agents (SnCl₂ orNaBH₄), the type and flow rate of purge gases (Ar, N₂ or Air), the type of quartz cell used (open or closed), and stirring of the separation chamber during vapor generation, which has been less attention in literature, were the unique properties of this study.

As it is shown in Figure 2, by increasing the flow rate of Hg (II) solution up to 2.5 ml min⁻¹, the absorbance of the fixed amount of Hg almost linear increased and then out of linear mode, shown that larger concentration make Hg⁰ release more difficult. Thus, according to the initial mercury concentration (100 µg l⁻¹), the use of proposed system was a linear range between0.125-2.5 ml min⁻¹ and had good sensitivity (Table 1).The effect of mercury solvent volume on the sensitivity of the sequential injection system measured in put has been studied in other researches [9,12,17]. The study of Anthemidis et

al.(2004) established that, despite larger sample volumes offer increased overall sensitivity, with developing a sequential injection system for trace mercury determination by CVAAS[9]. This is close to the results of the present study.

On the other hand, the vapor generation initiates into the separation chamber, which functions also as reaction chamber. Thus, in present system, it is more convenient and less time consuming, to load mercury and the reducing agents directly into the separation chamber, especially when large volumes are used. Consequently, the liberated mercury vapor can be delivered with the lower dispersion into the absorption cell. Based on these considerations, in the proposed system, in order to start the reaction with Hg (II) solution loading the reductant solution excess there was already inside the chamber (Figure 1).The efficiency of Hg reduction and purging was checked by pumping the Hg (II) for long and short period into the reaction vessel containing Sn (II) ions. After stopping the pump which delivers the mercury solution, the signal decrease since mercury free gas passes through the system. The difference of the tendency decreasing of the signal gives information about the accumulation of the mercury in the generator. Since a marginal difference found, it can be stated that, all of the delivered Hg (II) has been changed to mercury vapor.

As it has been reported in the literature, the concentration and flow rate of the reductant are critical in optimizing the mercury signal in CVAAS [13,14]. In the present study peak height of the Hg^0 as a function of the concentration and flow rate of both $SnCl_2$ and $NaBH_4$ were obtained, keeping mercury concentration and flow rate at 100 µg l^{-1} and 1 ml min^{-1}. As it is shown in Figure 3, low reductant concentration results in incomplete vapor generation of Hg^0. As the $SnCl_2$ and $NaBH_4$ concentration increased up to 2.5% and 1% respectively, all of in organic mercury was reducedto Hg^0. This difference may be attributed to the variation of the vapor generating efficiency of the reducing agents, which other studies have referred to in[12]. Also, it was observed that reproducibility was decreased. Balarama Krishna et al. (2010), in study with the aim of speciation of inorganic and methyl mercury showed that peak area of mercury species decreases when $NaBH_4$ concentration was increased further to 3%[18], which confirms the results of present study.

The purge gas flow rate will affect mainly the determination by CVAAS and final mercury vapor concentration and consequence the detection limit and sensitivity of sequential injection system[8,9]. The obtained results clearly indicate that flow rate increases to 200 ml min^{-1}, peak height increases and then remains constant. Therefore, it is concluded that saturation of mercury was completed and mixing time for analyte dilution was sufficient. While the observed deterioration of reproducibility in flow rate higher than 400 ml min^{-1} probably was related to leak fitting.

The significant relationship between the stirring of separation chamber and peak height especially when the air was used as purge gas, can be linked to form an oxide layer on the undisturbed surface, which causes a slow shifting of the peak height. Stirring of the reductant and mercury in the container has restored the initial mercury signal, and by using the renewable surface, constant mercury vapor concentration can be achieved, and if the flow rate of gas is not extremely high, the saturation can be achieved. Constant mercury vapor concentration could be achieved by using of the renewable surface.

As it is observed in the results, the increase in flow rate of Hg (II) solvent from 1.25 to 2.5 ml min^{-1} resulted in a significant decrease in the breakthrough time and mercury adsorptive capacity (Figure 4, Table 2). This can be attributed to the effective pore diffusivity decrease which in other studies referred to in[5,16]. Skodras et al. (2008), by study of two types of carbon active with different pore indicated that increase of the initial concentration from 0.1 to 0.35 ng/cm^3 causes the decrease in breakpoint from 52 to 22 min[19]. It seems that carbon active particle produces a delay of the breakthrough, compared with bone char. That is, in the carbon active particle, adsorption breakthrough curves follow a much more efficient profile than that in bone char (Figure 4).
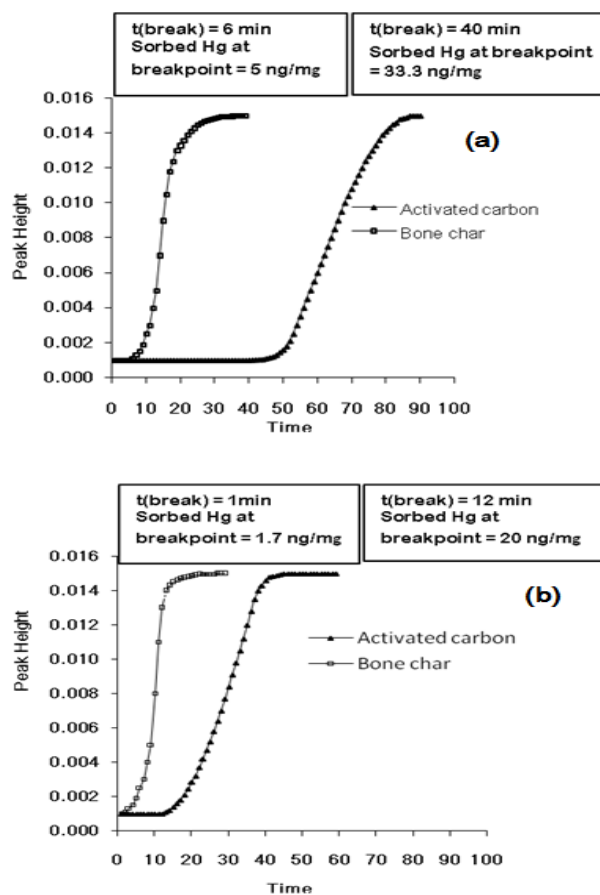
Figure 4: Compression of mercury vapor adsorption on both activated carbon and bone char; 100 (µg l^{-1}) Hg(II)initial concentration,185.6 mm column length, 4.9 mm column diameter, 50^{0}C adsorption temperature, 150 mg sorbent mass, 200 ml min^{-1} Ar flow rate. (a) With

1.25 (ml min^{-1}) Hg (II)flow rate. (b) With 2.5 (ml min^{-1}) Hg (II)flow rate

Conclusion

A novel mercury vapor generation unit based on CVAAS, undertaken to provide the advantages such as simplicity, use facilitating, small dead volume, quickly of mercury ions reduction, and the use of new separation chamber resulting thus to minimum vapor dispersion, it facilitates the successful manipulation of mercury loading in sorbent types is the ideal system for mercury vapor generation and as well as appropriate alternative for pre-concentration method. The above setup can successfully manage a wide range of mercury solution loading for varied sensitivity while its performance was stable during all experiments. This setup is adaptable to an on-line study of elemental mercury adsorption and the determination of breakthrough time and adsorption capacity. It could be applied to the time based studies.

Acknowledgments

Conflict of interest statement

The authors have no conflict of interests to declare.

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