

Electrochemical measurement and speciation of inorganic arsenic in groundwater of Bangladesh

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Abstract

The presence of arsenic in groundwater above the maximum permissible limit of $50 \mu\text{g l}^{-1}$ has threatened the health of more than 50 million people in Bangladesh and neighboring India. We report here the development of an inexpensive anodic stripping voltammetric (ASV) technique for routine measurement and speciation of arsenic in groundwater. The measurements are validated by more expensive atomic absorption, atomic emission and other techniques. To understand the present situation in Bangladesh, we measured As(III) in 960 water samples collected from 18 districts. A random distribution of 238 samples was used to measure both As(III) and As(V). The results from the present study indicate that most toxic form of inorganic arsenic, As(III), has the broad range of 30–98%. It shows 60% of the samples have $10 \mu\text{g l}^{-1}$ and 44% of the samples have $50 \mu\text{g l}^{-1}$ or more As(III). The fractional distribution pattern shows significant skew towards high percent occurrence which may indicate a progressive reduction process with a single source or a single mechanism for the formation of As(III). For direct consumption, this is possibly one of the most toxic groundwater known today. Speciation distribution at groundwater pH value shows H_3AsO_3 is the predominant species including H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$ whose distribution is significantly pH dependent. This is also supported by E_h -pH measurements. The depth distribution for Kushtia shows most of the As(III) is located within 100–200 ft deep aquifers. Similar fractional distribution of As(III) is found in deeper aquifers and may indicate contamination by leakage from upper aquifer. This study clearly demonstrates the aquifer environment is reductive and conducive to the formation of As(III) species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic; Groundwater; Bangladesh; Anodic stripping voltammetry; Speciation

1. Introduction

According to World Health Organization (WHO): “the contamination of groundwater by

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arsenic in Bangladesh is the largest poisoning of a population in history” [1]. The presence of naturally occurring inorganic arsenic in groundwater of Bangladesh and India was extensively studied by a research group led by Chakraborti [2–4]. Hyperkeratosis on the palms and feet is the common symptom of arsenic poisoning. Long term exposure to low concentrations of arsenic has been reported to cause cancer of bladder, skin and other internal organs [5–7]. Also, arsenic in its various ionic form is known to be very toxic to most microorganisms [8]. WHO reports that there are about 2.5 million tubewells in Bangladesh (unofficial estimate is about 10 million) and more than 30–60% of the Bangladesh population of 125 million drinks well water containing the maximum contamination level (MCL) $50 \mu\text{g l}^{-1}$ (or ppb: part-per-billion) of arsenic where $10 \mu\text{g l}^{-1}$ is a provisional guideline value [9]. Total arsenic measurement shows that about 60–70% of water from shallow and deep tubewells (wells with a metal or plastic casing) has above the $10 \mu\text{g l}^{-1}$ guideline value [10]. In comparison, a 1995 USEPA assessment shows about 32 million Americans in western states consume water that contains $2\text{--}50 \mu\text{g l}^{-1}$ arsenic [11]. About half of the US drinking water comes from groundwater and 2.5 million people in the US may be supplied with water with more than $25 \mu\text{g l}^{-1}$ arsenic.

The present work is motivated by the need to develop a reliable methodology for routine measurement of arsenic in the affected areas of Bangladesh, to understand the chemistry of arsenic pollution by speciation analysis and to establish a foundation for further research in this area. Since the present crisis is likely to remain for a very long time, the authors have started an environment initiative (SDCEI, Kushtia) to help understand the present situation and its possible solution [12]. Except for some validation measurements, all experimental data reported here was obtained under the environment initiative.

In particular, the need for speciation studies is not only important to understand the toxicity of arsenic but also its bio-geochemical origin [13]. In order of toxicity the +3 (As(III) in arsenite) is 25–60 times as toxic as +5 (As(V) in arsenate)

and several hundred times as toxic as methylated arsenicals [14,15]. Extensive studies on the toxicity and biochemistry of arsenic have demonstrated the importance of chemical speciation of this element [16,17]. The speciation of trace heavy metals determines their bioavailability. Metal ions strongly bound to other chemical species are not as bioavailable as labile metal ion species. The measurement of inorganic arsenic species is also important to understand the origin and fate of arsenic in geochemical cycling [18]. Several recent studies show that dissolution and mobilization of arsenic are accomplished by quantitative reduction to As(III) [19].

We have chosen the electrochemical technique because it has been proven to be very sensitive and selective for trace analysis of arsenic and other heavy metal ions for more than a decade [20–24]. Recent technical developments in field deployable electrochemical instruments further enhance the possibility of on-site analysis [25–27]. There are two primary reasons to select the anodic stripping voltammetry (ASV) for the measurement of As(III) and As(V). First, the ASV with a gold coated glassy carbon electrode can be used to measure As(III) selectively in presence of a large excess of As(V) and without interferences from species normally present in groundwater. As(V) can be measured after chemical reduction to As(III) and thus the total inorganic arsenic can be found. Secondly, the technique is inexpensive and can be decentralized for a wider application. Since the present arsenic pollution is widespread and occurring in places where expensive instruments such as atomic absorption spectroscopy (AAS) are prohibitive from the point of cost and logistics, the electrochemical technique is an ideal choice. Finally, the accuracy and sensitivity of the technique is comparable to that of Inductively Coupled Plasma Spectrometry (ICPS), Graphite Furnace and Hydride Generation AAS. We believe the implementation of the technique for the measurement of about 1000 samples in a remote area of Bangladesh shows the utility of the technique and possibly a first of its kind example in application of electrochemical technique for environmental trace analysis.

2. Experimental section

2.1. Apparatus

A Model HQ-2040 (Advanced Analytics, VA, USA) personal computer controlled electrochemical analyzer was used for all voltammetric experiments. This multifunctional computer controlled potentiostat is capable of performing a variety of electrochemical experiments and has a magnetic stirrer controlled by the computer [28,29]. For arsenic analysis the instrument uses a staircase ASV which has been shown to be more sensitive than differential pulse anodic stripping voltammetry (DPASV) [30,31]. A 15 ml glass electrochemical cells with Teflon top and Teflon magnetic stir bar were used throughout the experiment. The Teflon top has holes for a Teflon purging tube and a micropipette tip for standard additions without disturbing the electrodes. A thin gold film coated glassy carbon (3.0 mm diameter) was used as the working electrode. A platinum wire (53 mm long) was used as the counter electrode. The reference electrode was an Ag/AgCl in saturated KCl isolated from the test solution by a porous Vycor junction. Platinum electrode redox potential (E_h) was measured on the same system by the open circuit potential procedure. Groundwater pH for some samples was measured before sample acidification.

A Perkin–Elmer Model 5100 Zeeman-effect atomic absorption spectrometer with a graphite furnace (ZAASGF) and a Model A-60 autosampler were used to validate the well water arsenic concentration. An American Research Laboratory, Model ARL 3500 inductively coupled plasma (ICP) emission spectrometer and a Model VE-IV ultrasonic nebulizer were used for multi-element trace analysis. A Flow Injection HGAAS (Model 210VGP, Buck Scientific, USA) was also used for the validation measurement. Arsenic was also measured by insitu AsH_3 gas generation and subsequent monitoring by a commercial single point arsine monitor (SPMH, Hydride Chemcasette™ Detection System by Zellweger Analytics, Inc., Licolnshire, Illinois) based on the methodology developed by us [32]. The instrument works by measuring the change in color of a proprietary

reagent (silver nitrate as the main component) on a paper tape by reflectance photometry.

2.2. Reagents and chemicals

Primary standards for As(III) were prepared from either high purity As_2O_3 (Aldrich) or reagent grade NaHAsO_3 (Fisher). Primary standards for As(V) were prepared from Na_2HAsO_4 (Fisher). All samples and reagents were prepared in distilled deionized water with HCl (AnalaR). Trace metal grade HCl (Fisher) was used for sample preparation in ZGFAA, ICP and SPMH. Metallic gold foil (min 99.99%) was used for the preparation of Au^{3+} stock solution. Reagent grade Na_2SO_3 (Fisher) was used as the reductant for As(V).

2.3. Methods and procedure

Au^{3+} solution was prepared by dissolving 0.500 g Au in a minimum volume of aqua-regia (2 ml nitric acid then 6 ml HCl dropwise). The solution was carefully heated to reduce the volume to a minimum before spattering. Then 5 ml concentrated HCl was added and diluted to 100 ml in a volumetric flask. The solution was purged with water-saturated nitrogen (99.99% pure) for 10 min to get rid of residual oxidizing impurities such as Cl_2 and NO_2 . The final solution was bright golden yellow in color.

The glassy carbon electrode was polished with a 0.3 μ polishing grade alumina on a fine polishing pad to a mirror finish and rinsed free of adhering alumina particles. The gold deposition solution was prepared by adding 300 μ l of gold stock solution into 12.0 ml of 0.5 M HCl in the electrochemical cell. The solution was then purged with nitrogen for 10 min and a constant nitrogen flow was maintained above the solution to prevent oxygen reabsorption. The gold film deposition was carried out at a deposition potential of -150 mV for 100 s without stirring. These conditions ensured complete reduction of Au^{3+} to metallic Au under a nonsteady state diffusion. The electrode potential was then returned to 500 mV and held there for a minute to ensure complete removal of trace metal impurities from the gold

film. The procedure can be repeated to obtain a shiny gold film on the GC electrode. A dull deposit is not desirable. A mirror underneath the cell was used to observe the bottom of the electrode without taking the GC electrode out of the solution. The electrode was washed with 1.0 M HCl and hung in an empty cell. The deposition solution was stored for future reuse. The shiny gold electrode can be used for more than 20 measurements before the response starts to diminish. Between analyses, the electrode was rinsed with a blank 6.0 M HCl solution to minimize carry over. A new electrode can be prepared by simply wiping off the previous Au-film and following the above procedure.

A 100 mg l⁻¹ As(III) stock solution was prepared by dissolving As₂O₃ in a minimum volume of 1.0 M NaOH solution and then diluted with 1.0 M HCl. Lower concentrations of standards, 50 and 25 mg l⁻¹ As(III), were prepared by sequential dilution of the stock standard.

A flow-chart for arsenic analysis is shown in Fig. 1. Groundwater samples from tubewells (shallow or deep) were collected in a 250 ml high-density polyethylene bottle containing 1.0 ml 32% HCl without a headspace. The tubewell was pressed for 10 min before the sample was collected. All necessary information such as the location, depth, and condition of the tubewell was noted. Samples were analyzed within 2 weeks of collection and some representative samples were preserved in the refrigerator for method intercomparison studies. The sample collection and preservation procedure were very effective in retaining the As(III) and As(V) stable for months [33,34].

In a typical ASV experiment, the following values for the parameters were used: initial potential -150 mV, final potential 500 mV, step potential 5 mV, scan rate 50 mV s⁻¹, initial delay 60 s (deposition time), quiet time delay 30 s, and a stirring rate 600 rpm. The resulting oxidation current was sampled at the end of each staircase step (average of 100 samples collected for 20 ms) and the stripping voltammogram was recorded for further analysis. If the signal was within the analytical range then an aliquot (5.0–20.0 µl) of the As(III) stock was added and another stripping voltammogram was recorded. The same was re-

peated with another aliquot addition. The standard addition procedure just outlined was used for final determination of As(III). Fig. 2 shows typical stripping voltammograms and a standard addition plot. If the sample As(III) concentration was higher than 100 µg l⁻¹, the standard additions showed a small increase in the peak current due to gold film saturation. At a much higher concentration split peaks could appear. In such cases the samples were diluted. For concentrations lower than 10 µg l⁻¹ As(III) deposition time higher than 60 s was used. As(III) concentration below the detection limit of the technique was shown by a background signal and required no further analysis.

The measurement of total inorganic As was done by reducing As(V) to As(III) with SO₂ (g) produced *in situ* by the acid decomposition of Na₂SO₃. After investigating several other reducing

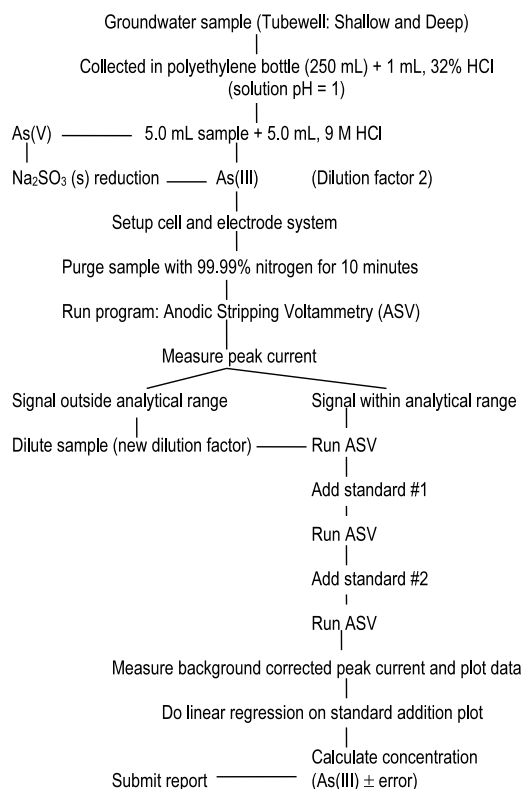


Fig. 1. Flow-chart for analytical measurement of inorganic arsenic in groundwater by ASV.

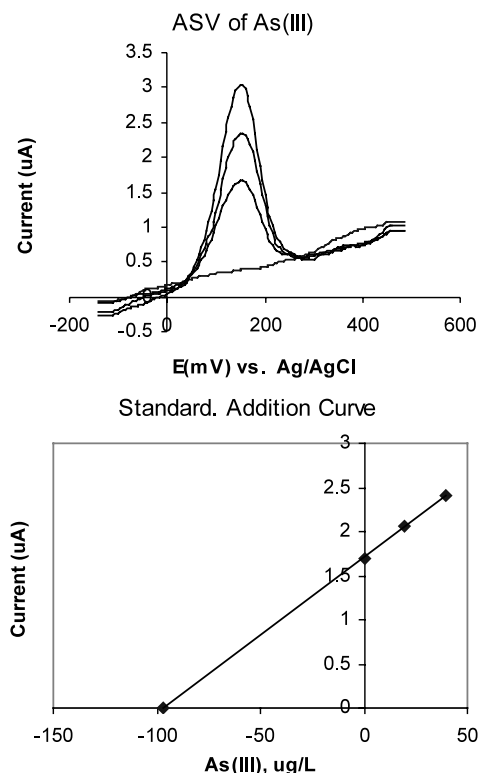


Fig. 2. Typical anodic stripping voltammogram and standard addition plot for the measurement of As(III) in a groundwater sample.

agents (ascorbic acid, hydrazine hydrochloride, and hydrazine sulfate) we found Na_2SO_3 is easier to implement and cost effective. For each 5.0 ml of sample 5.0 ml of 9.0 M HCl and 0.20 g of Na_2SO_3 was used. The solution was heated near boiling with occasional stirring until all excess SO_2 fumes cleared. The accuracy of chemical reduction of As(V) to As(III) was found to be 5–20%. Blank experiment showed no detectable arsenic added in the reduction process.

The analytical performance of the method can be summarized as follows: precision 1–10% relative standard deviation (rsd) of three replicate runs, accuracy 10% rsd (maximum) for $10 \mu\text{g l}^{-1}$ quality control standard, three standard deviation of the signal detection limit $1.2 \mu\text{g l}^{-1}$ at 95% CL at 120 s deposition time, and sample carry over $0\text{--}4 \mu\text{g l}^{-1}$ max. Sample measurement error was calculated from the linear least-squares errors of the standard

addition plot. The system throughput was 20–30 samples per day for As(III) or As(V) and 10–20 samples for both species in the same solution. The low throughput was due to the implementation of standard addition technique and the chemical reduction procedure. However, the most important advantage of ASV is the lowest cost per sample without using or producing any significant toxic substances such as arsine. Work is in progress to increase the throughput by implementing an analytical flow system.

The method described above is a significant improvement over EPA method 7071: arsenic in aqueous samples and extracts by ASV [35]. It is noted that EPA methods are given as general outline of the process where experimental details are left to the users to explore. The reduction procedure in EPA method is also not clear. Although EPA has used direct calibration method it is well known that standard addition is the method of choice to eliminate matrix effect on the analysis. This is true for groundwater and waste-water samples containing minerals and dissolved organic species at different concentrations.

2.4. Sampling locations

To understand the present situation we have measured As(III) in 960 water samples collected from 18 districts covering 71 thanas (small administrative units of a district). A detail geographical locations of the districts listed in Table 1 can be found elsewhere [36]. The samples were collected at random by various nongovernmental organizations and by our own team from 1997 to 1999. A distribution of 215 samples from Kushtia and 50 samples from other districts covering a wide range of As(III) from initial measurements was used to measure total arsenic and thus the concentration of As(V). About 80% of samples were collected from the western part of Bangladesh located west of two major rivers, Padma and Jamuna. The remaining 20% of samples were obtained from three districts in the south eastern region east of Jamuna river known as the Gangetic alluvial plain. It is believed that the majority of these areas are now severely affected by arsenic in the groundwater where patients are identified with arsenicosis.

3. Results and discussion

3.1. Method verification

The ASV was extensively tested against modern methods for the measurement of arsenic. Table 1 shows the results. The first four samples are As(III) and As(V) standards prepared as discussed earlier. Sample 5 is a mixture standard of As(III) + As(V). The ASV experiment shows good agreement with all the standards. The composite standard shows excellent agreement with ZAASGF, FIHGAA and ICP.

We note that groundwater samples studied here are not digested or filtered. Since the groundwater samples were preserved in dilute HCl, and no apparent particulates were observed during extensive studies by ASV, sample filtration or digestion was not necessary. The methodology is also provoked by the fact that groundwater obtained from tubewells are consumed directly without filtration

and, most often, without aeration. Therefore, the present work is relevant to the direct consumption of arsenic species from drinking water.

Four distinct instrumental techniques are used for the validation of our measurement. The first is the ASV which is based on the electrochemical redox reactions, the second is based on the absorption or emission of atomic species (ZAASGF, ICP, and FIHGAA), and the third is based on in-situ arsine generation and molecular absorption spectrometry. However, only ASV is capable of providing direct As(III) speciation information. The agreement between ASV and other techniques are generally within experimental error at concentrations below $100 \mu\text{g l}^{-1}$. The linear dynamic range (LDR) for ASV, FIHGAA, and SPMH is $2\text{--}100 \mu\text{g l}^{-1}$. The LDR for ZAASGF is $2\text{--}40 \mu\text{g l}^{-1}$ and for ICP $16\text{--}200 \mu\text{g l}^{-1}$. For concentrated samples the LDR can be easily achieved by sample dilution. The upper range is somewhat low in AA techniques. The lower limit

Table 1
Method comparison for the measurement of arsenic in groundwater samples

#	Sample description	ASV, As(III)	ASV As(total)	ZAASGF	ICP	FIHGAA	SPMH
1	$10 \mu\text{g l}^{-1}$ As(III)	12 ± 2		11 ± 2	<	12 ± 1	
2	$20 \mu\text{g l}^{-1}$ As(III)	22 ± 2		24 ± 2	23	21 ± 2	
3	$20 \mu\text{g l}^{-1}$ As(V)		19 ± 2	24 ± 2	22	20 ± 1	
4	$50 \mu\text{g l}^{-1}$ As(V)		46 ± 4	50 ± 3	54	49 ± 2	
5	$50 \mu\text{g l}^{-1}$ As(III) + $50 \mu\text{g l}^{-1}$ As(V)	55 ± 4	93 ± 5	96 ± 2	98	102 ± 5	
6	Groundwater	83 ± 1	188 ± 12	154 ± 4	180	190 ± 5	
7	Groundwater	24 ± 3	40 ± 2	31 ± 3	40	42 ± 2	
8	Groundwater	27 ± 0.2	32 ± 6	22 ± 6	34	36 ± 2	18
9	Groundwater	38 ± 8	49 ± 2	33 ± 4	30	52 ± 2	35
10	Groundwater	33 ± 8	54 ± 7	58 ± 4	56	58 ± 2	58
11	Groundwater	242 ± 15	282 ± 8	170 ± 4	245	290 ± 5	
12	Groundwater		296 ± 10	320 ± 10	310	306 ± 4	285

All Concentrations are in $\mu\text{g l}^{-1}$. Explanation of terms and conditions: ASV, anodic stripping voltammetry, As(tot) is the total arsenic based on the reduction of As(V) to As(III). With ASV samples were diluted at least twofold. Errors shown in ASV measurements are calculated from the linear least-squares fitting of the standard addition plot at 99.5% confidence level. ZAASGF: Zeeman atomic absorption spectroscopy with graphite furnace. Wavelength 193.7 nm, slit 0.7 low, integration time 6 s and three replicates for standards and samples. Linear concentration calibration range: $0\text{--}40 \mu\text{g l}^{-1}$ arsenic, slope, 0.0039, intercept, 0 and r^2 , 0.99979. Samples were not diluted before measurement. $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ is used as matrix modifier. ICP: Inductively Coupled Plasma Spectroscopy. Applied Research Laboratory Model 3500 with VE1-V Ultrasonic Nebulization. Samples were diluted 5–10-fold depending on the concentration. The results are the average of duplicate runs. Calibrations were performed with 46 and $100 \mu\text{g l}^{-1}$ composite standards. The method detection limit was $16 \mu\text{g l}^{-1}$. FIHGAA: Flow Injection Hydride Generation Atomic Absorption Spectroscopy (Model 210VGP, Buck Scientific, USA). Initial sample measurement above $100 \mu\text{g l}^{-1}$ was diluted 2–5-fold. Measurement errors are ± 1 stdev. SPMH: Single Point Monitor Hydride Chemcassette™ Detection System. The calibration slope = 564.6 ppbv-s/ppb and intercept = -139 ppbv-s were used to calculate arsenic concentration. Samples were diluted fivefold.

Table 2
Percent of total samples containing As(III) in the concentration ($\mu\text{g l}^{-1}$) range as indicated in the first row

#	District	# of Thana	Total sample	<3	4–9	10–49	50–99	100–499	> 500
1	Kushtia	6	269	29.0	10.4	24.2	17.8	15.2	3.3
2	Meherpur	2	30	20.0	6.7	16.7	26.7	26.7	3.3
3	Chuadanga	4	39	15.4	5.1	48.7	20.5	10.3	0.0
4	Pabna	9	77	70.1	6.5	6.5	5.2	11.7	0.0
5	Jessore	8	85	25.9	10.6	31.8	18.8	11.8	1.2
6	Narail	3	26	23.1	0.0	19.2	11.5	46.2	0.0
7	Magura	4	37	70.3	0.0	8.1	18.9	2.7	0.0
8	Jhenidah	6	59	39.0	20.3	23.7	13.6	0.0	3.4
9	Faridpur	8	72	38.9	5.6	12.5	19.4	23.6	0.0
10	Rajbari	4	39	64.1	5.1	10.3	7.7	7.7	5.1
11	Bagerhat	5	45	2.2	4.4	20.0	22.2	42.2	8.9
12	Khulna	5	22	22.7	31.8	13.6	18.2	9.1	4.5
13	Chandpur	1	25	12.0	0.0	0.0	0.0	44.0	44.0
14	Lakshipur	1	14	0.0	0.0	7.1	21.4	64.3	7.1
15	Noakhali	1	9	0.0	0.0	11.1	33.3	33.3	22.2
16	Chittagong	1	18	0.0	5.6	22.2	16.7	55.6	0.0
17	Nilfamari	2	63	36.5	23.8	22.2	14.3	3.2	0.0
18	Lalmonirhat	1	31	58.1	35.5	6.5	0.0	0.0	0.0
	All	71	960	29.3	9.5	16.9	15.9	22.6	5.7

is determined by the method detection limit. While a direct standard calibration was used for AA techniques, a standard addition procedure was used with ASV. Therefore, any significant matrix effects at high concentration may have been manifested in AA techniques, ZAASGF in particular. The rsd in ASV for As(III) and As(V) are 0.7–20% and 4–14%, respectively. The measurement errors appear to have no systematic trend with respect to the concentration and therefore are purely stochastic in nature. Since electrochemistry is very dependent on the surface characteristic of the working electrode, we suspect the measurement error is affected by the purity of the gold film and the run-to-run homogeneity of the arsenic deposit. However, electrochemical interference was nonexistent from other redox couples including $\text{Fe}^{3+}/\text{Fe}^{2+}$, which may be present in groundwater at $1\text{--}10\text{ mg l}^{-1}$. The ZAASGF showed an error range 2–27% rsd. The SPMH and ICP have errors between 2 and 10% rsd with SPMH having the most variability. The FIHGAA has the best precision (rsd 1–10%) and accuracy. The error range encountered in this study is not unusual. An extensive interlaboratory comparison of two atomic spectroscopic techniques (HGAA

and GFAA) showed precision of 0–25% rsd and accuracy of 0–15% rsd at 95% confidence level [37]. In addition, in 1992 USEPA notice on the phase V regulation sets the accuracy limit of $\pm 30\%$ for GFAAS based on an analysis of performance evaluation from several studies of very low concentrations ($2\text{--}10\ \mu\text{g l}^{-1}$) of arsenic in drinking water [38]. Considering these, the ASV technique is well within the EPA's evaluation range. Most importantly, in a recent first-phase interlaboratory comparison studies the ASV technique has performed very well and has been recommended for routine sample analysis [39].

3.2. As(III) distribution

The concentration distribution of arsenic in 18 districts is shown in Table 2. Geographically, the first 12 districts are situated in the southwestern part of Bangladesh and the last two districts are in the northwestern part. Districts 13–16 are located in the middle southern most regions primarily in the confluence of deltaic plateau. The overall distribution of As(III) is shown at the bottom of Table 2. It shows 60% of the samples has $10\ \mu\text{g l}^{-1}$ or more As(III). About 44% of the

samples has $50 \mu\text{g l}^{-1}$ or more As(III). These results may be compared with that of 73% of samples (22 003 analysis) having total arsenic above $10 \mu\text{g l}^{-1}$ and 53% above $50 \mu\text{g l}^{-1}$ [40]. Our results are low because we have analyzed only As(III). About 6% of samples have $500 \mu\text{g l}^{-1}$ or more As(III). Table 2 shows Kushtia has the highest number of samples analyzed and thus determines the modal tendency of the distribution. This is further illustrated in Fig. 3 by the distribution of As(III) for four districts. The districts are located farthest from Kushtia and represent four distinct geologic regions. The overall distribution shown in Table 2 is very similar to that of Kushtia. Table 2 shows that the least affected areas are Lalmonirhat and Nilfamari situated in the northwestern part of Bangladesh. The most affected areas are Chandpur, Lakshipur, Noakhali, Bagerhat, and Chittagong—generally located in the southern alluvial plain. The highest concentration of $1900 \mu\text{g l}^{-1}$ As(III) was found in Lakshipur. Analyzing spatial data (thana level data) shows that arsenic contamination is localized and not uniformly distributed.

Because the number of samples analyzed is small for most districts (except Kushtia) the conclusion on As(III) distribution should be taken as provisional.

3.3. As(total)–As(III) distribution

About 238 samples were analyzed for both As(III) and As(total) of which 215 were collected from Kushtia and 23 from Lakshipur and Noakhali. Fig. 4 shows the As(III)–As(total) distribution. The distribution is primarily confined within upper and lower lines showing 50 and 100% As(III), respectively. Actual data shows 30–98% of the total arsenic in the form of more toxic As(III). Fractional distribution of As(III) for more localized Kushtia data shows 40% As(III) in 34% of the samples and 80% As(III) in 5% of the samples as shown in Fig. 5. The fractional distribution with significant weighting towards high percent occurrence may indicate a progressive reduction process with a single source or a single mechanism for the formation of As(III). This may have already happened in the southern alluvial

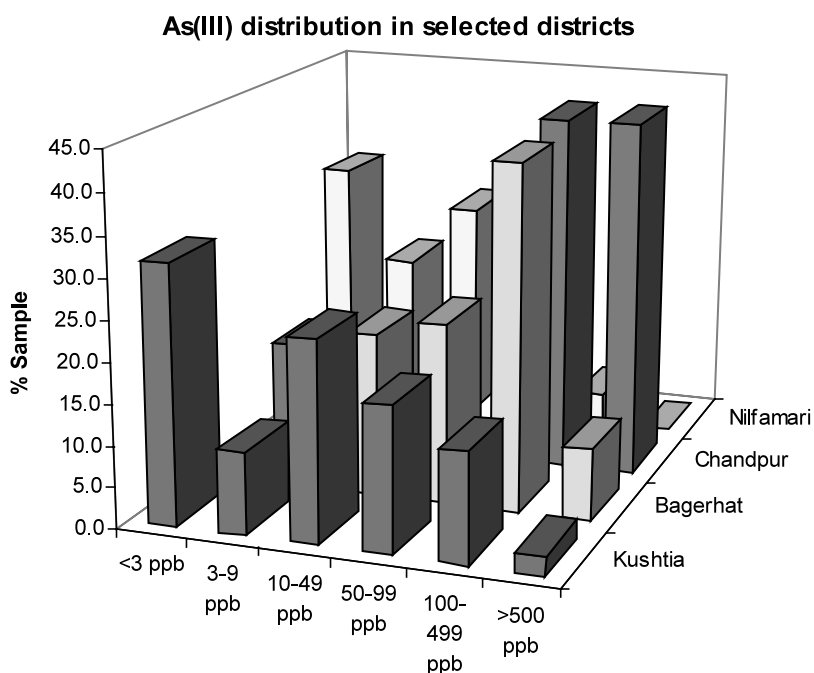


Fig. 3. Distribution of As(III) in four representative districts of Bangladesh.

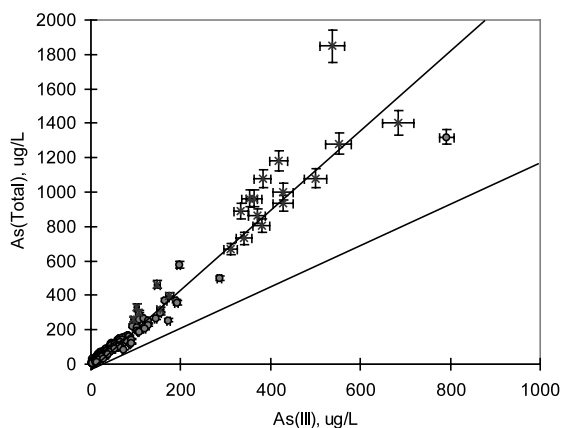


Fig. 4. As(III)–As(total) distribution. The upper and lower lines are showing 50 and 100% As(III), respectively. (o), Kushtia; (x), Lakhipur and Noakhali.

plain, such as Chandpur, Lakshipur, Noakhali and Chittagong where 90% of the samples has more than $10 \mu\text{g l}^{-1}$ of As(III). These are already designated as one of the most affected areas. The current arsenic crisis is possibly far more serious than previously thought, because As(III) is the most toxic form of arsenic present in the groundwater at a much higher level than normally expected on the basis of thermodynamic stability of inorganic arsenic species [41]. Clearly, a reduction process is responsible for the conversion of As(V) to As(III) [42]. The presence of such a high concentration of As(III) and its widespread occur-

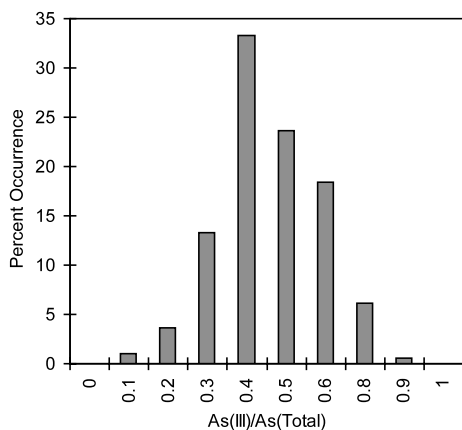


Fig. 5. Histogram showing fractional distribution of As(III) in Kushtia.

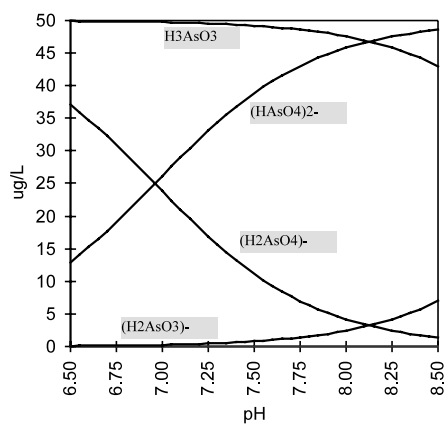


Fig. 6. Distribution of major inorganic arsenic species in groundwater as a function of pH.

rence in groundwater of Bangladesh is not unique. Similar high As(III) resulted from natural process was found in wells in Missouri river alluvium [42] and alluvial aquifers in Vietnam [43].

Assuming $50 \mu\text{g l}^{-1}$ each of As(III) and As(V), we calculate the distribution of most stable oxoanion arsenic species as a function of groundwater pH values. This is shown in Fig. 6. Clearly, three major species, H_3AsO_3 , H_2AsO_4^- , $\text{H}_2\text{AsO}_4^{2-}$, are evident. Even at 50% distribution level the concentration of H_3AsO_3 remains relatively unchanged at groundwater pH values (6.9–8.0) as the predominant species. Whereas the distribution of H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$ are significantly depended on the pH. The E_h and pH measurements of 50 samples collected from Kushtia showed an average value of $54 \pm 5 \text{ mV}$ and 7.1 ± 0.1 , respectively. Indeed, these values on the E_h –pH diagram for As at 25°C and 1 atm with total arsenic 10^{-5} M and sulfur 10^{-3} M indicate H_3AsO_3 as the major species [44].

3.4. Depth distribution and speciation

In this study we have recorded the depth of the tubewells where available. The well depth is an indication of the location of the aquifer. The depth distribution of fractional As(III) for Kushtia is shown in Fig. 7. The dome shaped distribution indicates that 40–60% of As(III) is located within 100–200 ft deep aquifers. About 40% of

the samples were found in this depth region with $50 \mu\text{g l}^{-1}$ or more As(III). Based on the average distribution of As(III)/As(total), about 50% of the samples was found in the same region with As(total) concentration above $50 \mu\text{g l}^{-1}$. This is also consistent with findings based on the larger data set of SOES [40]. It should be noted that As(III) above $50 \mu\text{g l}^{-1}$ was also found in 80% cases below 200 ft. Fig. 7 indicates that major aquifers in this region are located around 100 and 200 ft depths. In deep tubewells, above 200 ft, As(III)/As(total) are very similar to the average. Could this mean a leakage of the upper aquifer and thus a source of contamination of deep tubewells remains an open question. The prevailing notion is that deeper aquifers are free from arsenic, therefore, attempts to sink deeper tubewells may not be well founded.

Clearly, the aquifers are significantly anoxic and reductive in nature. If the As(III)/As(total) is an indicator of an equilibrium quotient for a chemical process which has not reached the equilibrium, the fractional distribution of As(III) may still reach a constant value in the future. There are some indications of this process from the average value of As(III)/As(total) from Figs. 6 and 7. Both show a possible single source or a

single mechanism for the reduction process. It has been reported that the presence of unusually high levels of As(III) in the groundwater of Bangladesh is possibly due to the reductive dissolution of hydrous ferric oxide underground [45,46]. Whether the redox mechanism has significant contribution from iron reducing bacteria is yet to be found [47].

4. Conclusion

This work shows that ASV is a viable low cost instrumental technique for the measurement and speciation of arsenic in drinking water at $\mu\text{g l}^{-1}$ concentration. The method is particularly convenient to measure the most toxic As(III) at low $\mu\text{g l}^{-1}$ level even in the presence of high concentration of As(V). The use of this technique for the analysis of 960 samples in Bangladesh showed more than 64% of the samples have $10 \mu\text{g l}^{-1}$ or more As(III) and 30–98% of the total inorganic arsenic exists in very toxic As(III) species. Therefore, in terms of immediate toxicity the poisoning of drinking water by arsenic is probably more severe than previously believed. The depth profile of As(III) in Kushtia shows that wells 100–200 ft deep are most contaminated. The occurrence of As(III) also indicates that aquifers are reductive in nature and the dissolution of As(V) to more mobile As(III) as H_3AsO_3 species predominate. We suggest the use of As(III)/As(total) as a geochemical indicator for arsenic mobilization.

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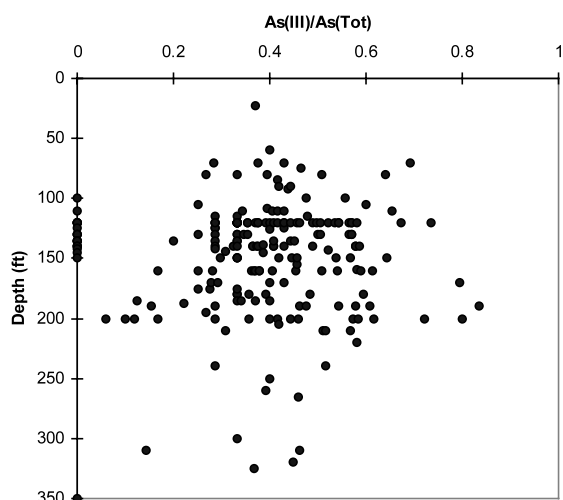


Fig. 7. Depth speciation of fractional As(III) in Kushtia.

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