Simultaneous Determination of Arsenic(III) and Arsenic(V) in Atmospheric Particulate Matter by Electrically Heated Quartz Hydride-Generation Atomic Absorption Spectrometry

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A method based on hydride generation atomic absorption spectrometry (HG-AAS) using an electrically heated quartz tube was developed for simultaneous determination of As(III) and As(V) associated with total suspended particles (TSP) and PM_{10} particles collected from urban and rural atmosphere. The concentrations of As(III) and As(V) associated with total suspended particles and PM_{10} were simultaneously determined. The monthly variation in atmospheric concentrations of As(III) and As(V) was investigated and indicated that the higher concentrations were found in December, January and February, respectively. The atmospheric concentration of total arsenic was also determined in rural and urban areas and the results showed the lower atmospheric concentrations in rural area with lower traffic density. An excellent co-variation in concentrations of arsenic, PM_{10} and CO indicated that arsenic is mostly released into the atmosphere from anthropogenic sources and especially from combustion of fossil fuels in automobile engines.

Key Words: Determination of arsenic, Speciation of arsenic, Air pollution, Simultaneous determination of As(III) and As(V).

INTRODUCTION

Arsenic is a well-known toxic element widely distributed in the environment including plants, animal tissues, water resources and urban atmosphere. Arsenic in urban air is mostly associated with airborne particulate matter[1,2]. Although arsenic and its compounds are released into the urban atmosphere from both natural and anthropogenic sources, the major sources responsible for releasing arsenic into urban air are man-made processes[3,4]. The anthropogenic sources of arsenic in urban air include; glass furnaces, metallurgical processes, garbage incineration and fuel and oil combustion[5-7]. Arsenic is recognized as cumulative and carcinogenic poison and the determination of its concentration in urban air is of great concern because of the size of population at risk in mega cities and the continuous nature of exposure[8]. Arsenic is one of the most important components of airborne particulate matter. They are ubiquitous components of the lower atmosphere[9]. The bioavailability and toxicity of an element is considerably depends on the physicochemical form which also governs the mobility of the element[10,11]. The individual determination of arsenic(III) and arsenic(V) in urban atmosphere is particularly important because of the variation in toxicity and carcinogenicity of the different species[12,13]. A variety of analytical methods currently exist for speciation of arsenic in environ-

mental samples such as atomic absorption spectrometry[14,15], electro-thermal atomic absorption spectrometry (ET-AAS)[16,17], gas chromatography (GC)[18,19], high performance liquid chromatography (HPLC)[20,21], spectrophotometry[22,23], inductively coupled plasma atomic emission spectrometry (ICP-AES)[24,25], inductively coupled plasma mass spectrometry ICP-MS[26] and neutron activation analysis (NAA)[27]. In considerable numbers of these methods hydride generation is linked to a technique for sensitive determination of arsenic species. Among the different techniques hydride generation atomic absorption spectrometry (HG-AAS) is the most popular technique because of its rapidity simplicity and sensitivity[28-30].

The aim of this work is to determine the levels of arsenic(III) and arsenic(V) in urban atmosphere simultaneously. In this context arsenic speciation was carried out in airborne particulate matter collected from the atmosphere of the city of Isfahan, Iran. The concentrations of arsenic(III) and arsenic(V) were determined in total particulate particles (TSP) and particles with diameter less than 10 μm (PM_{10}).

EXPERIMENTAL

All chemicals were of analytical grade or better. Hydrochloric acid (Merck Chemical Co.) was used for digestion of samples and preparation of standard solutions.

Distilled de-ionized water was used for preparation of standard solutions. It was prepared by a Waters Milli-Q water purification system. Standard stock solution (1000 mg/L) of arsenic(III) was prepared by dissolving arsenic(III) oxide (0.1320 g) in 20 mL of sodium hydroxide and then neutralized with 3 mol/L sulfuric acid and diluted to 100 mL by distilled de-ionized water.

Standard stock solution (1000 mg/L) of arsenic(V) was prepared by dissolving sodium arsenate (0.4165 g) in distilled de-ionized water and diluting to 100 mL. Standard solutions in the working range were prepared fro the stock standard solutions by proper diluting with distilled de-ionized water. Zinc slurry was prepared by dispersing zinc powder in double distilled water and agitation vigorously.

The standard solution of sodium tetrahydroborate solution was prepared by dissolving the appropriate amount of the reagent in 2 g/L sodium hydroxide solution just before use. All glassware was placed into 25% (v/v) nitric acid for 24 h before use. After removal from acid, the vessels were rinsed with distilled de-ionized water and dried.

Collection of samples: The samples of total suspended particulate (TSP) and particles with diameter less than 10 μm (PM_{10}) were collected from the atmosphere of the city of Isfahan, Iran. Particles were collected from the height of 1.5 m above the ground level and at a distance of 10 m from the road shoulder.

Total suspended particulate was collected on quartz fiber filters (QM-A) using a Greaseby, Model PS2 hi-vol air sampler. Sampling flow rate and sampling period were 1 m^3 min^{-1} and 24 h, respectively.

PM_{10} particles were collected using a PM_{10} high volume air sampler (Ecotech, Australia). PM_{10} particles was collected on quartz fiber filter. The flow rate and sampling period were 1 m^3 min^{-1} and 24 h in order to collect sufficient material for performing a sensitive analysis. Before the sampling all filters were maintained at 25 °C in a dry box for 24 h. The filters were then weighed and used for sampling. The exposed filters were also dried at the same condition and weighed. The difference filter weight after and before sampling indicates the weight of TSP or PM_{10} particles collected.

Preparation of samples: Digestion of particulate matter was performed with 1M hydrochloric acid. The exposed filter was located in a PTFE beaker and 10 mL of hydrochloric acid was added on that. The lid of PTFE beaker was closed and heated in an oven at 90 °C for 1 h. The digest was then cooled to room temperature and filtered into a 25 mL volumetric flask and made to the volume by 0.1M HCl and used for the determination of As(III) and As(V).

Instrumentation: The determinations were carried out on a Varian atomic absorption spectrometer, Model AA-220.

The spectrometer was linked to a hydride generation device and a Varian hollow cathode was used as the light source. The lamp current was 10 mA. The determinations were performed at wavelength of 193.7 nm, band pass of 1 nm. The absorption cell was a T-shaped quartz tube and located instead of the conventional air-acetylene burner. It was electrically heated by a Ni-Cr wire which was wrapped around the absorption cell. Fig. 1 shows the schematic diagram of the system used for the determination of arsenic.
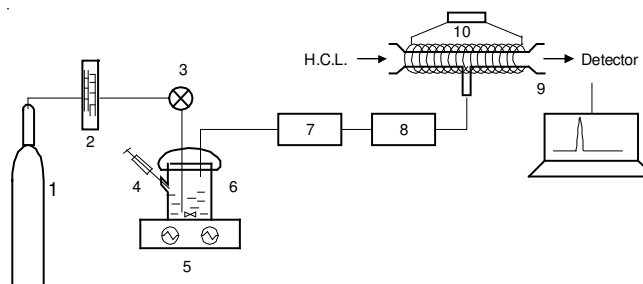

Fig. 1.   Schematic diagram of the system used for determination of arsenic. 1. Helium cylinder 2. Flowmeter 3. Triple-way valve 4. siringe 5. heater 6. hydride generator 7. H_2O adsorber 8. CO_2 adsorber 9. absorption cell 10. transformer

Determination of arsenic species: The determination of As(III) and As(V) in each digest was performed simultaneously by the a developed method using a two step reduction process. 5 mL of the digest was poured into the bubbler of the system and acidified with hydrochloric acid. 2 mL of the zinc slurry was injected into the solution to reduce As(III) and converted that to arsine and immediately after that 2 mL of $NaBH_4$ solution was injected into the solution to reduce As(V) to arsine. The absorption signal related to each step was recorded by the graphic printer individually and used for the determination of As(III) and As(V).

RESULTS AND DISCUSSION

Zinc powder in acidic media produces hydrogen and is able to reduce As(III) to arsine, but the process is not able to reduce As(V) to arsine as well, but $NaBH_4$ in acidic media is able to reduce both species of arsenic to gaseous arsine. The injection of Zn powder slurry and then $NaBH_4$ causes to separate the reduction processes of As(III) and As(V) and produces the individual absorption signals for the consequent reduction of As(III) and As(V).

A recovery test was performed to evaluate the reliability of the method by spiking standard solution of As(III) and As(V) on the exposed filters and then determination of As(III) and As(V) were performed by the proposed method. The results are summarized in Table-1 and indicates that the method is quite capable to be used for speciation of arsenic.

	TABLE-1					
	RECOVERY OF As(III) AND As(V) FROM AIRBORNE PARTICULATE MATTER (μg/FILTER)					
Sample	As(III) added	As(V) found	Recovery (%)	As(V) added	As(V) found	Recovery (%)
1	0.00	0.88	–	0.00	0.77	–
	1.00	1.86	99	1.00	1.74	98
2	0.00	0.98	–	0.00	0.87	–
	1.00	1.95	98	1.00	1.83	97
3	0.00	1.12	–	0.00	0.86	–
	1.00	2.13	100.5	1.00	1.82	97

Effect of diverse ions: The effect of interferences on the method was investigated by using a standard solution containing known amounts of As(III) and As(V) and various amounts of different ions. The mixtures were analyzed by the proposed procedure. The tolerance limit was defined as the maximum concentration of the concomitant ion that produced a determination error of < 5 %. The effects of Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Hg^{2+}, Na^+, K^+, Mg^{2+}, Mn^{2+}, Si^{4+} and Zn^{2+} were investigated at molar ratio of 1000 and no affect on the absorption signal of arsenic was found.

Determination of arsenic species associated with airborne particulate matter: The concentrations of As(III) and As(V) associated with total suspended particles and PM_{10} particles collected from the atmosphere of the city of Isfahan, Iran were determined. Figs. 2 and 3 represent the monthly average concentrations of arsenic species associated with total suspended particle and PM_{10}, respectively.
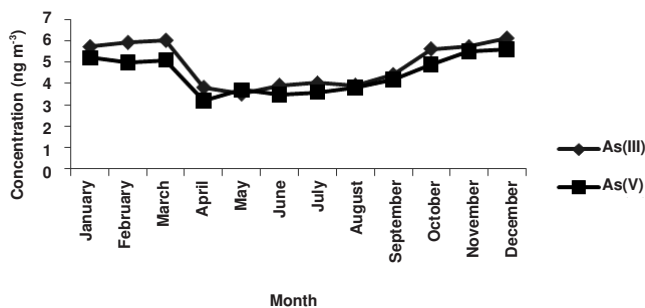

Fig. 2.　Monthly average concentrations of As(III) and As(V) associated with total suspended particle
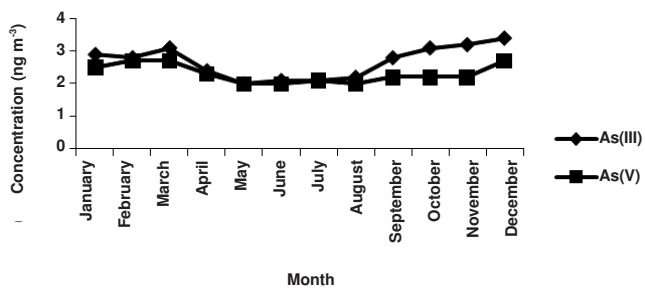

Fig. 3.　Monthly average concentrations of As(III) and As(V) associated with PM_{10}

The relationship between total suspended particles (TSP) and atmospheric and also the relationship between the concentration of PM_{10} was investigated and indicated that better correlation exist between the arsenic concentration and PM_{10}. Figs. 4 and 5 show the results obtained from this investigation.
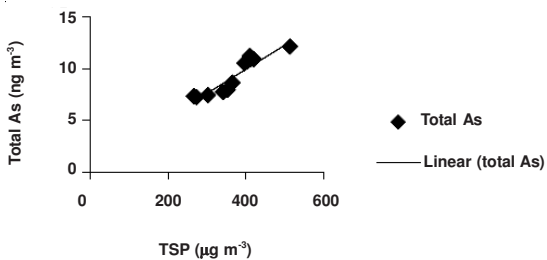

Fig. 4.　Correlation between total suspended particle and arsenic concentration in atmosphere
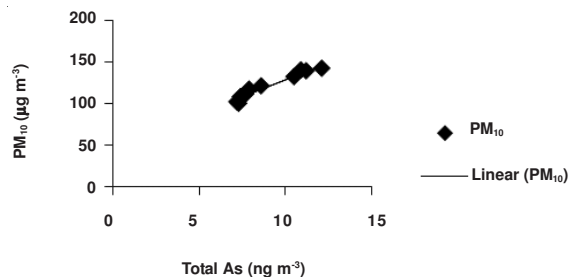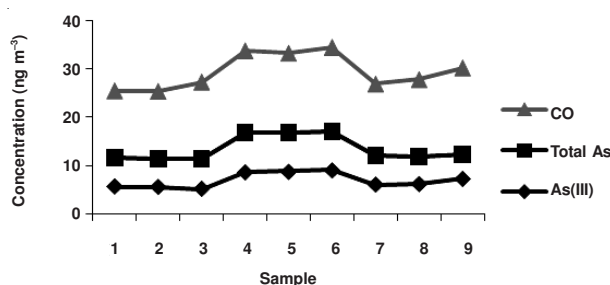

Fig. 5. Correlation between PM_{10} and arsenic concentration in atmosphere

The relationship between the variation in concentrations of arsenic species and CO was also investigated and an excellent agreement was found between them. Typical co-variation between the concentrations of these air pollutants is shown in Fig. 6.

Concentration of arsenic = ng m⁻³ concentration of CO = ppm

Fig. 6.　Co-variation between the concentrations of arsenic species and CO in Isfahan atmosphere

A continuous sampling and determination of TSP, PM_{10}, total arsenic and CO were performed for two months and the relationship between these parameters was investigated. Table-2 shows the equations and correlations between these parameters and indicates that variation in concentration of arsenic is more correlated to PM_{10} and CO.

TABLE-2		
Variable	Equation	Correlation (r^2)
As and TSP	Y = 33.91X + 55.63	0.789
As and PM_{10}	Y = 19.22X + 26.86	0.906
As and CO	Y = 1.67x + 8.00	0.975

A simultaneous determination of atmospheric arsenic concentration associated with airborne particulate matter was performed in urban and rural areas. The results obtain from this investigation are shown in Fig. 7 and indicates that in urban area with higher traffic density the arsenic concentration is much higher than that in rural area.
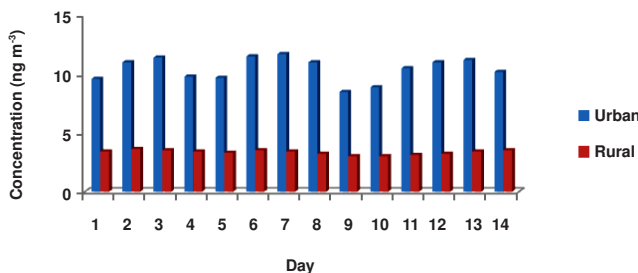

Fig. 7. Atmospheric concentrations of total arsenic in rural and urban areas

Conclusion

The proposed method developed for the simultaneous determination of As(III) and As(V) is a simple and precise method for sensitive determination of arsenic species in the atmosphere. The excellent agreement between the variation in concentrations of arsenic and CO and also arsenic and PM_{10} indicated that arsenic is mostly introduced into the atmosphere from anthropogenic sources. The total concentration of arsenic in urban and rural areas showed that area with lower traffic levels have lower atmospheric levels of arsenic that confirms the relationship between traffic and atmospheric concentration of arsenic.

REFERENCES

1. F. Tsopelas, L.A. Tsakanika and M. Ochsenkühn-Petropoulou, *Microchem. J.*, **89**, 165 (2008).
2. N.S. Thomaidis, E.B. Bakeas and P.A. Siskos, *Chemosphere*, **52**, 595 (2003).
3. S. Wang and C.N. Mulligan, *Sci. Total Environ.*, **66**, 701 (2006).
4. L. Gidhagen, H. Kahelin, P. Schmidt-Thomé and C. Johansson, *Atmos. Environ.*, **36**, 3803 (2002).
5. M. Wang, B. Zheng, B. Wang, S.L. Daishe and W.J. Hu, *Sci. Total Environ.*, **357**, 96 (2006).
6. R. Pérez-López, J.M. Nieto, M.J. López-Cascajosa, M.J. Díaz-Blanco, A.M. Sarmiento, V. Oliveira and D. Sánchez-Rodas, *Marine Pollut. Bull.*, **62**, 405 (2011).
7. Y.I. Tsai, S.C. Kuo and Y.H. Lin, *Atmos. Environ.*, **37**, 3401 (2003).
8. C.M. Liao, H.H. Shen, T.L. Lin, S.C. Chen, C.L. Chen, L.I. Hsu and C.J. Chen, *Ecotoxicol. Environ. Safety*, **70**, 27 (2008).
9. Y.I. Tsai, S.C. Kuo and Y.H. Lin, *Atmos. Environ.* **37**, 3401 (2003).
10. V.K. Sharma and M. Sohn, *Environ. Int.*, **35**, 743 (2009).
11. J. Ventura-Lima, M.R. Bogo and J.M. Monserrat, *Ecotoxicol. Environ. Safety*, **74**, 211 (2011).
12. D. Sánchez-Rodas, A.M.S. Campa, J.D. Rosa, V. Oliveira, J.L. Gómez-Ariza, X. Querol and A. Alastuey, *Chemosphere*, **66**, 1485 (2007).
13. A. Basu, J. Mahata, S. Gupta and A.K. Giri, *Mutation Res.*, **488**, 171 (2001).
14. A. D'Ulivo and J. Dedina, *Spectrochim. Acta B*, **57**, 2069 (2002).
15. F.L. Pantuzzo, J.C.J. Silva and V.S.T. Ciminelli, *J. Hazard. Mater.*, **168**, 1636 (2009).
16. É.C. Lima, J.L. Brasil and J.C.P. Vaghetti, *Talanta*, **60**, 103 (2003).
17. P. Liang and R. Liu, *Anal. Chim. Acta*, **602**, 32 (2007).
18. N. Campillo, R. Peñalver, P. Viñas, I. López-García and M. Hernández-Córdoba, *Talanta*, **77**, 793 (2008).
19. J. Kösters, R.A. Diaz-Bone, B. Planer-Friedrich, B. Rothweiler and A.V. Hirner, *J. Mol. Struct.*, **661**, 347 (2003).
20. P. Niedzielski, *Anal. Chim. Acta*, **351**, 551 (2005).
21. J.L. Gómez-Ariza, F. Lorenzo and T. García-Barrera, *J. Chromatogr. A*, **1056**, 139 (2004)
22. R. Raghavan, S.S. Murthy and C.S. Rao, *Talanta*, **36**, 951 (1989).
23. S.M. Talebi and M. Abedi, *J. Environ. Sci.*, **17**, 156 (2005).
24. D. Chen, C. Huang, M. He and B. Hu, *J. Hazard. Mater.*, **164**, 1146 (2009).
25. K. Jitmanee, M. Oshima and S. Motomizu, *Talanta*, **66**, 529 (2005).
26. Y.C. Sun, Y.J. Chen and Y.N. Tsai, *Microchem. J.*, **86**, 140 (2007).
27. Y.C. Sun and J.Y. Yang, *Anal. Chim. Acta*, **395**, 293 (1999).
28. I.B. Karadjova, P.K. Petrov, I. Serafimovski, T. Stafilov, D.L. Tsalev, *Spectrochim. Acta B*, **62**, 258 (2007).
29. A.N. Anthemidis, G.A. Zachariadis and J.A. Stratis, *Anal. Chim. Acta*, **547**, 237 (2005).
30. X. Li, J. Jia and Z. Wang, *Anal. Chim. Acta*, **560**, 153 (2006).