

# Determination of arsenic in air particulates and diesel exhaust particulates by spectrophotometry

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**Abstract:** A method was developed for the determination of trace arsenic by spectrophotometry. The proposed method is rapid, simple, and inexpensive. This method can be used for sensitive determination of trace arsenic in environmental samples and especially in air particulates. The results obtained by this method as a proposed method were compared with those obtained by hydride generation atomic absorption spectrometry as a popular reported method for the determination of arsenic and an excellent agreement was found between them. The method was also used for determination of arsenic associated with airborne particulate matter and diesel exhaust particulates. The results showed that considerable amount of arsenic are associated with diesel engine particulates. The variation in concentration of arsenic was also investigated. The atmospheric concentration of arsenic was different in different sampling stations was dependent to the traffic density.

**Keywords:** arsenic; air particulates; diesel exhaust particulates; spectrophotometry

## Introduction

Arsenic is a well-known toxic element emitted into the atmosphere from both natural and anthropogenic sources (Le, 1994). Appreciable amount of arsenic is released into the atmosphere from anthropogenic sources. The major anthropogenic sources of this element into the urban air include: glass furnaces, metallurgical industries, and fuel consumption in automobile engines (Coelho, 2002). Arsenic exists in the atmosphere in trace amounts associated with airborne particulate matter. Diesel exhaust emissions are also known as a source for distributing arsenic into urban air. Arsenic and its compounds are reported to be toxic, carcinogenic, and mutagenic in nature. However, distribution of trace arsenic is of much concern from both environmental and human standpoints. During last decades, the determination of arsenic in urban atmosphere has caused particular concern because of the continuous nature of exposure and the size of population at risk (Bavazzano, 1996). The most popular method for the determination of arsenic is hydride generation atomic absorption spectrometry (HG-AAS). The hydride generation (HG) was first introduced by Holak to atomic absorption spectrometry. So far, this hyphenated technique has been widely used for the determination of arsenic in environmental and biological samples (Zhang, 2001; Baluja-Santo, 1992; Yen, 1994). Hydride generation atomic absorption spectrometry is a time-consuming and tedious technique. Obtaining reliable results with lower RSD by HG-AAS need careful optimizing of experimental parameters and minimizing the interferences. In recent years many different methods such as gas chromatography (GC), neutron activation analysis (NAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and graphite furnace atomic absorption spectrometry (GFAAS) have been developed for the determination of trace arsenic in environmental samples

(Pozelon, 1998; Bouil, 1999; Dix, 1988). All of these methods need high primary investment and highly experienced technician to obtain reasonable results.

In this work, the determination of trace arsenic in airborne particulate matter and diesel exhaust particulate by spectrophotometric method has been investigated. This method is rapid, simple, and available in every laboratory. Determination of trace arsenic by this method is important especially in air pollution studies that a large number of samples should be analyzed in a short period of time.

## 1 Experimental

### 1.1 Reagents and chemicals

All chemicals were analytical grade or better. Aristar nitric acid was used for digestion of airborne particulate matter and diesel particulate. Stock standard solution of arsenic (1000 mg/L) was made from arsenic (III) oxide (Aldrich Chemical Company). Working standard solutions were prepared fresh daily from stock standard solution by proper dilution. Aqueous solution of KI was prepared by dissolving 20 g of KI in doubly distilled deionized water and the volume of the solution was then made to 100 ml. Aqueous solutions of rodamine-B (0.1%) and potassium iodide (3%) were freshly prepared and used. Double distilled de-ionized water was used for preparation of the standard solutions, dilution, and washing the vessels.

### 1.2 Collection of samples

Airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (Whatman QM-A) using a high-volume air sampler. Samples were collected from three different stations. Station A was located in an area with relatively low traffic density. Station B was located in the city center and close to the historical area of the city of Isfahan. Station C was located in a place close to a commercial area where the diesel engine automobile were mostly passing with high traffic density. Samples were

collected from a height of 1.5 m above the ground level. Sampling flow rate and sampling period were 1 m<sup>3</sup>/min and 12 h respectively. A continuous sampling was also performed in days and nights in order to investigate the variation in concentrations of arsenic in day and night times. The day samples were collected from 7 a.m. to 7 p.m. and the night samples were collected from 7 p.m. to 7 a.m.

Several samples of diesel engine particulate matter were collected on quartz fiber filters from the exhaust of a modified Perkins diesel engine under the two different working conditions, at high load 2200 r/min and at low load at 1500 r/min. The sampling temperature was 50°C. In each sampling 25 L of exhaust emission was passed through the filter. The specification of the modified diesel engine that used for collection of exhaust particulate samples is summarized in Table 1. Collection of the samples carried out while just one cylinder of the engine was in working position.

Table 1 Specification of the modified diesel engine used for exhaust emission collection

Model	Perkins
Cylinder	1
Discp, cc	965
Compression ratio	16:1
Power, kW	9.71
Dynamometer	Electrical

1.3 Extraction of arsenic from air particulates

Leaching of arsenic from the airborne particulate matter was performed by wet digestion procedure. An exposed filter was folded and placed in a 250 ml beaker. 20 ml of a mixture of nitric and sulfuric acids 2:1(v/v) was added, the beaker was covered by a watch glass and the mixture heated at 100°C for 30 min. The lid was then opened and the solution was heated at 100°C until the volume was reduced to a half. The sample solution was then cooled and 2 ml of potassium iodide were added and the mixture was shaken, in order to convert the As(V) to As(III). The solution was filtered into a 25 ml volumetric flask and 2 ml of rhodamine-B was added into the solution. The solution was kept for 15 min and then made to the volume with double distilled de-ionized water. The absorbance of the solution was measured at 553 nm.

Extraction and preparation of diesel engine particulates were performed in the same manner as mentioned for airborne particulate matter.

1.4 Calibration curve

Calibration curve of arsenic by proposed method was performed by using a series of standard solutions containing 1–5 µg of arsenic (III). The standard sample was transferred into a 25 volumetric flask and 2 ml of potassium iodate and 1 ml hydrochloric acid(0.5 mol/L) were added and the mixture was shaken gently. Finally 2 ml of rhodamine-B was added into the solution and it was kept for 15 min. The solution was made to the volume with double distilled de-ionized water. A blank solution was prepared

exactly in the same manner as standard solution but without arsenic. The absorbance of the sample solution was determined against the blank at 553 nm.

2 Results and discussion

The recovery of the method was determined by spiking different amounts of arsenic on the exposed filters containing airborne particulate matter. The exposed filters were exactly cut into two equal pieces. One piece of each filter was spiked with an especial amount of arsenic. The filters were analyzed for arsenic according to the procedure described above. The results obtained from this investigation are summarized in Table 2.

Table 2 Recovery of arsenic by the proposed method

Sample	Amount of As in sample, ng/filter	Amount of As added, ng/filter	Amount of As found, ng/filter	Recover, %
1	2.36	–	2.3	–
2	2.85	2	4.74	97.7
3	2.92	3	5.76	97.3
4	3.25	4	7.04	97.1
5	2.83	5	7.56	96.2

The accuracy and precision of the method were investigated by analyzing the standard reference material, SRM-1648 and SRM-1649. The samples were prepared in the same way as that described for airborne particulate matter. The results are shown in Table 3 and it is shown that the method is quite capable to determine the concentration of arsenic accurately with a RSD.

Table 3 Concentration of arsenic in reference standard samples

Reference sample	n	Certified concentration, µg/g	Found concentration, µg/g
SRM-1648	8	115.0	113.5 ± 1.48
SRM-1649	8	67.0	69.8 ± 1.52

Several exposed filters were digested and analyzed by both spectrophotometry and hydride generation atomic absorption spectrometry (HG-AAS). Spectrophotometry supposed as proposed method and HG – AAS as reported and popular method for the determination of arsenic. The results obtained from this investigation are summarized in Table 4 and showed that results obtained by the two techniques were in an excellent agreement.

Table 4 Comparison of spectrophotometry and hydride generation atomic absorption spectrometry for determination of arsenic (Unit: µg/filter)

Sample	Concentration of As by proposed method	Concentration of As by HGAAS	Proposed method over HGAAS
1	2.71 ± (0.006)	2.63 ± (0.008)	1.03
2	3.19 ± (0.009)	3.15 ± (0.007)	1.01
3	2.85 ± (0.008)	2.79 ± (0.007)	1.02
4	2.36 ± (0.009)	2.47 ± (0.007)	0.96
5	2.89 ± (0.007)	2.78 ± (0.008)	1.03
6	2.93 ± (0.008)	2.87 ± (0.005)	1.02

The concentration of arsenic in diesel engine particulate was determined. The results are shown in Table 5. The

results showed that considerable amount of arsenic is associated with diesel engine particulate.

**Table 5** Concentration of arsenic in diesel engine particulate matter

Sample	Volume of emission	Concentration of As at 1500 r/min	Concentration of As at 2200 r/min
1	25	81.0	134.5
2	25	83.2	136.7
3	25	79.8	132.9
4	25	82.6	133.1

The concentration of arsenic associated with airborne particulate matter collected from the atmosphere of the city of Isfahan was determined. The results of this investigation are shown in Table 6. The results indicated that the concentration of arsenic in samples collected from station C with higher traffic density and where the diesel engine automobile passing were much more than those collected in the other stations.

**Table 6** Mean concentration of arsenic in different sampling sites

Sampling site	Concentration of arsenin, ng/m <sup>3</sup>
A	3.2
B	4.1
C	6.8

A continuous sampling in station C was performed and airborne particulate matter was collected in the day(7 a.m. to 7 p.m.) and at the night(7 p.m. to 7 a.m.). The concentration of arsenic in the samples was determined. Fig.1 shows the results obtained from this investigation and indicates that the concentration of arsenic in the day with two rush hours is higher than those at the night.

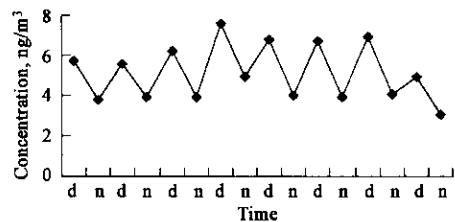


Fig. 1 Variation in atmospheric concentration of atmospheric arsenic in the day time and the night time, ng/m<sup>3</sup>

The same variation in concentration of arsenic was found in the other sampling sites.

### 3 Conclusions

Spectrophotometry is a rapid, simple and sensitive method which can be used for determination of trace arsenic in environmental samples and especially in air pollution studies.

The concentration of arsenic associated with diesel exhaust particulate and also with airborne particulate matter in the atmosphere of the city of Isfahan is high enough to be worried about. Concerning to the continuous nature of exposure and the population at risk, monitoring, control and reduction of atmospheric concentration of arsenic is necessary.

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