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On-line Pre-Concentration and Separation of Inorganic Arsenic Based on Nano Platinum-Multiwall Carbon Nanotubes

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Abstract

On-line solid phase extraction (SPE) based on nano adsorbent for pre-concentration of inorganic arsenic in water and waste water samples was developed prior to determine by hydride generation atomic absorption spectrometry (HG-AAS). By hydride generation simulation system (HGSS), the inorganic arsenic in liquid samples changed to hydride form and pass through nano platinum multi wall carbon nanotube (3 wt % Pt, NPt-MWCNT,). The hydride form of arsenic (AsH_3), pre-concentrated on NPt-MWCNTs and then completely desorption by electric heater accessory at 200^{o}C for determining. The detection limit (LOD) and linear range of perposed method were obtained 0.4 ng L^{-1} and 6 –410 ng L^{-1} respectively(R^2 = 0.9988). The relative standard deviations (%RSD) at 100 ng L^{-1} of analyte were found less than 5%. The capacity and efficiency of nano adsorbent were 75 mg g^{-1} and 96% at argon flow rate less than 100 ml min^{-1}. The developed method was applied successfully to determination of ultra trace of inorganic arsenic in environmental samples by HG-AAS.

Keywords: Arsenic; Nano Platinum; Multiwall Carbon Nanotubes; Pre-concentration; Water Samples; Cold Vapor Atomic Absorption Spectrometry.

1.Introduction

Arsenic (As) has two forms (inorganic and organic) in human body. Arsenic can be very toxic to the central nervous system (CNS). The toxicity of arsenic compounds is generally linked to the soluble inorganic trivalent forms (arsenite), which is controlled by pH [1]. Symptoms of arsenic poisoning may include headaches, diarrhea, vomiting and cancer [2].

Arsenic is a ubiquitous element in the environment originating from natural sources as well as human activities. Major anthropogenic sources of arsenic include wood preservatives, agricultural uses, industrial uses (catalysts, pyrotechnics, antifouling paints, and pharmaceutical substances), mining and smelting.

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Due to its natural and anthropogenic occurrence the entire population is exposed to (low levels of) arsenic through food, water and air. It has been reported that the same metal ion may possess different toxicity in its different oxidation states which are responsible for their different physico-chemical and biological activities. This indicates that it is very important to be able to measure inorganic arsenic in water sensitively and reliably. Although the above mentioned risks do not distinguish between the toxic effects of the inorganic arsenic species arsenite [As (III)] and arsenate [As(V)] individually. It is important to note that the toxicity of As (III) is greater than the toxicity of As (V) [3].

Determination of ultra trace arsenic concentrations in water samples required a sensitive analytical techniques such as; ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS), high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [4-6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7], hydride generation atomic absorption spectrometry (HG-AAS) [8], electro-thermal atomic absorption spectrometry (ET-AAS)[9], chemiluminescence method(CM)[10] and hydride generation and atomic fluorescence spectrometry (HGAFS) [11] have been recommended for the purpose. Among them, HG-AAS and ET-AAS is probably the most common technique used for low level concentrations of As in water samples. But in order to achieve accurate, sensitive and reliable results at sub-ppb levels, pre-concentration of arsenic are required prior to analyte determination. Sample preparation procedures such as liquid-liquid micro-extraction (LLME) [12, 13], homogeneous liquid-liquid extraction [14], solid phase extraction (SPE) [15,16], liquid-phase micro-extraction (LPME) [17] and Cloud point extraction (CPE) [18] are developed.

Among variety of methods, the solid phase extraction (SPE) and solid phase micro-extraction (SPME) are widely applied for the elimination of metals. SPE and SPME have some advantages, such as, lesser waste generation, lesser matrix effect, availability and easy recovery, achievement of higher pre-concentration factors, speed and simplicity, feasibility of sampling in the field, safety and ease of automation and easy adaptation of solid phase in a mini column coupled to a continuous flow pre-concentration system[19]. The solid phase extraction (SPE) and solid phase micro-extraction (SPME) are widely applied for the elimination of metals among a variety of methods [19-21]. Many adsorbent were used for elimination of metals in water samples by SPE or SPME technique.

In this research, arsenic ions in water samples changing to hydride form ($As H_3$) by hydride generation simulation system (HGSS) and As(III) was on-line determined by HG-AAS after pre-concentration on Pt-MWCNT adsorbent.

2. Experimental

2.1. Synthesis of hybrid of MWCNT with platinum

Multi wall carbon nanotubes (MWCNTs) were prepared through a special CVD method. The catalytic reactions for synthesis of MWCNT were carried out using the synthesized Co-Mo/MgO as the catalyst. The CVD technique was carried out in a horizontal furnace consisting of a quartz tube with 45 mm in diameter and 1 mm in length. The furnace provided controllable heating up to 1200 ˚c with a non-gradient temperature zone (reaction zone) of 30 cm in length. 20 g catalyst was placed in a quartz tube. The catalyst was purged in the hydrogen stream at the flow rate of 300 ml/min for 3 hours in order to reduce the catalyst. The reaction was carried out using methane as the carbon source with a flow rate of 50 ml/min, and hydrogen was used as carrier gas with a flow rate of 250 ml/min at 900 ˚C for 1 hour. The furnace was then cooled to room temperature under a hydrogen stream and the final product formed after the completion of the reaction was a black material. After synthesis of MWCNT, hybrid of MWCNT with platinum was occurred.

In this method stainless steel tubing was attached to a nozzle which was used to obtain a mist of small drops of hydrocarbon/catalyst. Argon was used as carrier gas to generate the dichloride platinum (II) /toluene mist in the rector. The reactor was inserted into a furnace that provided controllable heating up to 1080°C with a non-gradient temperature zone. The precursor solution was sprayed into Stainless steel tubing. Nebulizer container was filled with 250 mL of the mixture of $C_8H_{12}Cl_2Pt$ (98%, CAS Number 12080-32-9, Aldrich) and toluene (99.5%, Fluka).

After temperature on furnace was stable at 900˚c, the argon was feed to nebulizer and the mixture Argon/organoplatinum/toluene entered stainless steel tubing without any previous heating. Once stainless steel tubing was exposed to spray pyrolysis, oven is cooled under argon flow to ambient temperature. Thereafter, black film made of MWCNT formed at inner surface of stainless steel tube is removed mechanically with a brush. Concentration 3% wt $C_8H_{12}Cl_2Pt$ was used for synthesis of hybrid multi wall carbon nanotubes and platinum.

2.2.Instrument

The experiments were performed using a GBC-932 atomic absorption spectrometer equipped with hydride generation system (HG-AAS, 3000, AUS). A hollow cathode lamp operated at a current of 8 mA and a wavelength of 193.7 nm with a spectral band width of 1 nm and deuterium background corrector was applied. All containers (quartz crucibles, plastic tubes) were cleaned with detergent and treated successively by the hydrochloric acid and rinsed with de-ionized water. Argon was used as the pure gas (99.99%). SKC air sampling pump (1-5 L/min) with flexible connecting tubing was used. Flasks, volumetric (50- 100 mL), Pipet and Micro Pipet were also used. A scanning electron microscope (SEM) model S-4160 (Hitachi, Japan) was used for surface image analysis. In bench scale, arsenic vapour system, nano sorbent, electric heater power supply accessory (50-250 AC Voltage, 10A, 20-700 ^{o}C), on-off pneumatic valves and argon flow rate and removal conditions were optimized The stainless steel round tube (SSRT, N304, 8Cm) with a smooth surface in inside and outside diameters and heat resistance was selected as a sorbent column. SSRT is the most widely used stainless steel grade.

2.3. Reagents

All reagents and standards were perchased from Merck (Germany). Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly was added this solution to 100 mL deionized water and mixed well. Arsenic(III) standard solutions were prepared from a stock solution of 1000 mg L^{-1} as ultra trace in 1% nitric acid from Fluka Switzerland. Working standard solutions were prepared by dilution of stock and intermediate standards. Stannous chloride Prepared fresh daily. De-ionized water obtained from a Milli Q-water purification system (Millipore, Bedford, MA, USA) was used for preparing all solutions

2.4. General Procedure:

For ultra-trace analysis of inorganic arsenic ions in water samples, new method based on solid phase extraction with nano platinum adsorbent (SPE-NPt-MWCNT) were used. In pilot setup, arsenic ions in liquid change to hydride form (As H_3) by hydride generation simulation system (HGSS). The producer continue as follows, As(III) standard solution (1 mL/min.), the hydrochloric acid (5 mL/min, 5%) and the reducing agent solution at 3 mL/min are introduced separately through tubing's with the aid of a peristaltic pump. Only 2mL water sample, AsH_3 is generated in the reaction loop and pumped into SSRT micro column with NPt-MWCNT. Arsenic pre-concentrated on Pt-MWCNT and online determined by HG-AAS after thermal desorption of nano adsorbent (180 mm, i.d. 8 mm) by electrically heated to 200°C. Peak area were performed with the aid of the software of the GBC spectrophotometer.

3.Results and Discussion

3.1. Repeatability and capacity of NPd-MSN

In this work, the maximum capacity and repeatability of Pt-MWCNT sorbent were studied. The maximum capacity and repeatability of sorbent were 75 mg g^{-1} and 32 respectively. After adsorbing a certain mass of As (III) on Pt-MWCNT sorbent tube, the two ends of tubes tying tightly with paraffin and kept at a temperature of 25^{o}C. Then, in various times (min, hour, day), thermal desorption of Pt-MWCNT were examed. The maximum efficiency of As (III) desorption obtained in 28 days at optimized condition (96% ± 2.21).

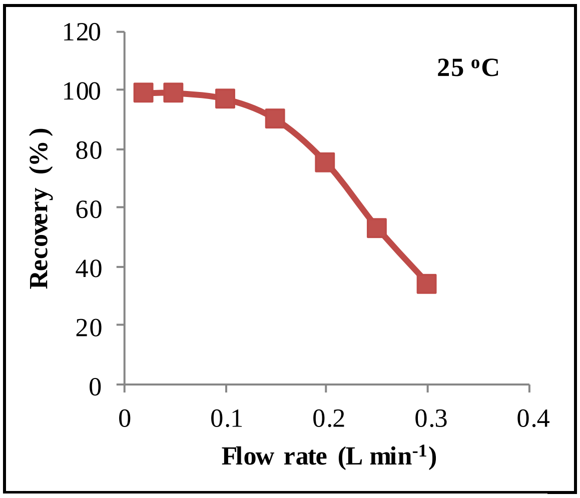


Fig. 1. Influence of flow rate on recovery

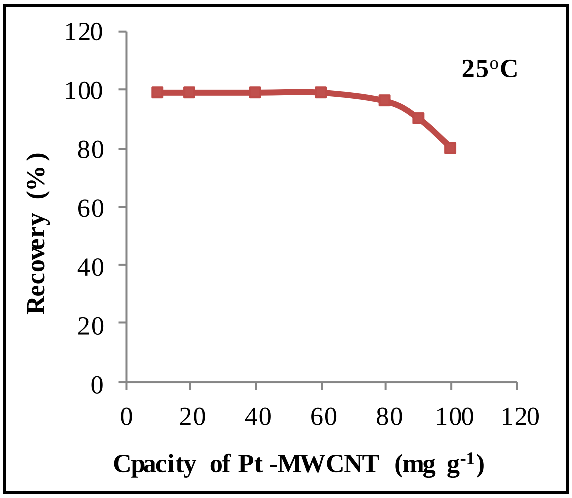


Fig. 2. Capacity adsorption of Pt-MWCNT for arsenic

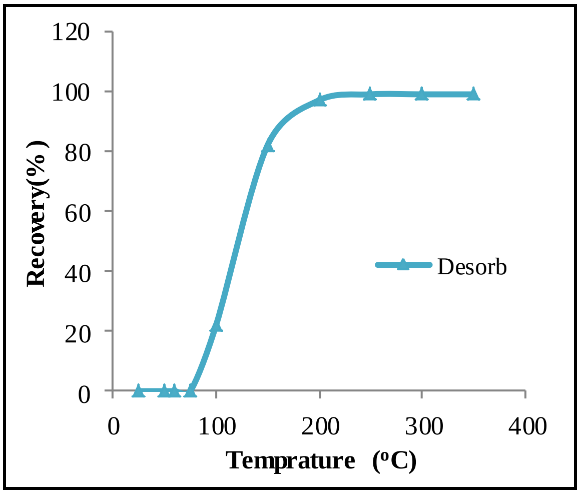


Fig. 3. Influence of temperature on arsenic desorption from Pt-MWCNT

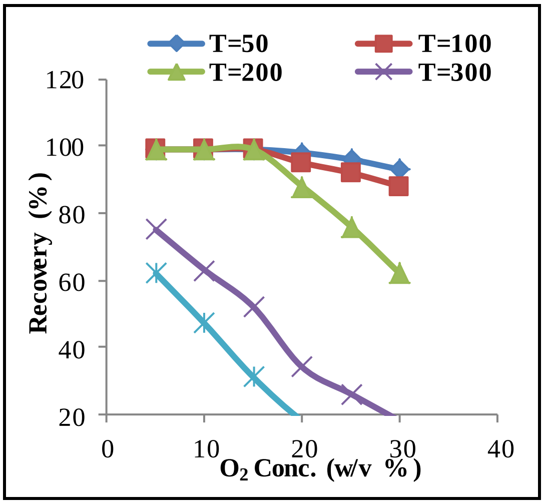


Fig. 4. Influence of O_2 on arsenic adsorption by Pt-MWCNT

3.2. Effect of temperature on absorption and desorption of sorbents

AsH_3 adsorption on NPt-MWCNT depended on various temperatures. In the presence of O_2 and H_2O vapor, AsH_3 could be adsorbed by NPt-MWCNT (96%) and MWCNT (17%) with 0.5 µg L^{-1} concentration (Ar flow rate 0.1 L/min). The effects of temperature on AsH_3 were evaluated in the range of 0–400 °C and optimized temperature was selected at 200 °C and 185°C for NPt-MWCNT and MWCNT respectively. However, the increase of temperature within 310–540°C led to a decrease of catalytic activity. In NPt-MWCNT sorbent, maximum thermal desorption were observed at 200°C. The experimental parameters such as, amount of sorbent, flow rate, O_2 and temperature have been optimized and were shown in figure 1 to 4.

3.3. SEM and EDX of NPt-MWCNT

Scanning electron microscopy was used to show the morphology of the nano Pt-MWCNT and MWCNT. A scanning electron microscope (SEM) model S-4160 (Hitachi, Japan) was used for surface image analysis. SEM images of the samples are illustrated in Figs. 5 and 6 specify that the morphology of PT is like to semispherical particles lied in the nanoscale range. The EDX peak, showed that the adsorption of arsenic on Pt-MWCNT and mass weight of As /Pt-MWCNT (%Wt) (Fig. 7).

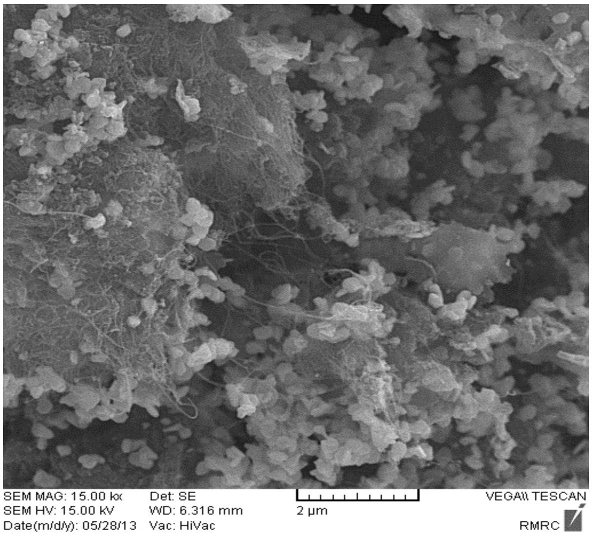


Fig. 5. The SEM image of As-Pt-MWCNT

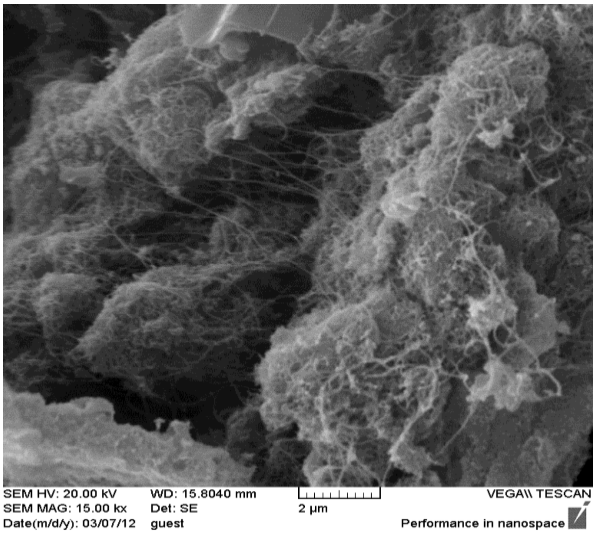
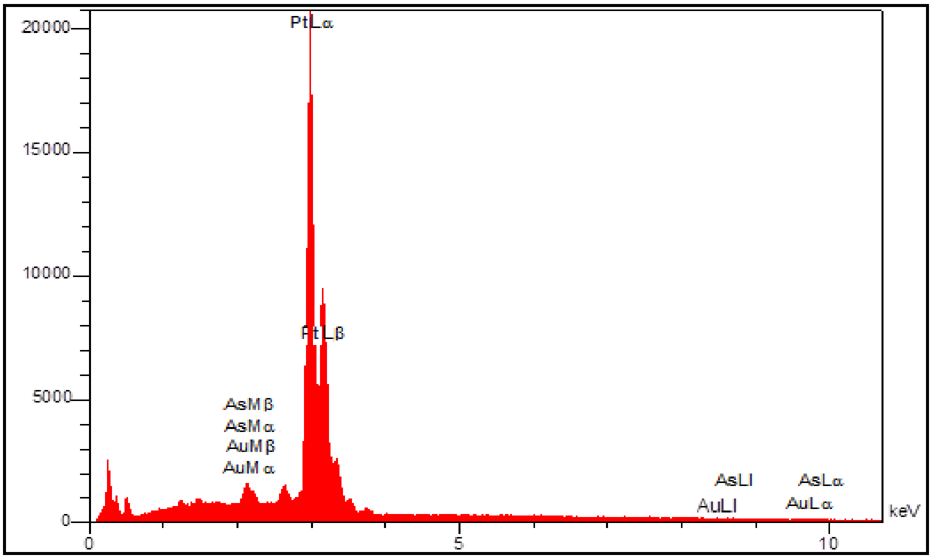


Fig. 6. The SEM image of Pt-MWCNT



Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Ox%	Pk/Bg	Class	LConf	HConf
Pt	La	2592.6	12.2820	0.9210	0.8821	91.05	94.90	0.9688	0.00	35.03	A	90.52	91.58
Au	La	6.1	0.3765	0.0693	0.0664	7.91	4.52	0.8391	0.00	2.23	B	6.96	8.87
As	Ma	30.8	12.2820	0.0096	0.0092	1.04	0.58	0.8893	0.00	3.04	B	0.98	1.09
				1.0000	0.9578	100.00	100.0		0.00				

Fig. 7. The EDX peak for As ,C and Si in NPt-MWCNT adsorbent (chemical adsorption of As on Pt)

3.4.Method Validation

In HGSS, AsH_3 were generated from water samples(Recovery 95%). The arsenic ions in water samples change to gas forms and flow to NPt-MWCNT. After pre-concentration of arsenic vapor in NPt-MWCNT adsorbent, completely desorption by electric heater accessory at 200°C and determined by HG-AAS.

Validation of the methodology was performed by a standard addition to samples (Table1). This method has been developed based on 100 mg of nano Pt-multiwall carbon nanotubes.

Table 1. Determination of As(III) in real samples by purposed method

Sample	Added (ngL^{-1})	^{a}Found (ngL^{-1})	Recovery (%)
Industrial effluent water	---	212.3 ± 9.1	---
	50	248.5 ± 10.9	98
Well water	---	174.2 ± 7.3	---
	20	198.3 ± 9.5	102
Municipal effluent water	---	353.3 ± 12.3	---
	50	398.4 ± 15.8	99
Drinking water	---	73.4 ± 3.8	---
	100	168.1 ± 6.5	97

^{a}Mean of three determinations ± confidence interval (P = 0.95, n =5)

4. Conclusions

The aim of this work was to develop a new, simple and sensitive method for pre-concentration of ultra-trace arsenic prior to determine by HG-AAS. In this study, SPME method has been developed based on 100 mg of Pt-MWCNT for pre-concentration of ultra-trace arsenic. The experimental parameters such as, amount of sorbent, argon flow rate and volume of sample have been optimized. The perposed method had high precision and accuracy results with low LOD and high pre-concentration factor (PF). The developed method was applied successfully to determination of arsenic in water and waste water samples. The pre-concentration factor was 148.

5. References

1. M.F. Hughes, Toxicol. Let., 133, 1 (2002).
2. Arsenic, Agency for Toxic Substances and Disease Registry(ATSDR), January, (2006).
3. P. A. Gallagher, J.A. Shoemaker, X. Wei and C.A. Brockhoff-Schwegel, F. J. Anal.Chem., 369, 71 (2001).
4. S.H. Nam, H.J. Oh, H.S. Min and J.H. Lee, Microchem. J., 95, 20 (2010).
5. L. Kuenstl, S. Griesel, A. Prange and W. J. Goessler, Environ. Chem., 6, 319 (2009).
6. S. Dobran and G.J. Zagury, Science of the Total Environment Sci. Total Environ., 364, 239 (2006).
7. J. Koh, Y. Kwon and Y. Pak, Microchem. J., 80, 195 (2005).
8. A.R. Kumar and P. Piyazuddin, Int. J. Environ. Anal. Chem., 88, 255 (2008).
9. I. Serafimovski, I. Karadjova, T. Stafilov and D. L. Tsalev, Microchem. J., 83, 55 (2006).
10. A. R. Kumar and P. Riyazuddin, Int. J. Environ. Anal. Chem., 87, 469 (2007).
11. F. El-Hadri, A. Morales-Rubio and M. Guardia, Food. Chem., 105, 1195 (2007).
12. H. Shirkhanloo, A. Rouhollahi and H.Z. Mousavi. J. Chin. Chem. Soc., 85, 623(2011).
13. H. Shirkhanloo, A. Rouhollahi and H.Z. Mousavi. Bull. Korean Chem. Soc., 32, 1 (2011).
13. Y.K. Agrawal and K.R. Sharma, Talanta., 67, 112(2005).
14. H. Ebrahimzadeh, Y. Yamini, F. Kamare and S. Shariati, Anal. Chim. Acta., 594, 93 (2007).
15. Z. Li, X. Chang, Z. Hu, X. Huang, X. Zou, Q. Wu and R. Nie, J. Hazard. Mater.,166, 133 (2009).
16. I. Narin, A. Kars and M. Soylak, J. Hazard. Mater. 150, 453 (2008).
17. C. Zeng, Y. Lin, N. Zhou, J. Zheng and W. Zheng, J. Hazard. Mater., 237, 365 (2012).
18. P. Liang and H. Sang, J. Hazard. Mater., 154, 1115 (2008).
19. E. M, Soliman, M.B. Saleh and S. Ahmed, Talanta., 69, 55 (2006).
20., H. Shirkhanloo,M. Osanloo and O. Q. Dadrass, Int. J. Occup. Hyg., 6, 1 (2014).
21. H. Shirkhanloo,M. Osanloo and O. Q. Dadrass, J. Health. Safety work.,(in press).