Distribution of Arsenic Species in Surface Water Using Flow Injection Hydride Generation Atomic Absorption Spectrometry and Furnace Method

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Abstract

Arsenic has been considered detrimental to human health when accumulated in the body beyond the tolerance level. The toxicity level of certain species (like As^{3+}) of Arsenic is higher than others, making the situation worse for human health with its presence. In this study, we used a combination of two principal atomic absorption spectroscopic methods, namely Flame-FIAS and the Furnace technique, to determine the distribution of inorganic Arsenic species in a synthetic sample. The Flame-FIAS technique was employed to determine the amount of toxic As^{3+} present in the samples and the Furnace method was used to measure the total Arsenic content. Following standardization of this experimental process, we used the technique to determine the distribution of inorganic Arsenic species in environmental samples with high total Arsenic content. Since the samples were collected from surface water systems, the conditions are supposed to be oxidizing. As per the natural geochemical distribution phenomena of Arsenic species, As^{5+} was found predominantly (around the range of 10-18 µg/l) in all samples, validating the process of species identification. In groundwater samples, conditions being reducing, the As^{3+} species is supposed to be predominant. These findings can guide future bioremediation strategies to be effectively designed, as per the distribution of Arsenic species in the surface water.

Keywords: As3+; As5+; FIAS; Furnace; Environmental Samples; Arsenic Speciation

Highlights

a) Standardization of Arsenic speciation in synthetic samples using FIAS (Flame Ionisation Atomic Absorption Spectrometry) and Graphite Furnace methods.

b) Application of Arsenic speciation in environmental samples with total arsenic content.

c) Determination of predominant inorganic Arsenic species in surface water system.

Introduction

Arsenic is a ubiquitous metalloid found in lithosphere, hydrosphere, atmosphere and biosphere [1]. Natural minerals are the key source of arsenic. The soil arsenic concentration ranges from 0.1 to 40 mg/kg around the world, while, in water, it ranges from <0.05 to 5000 µg/l [2,3]. Arsenic and its compounds are highly toxic. Studies have shown that consumption of water with high arsenic content can lead to arsenical skin lesions [4]. According to the World Health Organization (WHO), the recommended arsenic concentration in potable water is 10 µg/l. Prolonged exposure to arsenic can lead to skin cancer, neurological disorders, lung cancer, liver cancer and adverse obstetric effects [5-9]. Groundwater arsenic contamination has become an issue of great concern across the world. A number of countries have been affected by high arsenic concentration in groundwater, when it is a source of drinking water. Of them, Bangladesh and India (West Bengal) have been affected the worst [4,10,11]. The elevated presence of arsenic in the groundwater of the Bengal Delta Plain (BDP) has been termed as "the worst mass poisoning in human history" [12]. Other affected countries are Vietnam, Thailand, Cambodia, Taiwan,

Mongolia, China (Xinjiang region), Chile, Argentina, Bolivia, Brazil, Mexico, Ghana, Germany, Greece, Spain, Canada and the United States [13]. In West Bengal, six districts are adversely affected by arsenic contamination in groundwater: North 24 Parganas, South 24 Parganas, Nadia, Burdwan, Murshidabad and Malda. The total affected area is around 34,000 km² with a population of about 30 million (44.4% of the total population of West Bengal). About 800,000 people in this region drink arsenic contaminated water and about 175,000 people are suffering from arsenic related diseases [10]. Other Indian states such as Bihar, Jharkhand, Madhya Pradesh and Assam are also affected by the issue. Out of 64 districts in Bangladesh, 51 have been detected with arsenic contamination. The total area of these 51 districts is 121,145 km² and population of about 113 million (87% of the total population of Bangladesh) [5]. Excessive use of hand tube wells for drinking water and other purposes has caused the major outbreak of arsenic contamination in these regions. The biogeochemical cycle of arsenic involves a number of physicochemical processes, such as redox reactions, adsorption, desorption, ion exchange, solid

phase precipitation and dissolution. Microbiological processes play a crucial role in these processes [14]. Several factors like redox potential, pH, organic carbon and chemical speciation play important roles in these processes [14,15]. Arsenic occurs in four oxidation states: elemental arsenic (As^0), arsenite (As^{3+}), arsenate (As^{5+}) and arsenide (As^{3-}). Among these species, As^{3+} and As^{5+} are the most common ones found in aquatic environment [16]. Distribution and mobility of these arsenic species depend upon local physicochemical conditions as well as biological processes. The pKa values of arsenic acid (H_3AsO_4; contains arsenic in the form of As^{5+}) are – pKa1 = 2.19, pKa2 = 6.94 and pKa3 = 11.5. Therefore, at low pH (i.e., below 6.9) and oxidizing condition, $H_2AsO_4^-$ is the predominant form, whereas, at higher pH levels, $HAsO_4^{2-}$ is the predominant form. Arsenate, being negatively charged, gets adsorbed easily on the oxidized minerals [17]. The lowest pKa value for As^{3+} is 9.22. In most natural water with pH below 9.2 as well as reducing condition, $As(OH)_3$ is the predominant form. Solubility of arsenic depends upon its speciation [18]. Elemental arsenic is not very common in the environment, and organic forms of arsenic are found only in extremely reducing conditions (within live biomass) [19].

Objectives of This Study

This study aims to identify the method of selective determination of As^{3+} and the total Arsenic in a solution where Arsenic exists in both trivalent and pentavalent state, by combining two methods:

a)   Hydride generation through Flame – FIAS technique. (PinAAcle 900H Atomic Absorption Spectrometer, Perkin Elmer)

b)   Furnace method (PinAAcle 900H Atomic Absorption Spectrometer, Perkin Elmer)

Application of the method in determination of As species in environmental samples (river water samples).

Subtracting the result of trivalent arsenic from total Arsenic, pentavalent Arsenic concentration of the solution can be measured. Presence of other forms of Arsenic is assumed to be negligible.

Methodology

Basic Reagent Preparation

a) As^{3+} standard 50 μg/l : From stock 1000mg/l NIST As^{3+} soln. 0.1 ml was added to 100 ml volumetric flask and volume made up to 100 ml with milli Q water resulting 1000 μg/L of As^{3+} solution. From it 5 ml was added to 100 ml volumetric flask yield to 50 μg/l of As^{3+} soln. by volume make up with milli Q water.

b) As^{5+} standard 50μg/l : From stock 1000mg/l NIST As^{5+} soln. 0.1 ml was added to 100 ml volumetric flask and volume made up to 100 ml with milli Q water resulting 1000 μg/L of As^{5+} solution. From it 5 ml was added to 100 ml volumetric flask yield to 50 μg/l of As^{3+} soln. by volume make up with milli Q water.

c)   Calibration standard: from 1000 μg/L of As^{3+} solution 4,10,20,30,40 μg/L of calibration standards were prepared.

d)   Tris - Buffer (2.5 M, pH 6.2) : 75.69 gm Tris Base was dissolved in 130 ml of milli Q water. Then Conc. HCl was added continuously by checking the pH in pH meter and final pH was maintained at 6.2. Then volume was made up to 250 ml with milli Q water in a 250 ml volumetric flask.

Specific Reagent for Flame-FIAS Method

Sodium Borohydride (Reductant): 6 gm of Sodium Borohydride was dissolved in 1000 ml vol. flask with 0.6 gm of NaOH with milli Q water.

Carrier Acid (3% HCl): 30 ml Conc. HCl is dissolved in 1000 ml milli Q water in 1 L volumetric flask.

Specific Reagent For Furnace Method

Chemical modifier :1%(10g/L) Pd stock solution & 1%(10g/L) Mg stock solution were prepared. 3ml of Pd stock & 0.3 ml of Mg stock solution is added to 10 ml of MQ water.

Collection of Samples:

Sampling Sites: The sampling sites were selected based on the As contamination results obtained from routine monitoring procedure undertaken by the West Bengal Pollution Control Board. Typically, two surface water streams in the lower Gangetic delta exhibited high Arsenic contamination, namely Churni and Jalangi. Three sampling points were identified in River Churni and one point from River Jalangi. Both rivers are trans-boundary and are tributaries of the River Ganges. Sampling points on River Churni are located at Majdia (23° 23' 60'' N, 88° 42' 0'' E), Shantipur-Ranaghat (23° 10' 12'' N, 88° 32' 60'' E) and Mathabhanga Govindapur (23° 23' 56.4'' N, 89° 43' 15.6'' E) of the Nadia district. Sampling points on River Jalangi (23° 49' 12'' N, 88° 28' 19.2'' E) are located at Krishnanagar of Nadia District.

Sampling Procedure: The water samples were collected from the sampling points in sterile containers and were transported to laboratory on ice for further analysis. The samples were immediately transported to the laboratory in ice cold condition in heat insulated container. The samples were refrigerated at 4^0C, if not processed immediately.

Experimental Procedure

1st Experiment

Two sets of mixed solutions were prepared according to the Table 1 – named as Set A (A1-A8) & Table 2 for Set B (B1-B8). 1 ml Tris buffer was added to each solution of Set A. The following experimental solutions are prepared from 50 μg/l of both As^{3+} and As^{5+} stock solutions.

Table 1: Preparation of Set A Solutions.

Solution ID	Volume (mL) of As³⁺	Volume (mL) of As⁵⁺	Volume (mL) of Tris	Set A Solutions		Conc. of As³⁺	Conc. As⁵⁺
				Volume (Ml) Of Water	Total Volume (mL)		
A-1	0	0	1	49	50	0	0
A-2	0	30	1	19	50	0	30
A-3	5	25	1	19	50	5	25
A-4	10	20	1	19	50	10	20
A-5	15	15	1	19	50	15	15
A-6	20	10	1	19	50	20	10
A-7	25	5	1	19	50	25	5
A-8	30	0	1	19	50	30	0

Table 2: Preparation of Set B Solutions.

Solution ID	Volume (mL) of As³⁺	Volume (mL) of As⁵⁺	Volume (mL) of Tris	Set B Solutions		Conc. of As³⁺	Conc. of As⁵⁺
				Volume (mL) of Water	Total Volume (mL)		
B-1	0	0	0	50	50	0	0
B-2	0	30	0	20	50	0	30
B-3	5	25	0	20	50	5	25
B-4	10	20	0	20	50	10	20
B-5	15	15	0	20	50	15	15
B-6	20	10	0	20	50	20	10
B-7	25	5	0	20	50	25	5
B-8	30	0	0	20	50	30	0

2ⁿᵈ Experiment

For checking interference, two sets of mixed solutions were prepared according to the Table 3 – named as Set C (C1-C7) & Set D (D1-D7). 1 ml Tris buffer was added to each solution of Set C. The concentrations of Set A, B, C & D solutions were measured by Flame FIAS method against the calibration curve.

Table 3: Preparation of Set C and D Solutions.

Solution ID	Volume (mL) As⁵⁺ of	Volume (mL) Of Tris	Volume (mL) of Water	Total Volume (mL)	Conc. of As⁵⁺ (µg/l)
C-1	5	1	44	50	5
C-2	10	1	39	50	10
C-3	15	1	34	50	15
C-4	20	1	29	50	20
C-5	25	1	24	50	25
C-6	30	1	19	50	30
C-7	0	1	49	50	0
D-1	5	0	45	50	5
D-2	10	0	40	50	10
D-3	15	0	35	50	15
D-4	20	0	30	50	20
D-5	25	0	25	50	25
D-6	30	0	20	50	30
D-7	0	0	50	50	0

3rd Experiment

Two set of samples were prepared according to Table 4 & named as Set E (1-8) & F (1-8).Undigested synthetic samples were used in Set E. And in Set F, synthetic samples were digested with Conc. HNO_3 by Microwave Digestion System (Anton PAAR). (Digestion Method: 15 ml sample + 0.75 ml conc. HNO_3. Run Program- USER 004M) Then Set E & F, are analyzed by furnace method.

Table 4: Furnace Method.

Soln. ID	As³⁺(50 µg/l)		As⁵⁺ (50 µg/l)		Water M.Q (ml)	Total Volume (ml)
(Sets E & F)	Vol (ml)	Conc. (µg/l)	Vol (ml)	Conc. (µg/l)		
1	0	0	30	30	20	50
2	5	5	25	25	20	50
3	10	10	20	20	20	50
4	15	15	15	15	20	50
5	20	20	10	10	20	50
6	25	25	5	5	20	50
7	30	30	0	0	20	50
8	0	0	0	0	50	50

4th Experiment Applied on Environmental Samples

Eight environmental samples were taken for Arsenic speciation study. 50 ml aliquot of each sample was taken in 50 ml test tube. The pH of each sample was checked to neutral. Then samples were analyzed by Flame FIAS method to get As^{3+} concentration.

The same 8 environmental samples were subject to digestion. 15 ml of sample was digested in MDS with 0.75 ml conc. HNO_3. Then samples were analyzed by Furnace method to get total Arsenic concentration. Subtracting As^{3+}concentration from total Arsenic concentration, As^{5+} concentrations were obtained.

Results and Discussion

Several mixtures (As^{3+} + As^{5+}) were analyzed both in the presence and absence of buffer. Reported values of As^{3+}in both set A2 & B2 are 4.632µg/l & 4.804µg/l, respectively. However, the mixture (As^{3+}/As^{5+} in sets A1 & B1) actually contains 0 µg/l As^{3+} & 30 µg/l As^{5+}. Hence, it may be assumed that a positive interference (artifact) may be due to reduction of any As^{5+}present or any impurities.

Whether the reported value of As^{3+}in sets A2 and B2 (at actual value of 0 µg/l of As^{3+} in mixed solution As^{3+}/As^{5+}) depends on As^{5+} concentration or not, can be ascertained by analyzing different solutions with varying concentrations of As^{5+} against As^{3+} calibration curve in Flame-FIAS method. Blank concentrations in the presence and absence of buffer, i.e for A1 & B1 are reported as 0.006 µg/l & 0.096µg/l respectively.

It can be presumed that a value due interference (obtained in case of seta A1 and B1) coming from As^{5+}NIST Standard in mixed solutions of As^{3+}/$As^{5+}$are appeared. To check the interference, the solutions of As^{5+} of different concentrations are may be measured against As^{3+} standard curve by Flame FIAS method.

Table 5: Results of Set A and B.

Soln. ID	As³⁺ Conc. (µg/l)	
	Set A, pH = 7	Set B, pH = 5
1	0.006	0.096
2	4.632	4.804
3	9.703	9.815
4	15.12	16.83
5	19.27	19.86
6	22.56	24.48
7	25.84	28.55
8	28.91	31.93

From the above experimental data (Table 5) it was observed that the interference value due to As^{5+} was not increasing proportionately & also reported below our lowest calibration standard value. Hence, the quantification of interference value due to As^{5+} is not possible at pH 6-7.

Chemistry Behind This Phenomenon

In the hydride generation method through Flame-FIAS, the total As (As^{3+} and As^{5+}) was reduced to As^{3+} (followed by simultaneous conversion to arsine, AsH_3 gas) using a reducing agent (Sodium borohydride). If the pH was maintained at near neutral range (6-
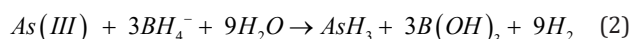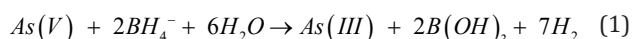
7), the reduction (As^{5+} to As^{3+}) did not occur, and only the portion of the As present in trivalent form was selectively converted to AsH_3. Using TRIS buffer, the pH of the solution was maintained at 6.2, where As^{5+} was expected not to get reduced to As^{3+}, and only the fraction of As present in trivalent form gets converted to AsH_3,

As^{3+} (and not total As) was selectively determined by Flame – FIAS method. In this study, several mixtures ($As^{3+} + As^{5+}$) are analysed both in the presence and absence of buffer to understand the effect of pH on the reduction of As^{5+} to As^{3+}.

Table 6: Results of Set C and D.

Soln. ID	As⁵⁺ Conc.(µg/l)	
	Set C, pH=7	Set D, pH=5
1	0.484	0.475
2	0.979	1.406
3	1.804	2.181
4	2.725	3.16
5	3.726	4.292
6	4.334	4.879
7	0	0

Chemical Reaction behind this conversion may be:

$$As(V) \ + \ 2BH_4^- + 6H_2O \rightarrow As(III) \ + \ 2B(OH)_3 + 7H_2 \quad (1)$$

$$As(III) \ + \ 3BH_4^- + 9H_2O \rightarrow AsH_3 + 3B(OH)_3 + 9H_2 \quad (2)$$

It was observed (as indicated in Figure 1) that on increasing the concentration of As^{3+} in the mixtures, the same was reflected in the spectrometric data, for both the sets (A & B), i.e. As^{3+} fraction in the solution gets converted to AsH_3. It was also observed (as indicated in Figure 2) increasing pH (in the experimental range

from pH 5 to pH 7) the interference of As $^{5+}$ decreased in arsenic solution in Flame FIAS method. From the Table 6, concentration of total Arsenic (given 30 µg/l) was varying from 23.25 to 24.6 µg/l in the undigested samples (set E) even at pH=2, due to unknown chemical interferences. But in case of digested samples at same pH (Set F) the concentration of Total As was around 30µg/l. In case of environmental samples the presence of total Arsenic went above the range of WHO standards (=10µg/l) but the more toxic species of Arsenic (i.e., As^{3+}) varied from 1.66 to 3.94 µg/l following natural chemical phenomenon (Tables 7 & 8).

Table 7: Results of Set E and F in Furnace Method.

Soln. ID	Total Arsenic Concentration (µg/l)	
	Set E, pH=5	Set F, pH=2
1	24.09	30.11
2	23.96	29.41
3	24.14	29.12
4	23.34	29.56
5	23.25	29.68
6	24.6	30.92
7	24.22	29.46
8	4.53	1.21

Table 8: Results of Environmental Samples.

Sample ID	As3+ Conc. (µg/l) by Flame FIAS Method (pH = 7)	Total Arsenic Conc. (µg/l) by Furnace Method (pH = 5)	Pentavalent Arsenic (As5+) Conc. (µg/l)
Blank	0	3.665	-
15/12 Govindapur	2.86	18.14	15.28
15/12 Majdia	2.49	18.2	15.71
14/12 Jalangi	3.01	19.63	16.62
14/12 Churni	3.43	20.23	16.8
15/11 Churni	1.66	12	10.34

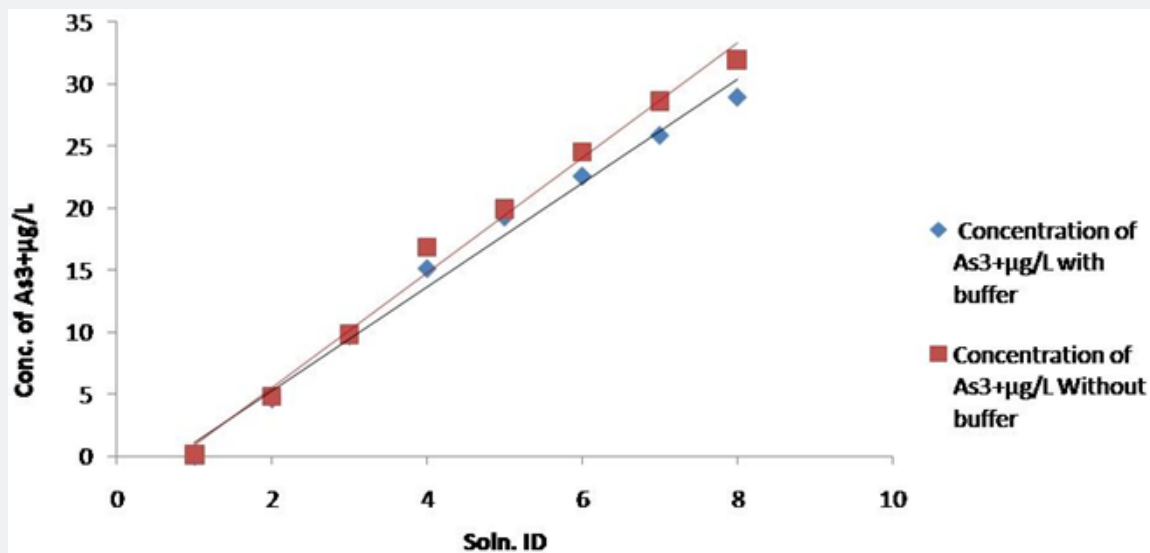| 15/11 Jalangi	2.34	13.05	10.71
16/11 Govindpur	3.94	22.26	18.32
16/11 Majhdia	3.89	22.32	18.43

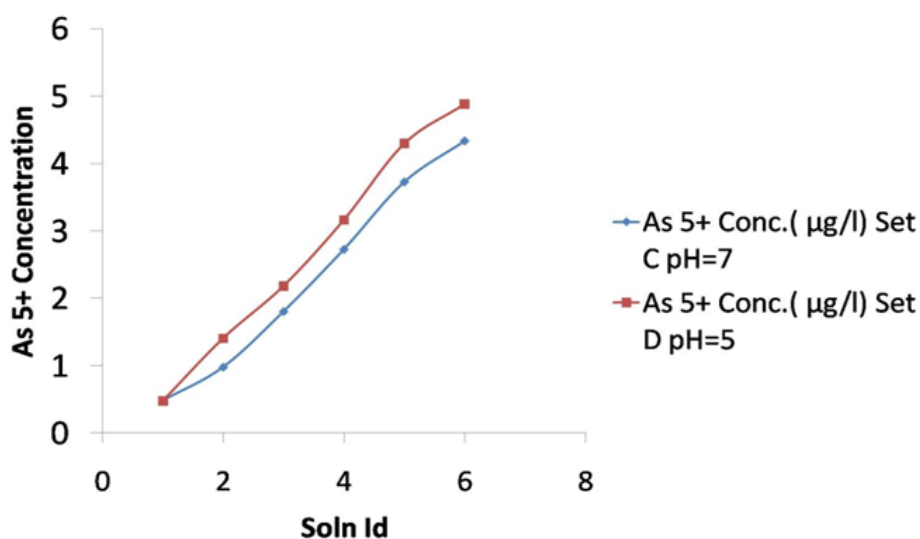**Figure 1:** Graphical Plot of the results of Set A and Set B.

Figure 2: Graphical Plot of the results of Set C and Set D.

Therefore, we can apply this method for speciation of Arsenic in this kind of environmental samples.

Conclusion

We conclude that the FLAME-FIAS method can be used to determine As^{3+} in the mixed solution of As^{3+}/As^{5+} at neutral pH as Arsenic speciation technique by plotting As^{3+} NIST standard calibration curve. An interfering value, due to transformation of As^{5+} to As^{3+} to some extent, is reflecting in the above experiment which cannot be nullified in this experimental condition. Additionally, in the case of the Furnace method, undigested synthetic samples have a certain amount of interference in comparison to the digested ones. Through application of this speciation study in environmental samples following standardized protocol, the concentration of As^{3+} is found to be low. Therefore, future remediation processes in this region should be planned according to the distribution of inorganic species reported here.

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