



Voltammetric Study of Arsenic (III) and Arsenic (V) in Ground Water of Hajigonj and Kalkini in Bangladesh

Samir Chandra Paul, Mohammad Arifur Rahman, Nur-E-Alam Siddique
and A. M. Shafiqul Alam*

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

Abstract

The speciation of arsenic in groundwater samples using Square Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Anodic Stripping Voltammetry (DPASV) and Normal Pulse Anodic Stripping Voltammetry (NPASV) are described. Good resolution of the species, arsenic (III) and arsenic (V) is achieved using SWASV. The reliability of the methods was checked by analyzing the total arsenic content of the samples by Hydride Generation Atomic Absorption Spectrophotometer and by analyzing prepared controlled laboratory standard solution. Since this technique is comparatively cheaper than other available techniques it could be a better analytical technique for arsenic speciation from water. In this study, the assessment of inorganic arsenic species in ground water of Kalkini (Madaripur) and Hajigonj (Chandpur) is reported. It shows that arsenic content in water in different locations is irregular. Most of the locations contain higher level of As(III) than As(V). The highest concentration of arsenic is found in Anayetnagar ($554.46 \pm 0.07 \mu\text{g/L}$) of Kalkini and Raichar ($562 \pm 0.50 \mu\text{g/L}$) of Hajigonj. However, the level of total arsenic and As(III) of most of the villages of the study areas are more than the WHO guideline value ($50\mu\text{g/L}$). Therefore a proper monitoring process should be evolved along with the development of methods to keep the water free from arsenic.

Introduction

Arsenic is ubiquitous in the environment, being naturally present in soil, air, water and food, and concentrations may be increased by anthropogenic contamination [1]. It is present in the environment in a number of different inorganic and organic chemical forms due to its participation in complex biological and chemical process. Some of the most important arsenic species from a toxicological perspective include the two oxidation states As(III), As(V), monomethylarsenic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine and arsenocholine [2].

In recent years, the presence of high levels of arsenic in ground water, the main source of drinking water in many countries around the world, has drawn attention of the scientific communities. Moreover, contamination of food chain by arsenic contaminated water is another threat [3]. Numerous recent investigations have demonstrated that arsenic constitutes a serious health risk spot in Bangladesh

[2-6]. Bangladesh, a country in south Asia with a population of about 150 million, is one of a number of countries that has arsenic contamination in its groundwater, which results from the underlying mineralogy and geology of the area. Arsenic contamination has been reported in groundwater in 41 out of 64 districts in Bangladesh [3]. About 61% of the water analysed from tubewells has arsenic content above 0.01 mg/L [4]. The average concentration of arsenic in contaminated water is about 0.26 mg/L with a maximum level of 0.83 mg/L. This is significantly higher than the World Health Organization (WHO) maximum permissible limit in drinking water which is 0.05 mg/L [7].

Moreover, Arsenic shows toxicity and chemical property depending on its oxidation state and physicochemical forms. Inorganic arsenic is known to be more toxic than organic ones, and As^{3+} is reported at least ten times more toxic than As^{5+} [8]. Thus it is important to determine each of arsenic species rather than the total amount. Rasul et al., and Hussam et al.,

*Corresponding Author: amsalam2004@yahoo.com

studied the As (III) and As (V) with the aid of anodic stripping voltammetry (ASV) and other metals with AASGF-Z (Zeeman Effect-Atomic Absorption Spectrometer with Graphite Furnace) from groundwater of Kustia, Bangladesh [9,10]. But there is no work has been reported with study of the As(III), As(V) with Square Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Anodic Stripping Voltammetry (DPASV) and Normal Pulse Anodic Stripping Voltammetry (NPASV) at Hajigonj and Kalkini of Bangladesh which are most endemic areas. Therefore, speciation of arsenic rather than quantification of total arsenic in drinking water present in groundwater are necessary.

Speciation of arsenic has been performed with different hyphenated techniques, often the coupling of ion chromatography or liquid-chromatography to detection system like: direct UV detection, direct coupling to atomic absorption spectrometry, AAS, on-line hydride generation AAS (Hg-AAS), ICP atomic emission spectrometry (ICP-AES), ICP mass spectrometry [11-13]. These techniques are very expensive. Several reports have appeared on electrochemical stripping procedures for the determinations of arsenic [9, 10, 14]. The instrumentation required is relatively simple and generally the cost is far less than that required for the other techniques. Another advantage of electrochemical techniques is their ability to distinguish between the different oxidation states of arsenic. The anodic stripping voltammetry is very sensitive [14] and compared with expensive multielement analysis techniques like ICP-MS, is an economical procedure for trace determination of arsenic down to the $\mu\text{g/l}$ level.

In the present work, there are three different electroanalytical methods such as Square Wave Anodic Stripping Voltammetry (SWASV), Differential Pulse Anodic Stripping Voltammetry (DPASV) and Normal Pulse Anodic Stripping Voltammetry (NPASV), were used for the determination of arsenic with speciation to satisfy the lack of proper analytical techniques and implement such analytical methods that can provide accurate and interference free measurements of arsenic at the $\mu\text{g/l}$ levels of concentrations in water of Hajigonj and Kalkini of Bangladesh.

Experimental

The study area

Tubewell water was collected from nine villages of Hajigonj and nine villages of Kalkini. Hajigonj Thana at Chandpur district is 53 kilometers away from Comilla district and Kalkini Thana at

Madaripur district is 260 kilometer away from Dhaka city.

Sampling

Tube well water was collected in polythene containers which were washed before collecting samples with 5% HNO_3 , distilled de-ionized water and finally with the tube well water at the sampling sites for several times. The information about the depth of the tube well, year of installation and also red or green marked were collected from the local inhabitants by supplying the questions-answers sheets.

Sample preparation

The samples collected from different points were filtered with a microfilter paper under vacuum and preserved in acid (1ml conc. HCl per 100ml of water sample). For the measurements of total arsenic, the samples were mixed with concentrated HCl and Na_2SO_3 (s) (10ml sample + 10ml conc. HCl + 30-40 mg Na_2SO_3 (s)) in an acid clean Pyrex glass electrolysis cell and heated at $70-80^\circ\text{C}$ for 20-30 minutes without stirring, then 15 minutes with stirring and also 15 minutes with purging nitrogen with stirring until all SO_2 fumes cleared. The sample was then cooled to room temperature and was thus made ready for the measurements of the concentration of total arsenic [14].

Preparation of stock standard solutions

Standard 1000 mg/L stock solutions of As^{3+} and As^{5+} were prepared by dissolving As_2O_3 (Merck, Germany, Analytical grade) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Germany, Analytical grade) in deionized water respectively. These solutions were made acidic by the addition of 2-3 ml conc. HCl acid. Fresh standard solutions of lower concentrations were made from the stock solution at the beginning of the everyday experiment.

Analytical procedure for quantification of As^{3+} and As^{5+}

At first the gold electrode was made shiny yellow, almost scratch free surface by polishing with fine alumina powder ($0.3\mu\text{m}$) on wet polishing cloth. Then the electrode was cleaned with deionised water and then 1M HCl and also stored in 6M HCl. For measurements of As^{3+} , the stair bar was put into the cell and the cell was filled with 10 ml sample and 10 ml 6M HCl [9]. The solution was purged for 10 minutes with nitrogen. All the electrodes were inserted and tapped off to remove any bubbles from them. A computerized electrochemical system, model HQ-2040 by *Advanced*

Analytics, USA was used for the analysis. The deposition potential (Initial potential), accumulation or deposition time (Initial delay), quit time delay is -150mV, 120sec. and 30 sec. respectively. The run replication (number of addition) is 3. In these analytical measurement procedures two standard additions were performed and corresponding currents were measured after subtraction of background current. The signal current was then plotted against concentration. The concentration of arsenic was calculated from the slope of the regression line drawn through the points using software sigma plot based on MS-Excel. Total arsenic was determined by same procedure after treatment of sample with NaHSO_3 as described in sample preparation method. As^{5+} was evaluated with subtraction of As^{3+} from total arsenic [14].

Results and Discussion

Pulse voltammetric techniques, introduced by Barker and Jenkin [15], are aimed at lowering the detection limits of voltammetric measurements. By substantially increasing the ratio between the faradaic and nonfaradaic currents, such techniques permit convenient quantification down to the 10^{-8}M concentration level. Because of their greatly improved performance, modern pulse techniques have largely supplemented classical polarography in the analytical laboratory. Among the voltammetric techniques Normal Pulse Voltammetry (NPV), Differential Pulse Anodic Stripping Voltammetry (DPASV), Square Wave Voltammetry (SWV) was checked to evaluate the sensitivity for the trace arsenic analysis and speciation from groundwater.

Analytical comparison between SWV, DPV and NPV

The SWAS, DPAS and NPAS voltammograms of arsenic (As^{3+}) for a 50 ppb standard solution at solid gold electrode (Au- button) are demonstrated in Fig. 1. Out of three ASV techniques in use, NPASV is considered to be least sensitive and selective method due to its highest signal to background ratio. In NPV, the non-faradaic current could not be avoided completely because the current is sampled once at the end of pulse amplitude. This charging current increases the signal current and for this reason NPV shows high signal current with respect to SWV and DPV where the current is sampled twice, just before the pulse application and late pulse life. Although in NPV, small amount of charging current is present it is also good sensitive method for As^{3+} analysis. Out of these techniques used for arsenic analysis, the SWASV technique is most sensitive and selective electroanalytical method because of its ability to enhance the analytical signal by removing non-faradaic

current. So less time is required for arsenic analysis and ultra trace analysis can be easily performed with this method. However, among these methods DPASV shows moderate signal for arsenic but it is also a sensitive method for arsenic analysis.

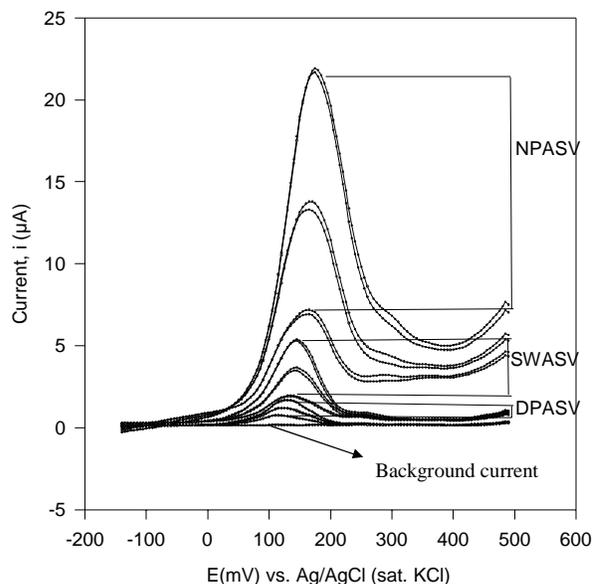


Figure 1: Comparison between three different electroanalytical methods for As^{3+} (same concentration) at solid gold electrode.

Speciation of arsenic in ground water

It is reported that shallow aquifer layer is contaminated with arsenic in almost all of the districts of Bangladesh (DPHE-BGS, 2000). In this study, arsenic level is determined in Hajigonj (Chandpur) and Kalkini (Madaripur) two contaminated areas of Bangladesh.

The different species of arsenic (As^{3+} and As^{5+}) content of ground water samples from different locations of the study area was measured with three different electroanalytical methods (SWASV, DPASV and NPASV) and the data thus obtained are represented in the Table 2 and Table 3. From the results, it is clear that the distribution of arsenic is not regular rather scattered due to the spatial variation. This is because of the variation in the depth of tube wells, amount of water withdrawn and also the geological phenomenon. In Hajigonj, the level of As^{3+} ranges from 48.19 to 285.28 $\mu\text{g/L}$. Among all the water samples collected from the nine different villages of Hajigonj, the highest arsenic (III) concentration was found in Raichar (285.28 $\mu\text{g/L}$) and the lowest was in Toraghor (48.19 $\mu\text{g/L}$). The value of As^{5+} is also the lowest in Satbaria (40.05 $\mu\text{g/L}$) and the highest in Raichar (276.95 $\mu\text{g/L}$). However, all of the

water samples contain total arsenic above the WHO guide line value (50 µg/L).

The level of As³⁺ ranges from 26.91 to 286.0 µg/L in Kalkini. Among the nine water samples collected from the nine different villages of Kalkini, the highest arsenic(III) concentration was found in

Anayetnagor (286.0µg/L) and the lowest was in Charluxmi (26.91µg/L). The lowest value of As⁵⁺ is in Shadipur (26.10µg/L) and the highest in Anayetnagor (268.46µg/L). Most of the water samples contain total arsenic above the WHO guide line value (50 µg/L).

Table 1. Concentration of As³⁺ and As⁵⁺ in ground water of the study area, Hajigonj (Chandpur)

Sample no.	Sampling location	Depth of tube wells	Methods	Conc. of As ³⁺	Conc. of total As (As ³⁺ + As ⁵⁺)	Conc. of As ⁵⁺
		(feet)		(µg/L ± SD)	(µg/L ± SD)	(µg/L)
1	Satbaria	90	SWASV	80.73 ± 0.05	120.78 ± 0.09	40.50
			DPASV	72.53 ± 0.12	119.90 ± 0.16	47.37
			NPASV	74.58 ± 0.70	116.54 ± 0.30	41.96
2	Khalpara	100	SWASV	72.71 ± 0.07	118.67 ± 0.70	45.96
			DPASV	76.56 ± 0.09	123.09 ± 0.17	46.53
			NPASV	78.75 ± 0.06	115.43 ± 0.18	36.68
3	Bolakhhal	140	SWASV	197.09 ± 0.21	320.87 ± 0.01	123.78
			DPASV	198.94 ± 0.08	307.27 ± 0.06	108.33
			NPASV	190.06 ± 0.09	312.12 ± 0.13	122.06
4	Bakila	100	SWASV	80.24 ± 0.30	129.45 ± 0.07	49.21
			DPASV	70.80 ± 0.70	115.56 ± 0.06	44.76
			NPASV	72.76 ± 0.16	121.49 ± 0.18	48.73
5	Raichar	120	SWASV	285.28 ± 0.90	562.23 ± 0.50	276.95
			DPASV	288.33 ± 0.60	594.53 ± 0.13	306.20
			NPASV	203.43 ± 0.23	437.60 ± 0.23	243.17
6	Uchaa gram	140	SWASV	276.57 ± 0.04	380.89 ± 0.60	104.32
			DPASV	296.34 ± 0.30	389.60 ± 0.30	93.26
			NPASV	280.98 ± 0.50	381.26 ± 0.04	100.28
7	Dherra	100	SWASV	83.56 ± 0.40	140.43 ± 0.40	56.87
			DPASV	85.90 ± 0.30	145.87 ± 0.30	59.97
			NPASV	84.37 ± 0.13	143.59 ± 0.60	59.22
8	Toraghor	70	SWASV	48.19 ± 0.70	94.54 ± 0.30	46.35
			DPASV	46.47 ± 0.15	91.01 ± 0.19	44.54
			NPASV	41.58 ± 0.50	82.92 ± 0.50	41.34
9	Shendra	110	SWASV	120.27 ± 0.20	209.76 ± 0.50	89.49
			DPASV	121.68 ± 0.40	209.0 ± 0.40	87.32
			NPASV	110.10 ± 0.14	187.23 ± 0.16	77.13

No. of analysis (n=3)

Table 2. Concentration of As³⁺ and As⁵⁺ in ground water of the study area, Kalkini (Madaripur)

Sample no.	Sampling location	Depth of tube wells	Methods	Conc. of As ³⁺	Conc. total As (As ³⁺ + As ⁵⁺)	Conc. of As ⁵⁺
		(feet)		(µg/L ± SD)	(µg/L ± SD)	(µg/L)
1	Charbivagdi	120	SWASV	166.29 ± 0.21	306.51 ± 0.05	140.22
			DPASV	161.17 ± 0.03	299.59 ± 0.09	138.42
			NPASV	166.64 ± 0.08	287.26 ± 0.13	120.62
2	Dharichar	90	SWASV	51.97 ± 0.12	98.20 ± 0.12	46.23
			DPASV	41.55 ± 0.30	89.67 ± 0.50	48.12
			NPASV	42.75 ± 0.40	72.81 ± 0.80	30.06
3	Charluxmi	70	SWASV	32.53 ± 0.08	47.59 ± 0.07	15.06
			DPASV	32.40 ± 0.10	51.84 ± 0.14	19.44
			NPASV	26.91 ± 0.14	42.42 ± 0.30	15.51
4	Shadipur	80	SWASV	75.96 ± 0.16	102.06 ± 0.80	26.10
			DPASV	95.16 ± 0.06	126.77 ± 0.17	31.61
			NPASV	82.16 ± 0.09	102.52 ± 0.07	20.36
5	Kashimpur	70	SWASV	46.30±0.70	76.27 ± 0.15	29.97
			DPASV	35.52±0.12	69.56 ± 0.19	34.04
			NPASV	30.60±0.15	64.02 ± 0.10	33.42
6	Shikar mangol	120	SWASV	110.71±0.05	197.31 ± 0.07	86.60
			DPASV	110.11±0.07	190.61 ± 0.40	80.50
			NPASV	89.96 ± 0.40	156.22 ± 0.08	89.96
7	Khishnanagor	70	SWASV	53.80 ± 0.50	76.24 ± 0.09	22.44
			DPASV	47.52 ± 0.09	67.76 ± 0.40	20.24
			NPASV	39.68 ± 0.08	51.72 ± 0.05	12.04
8	Alipur	120	SWASV	126.18 ± 0.4	186.20 ± 0.20	60.02
			DPASV	97.44 ± 0.07	160.51 ± 0.70	63.07
			NPASV	86.46 ± 0.23	138.90 ± 0.04	52.44
9	Anayet nagor	160	SWASV	286.0 ± 0.14	554.46 ± 0.07	268.46
			DPASV	275.45 ± 0.16	539.40 ± 0.20	263.95
			NPASV	268.21 ± 0.02	542.40 ± 0.09	274.19

No. of analysis (n=3)

The variation of arsenic concentration with depth of the different tube wells is presented in Table 1 and Table 2. It was found that the concentration of total arsenic was increased with the increase of depth within this range of 70 to 160 ft. This indicates high percentage of water was withdrawn from these aquifers. Moreover, it is interesting that the concentration of As (III) and As (V) varied with the depth of the tube well. This may be due to the change of geology with the variation of depth of soil. Hussam et al., [10] found the

concentration of As (III) and As (V) was present as AsO₃³⁻ (0.712 mg/l) and AsO₄³⁻ (0.973 mg/l) in groundwater at Kustia respectively [10].

From the Table 1 and Table 2, it is noticed that most of the locations of Kalkini and Hajigonj contain higher level of As(III) than As(V). This observation implies that more inorganic arsenic in ground water present in reduced form.

Table 3. Concentration of arsenic in water sample of manikgonj considered as controlled area (SWASV method).

Sample no.	Locations	Conc. of As ³⁺	Conc. of total As (As ³⁺ + As ⁵⁺)	Conc. of As ⁵⁺
		($\mu\text{g/L} \pm \text{SD}$)	($\mu\text{g/L} \pm \text{SD}$)	($\mu\text{g/L}$)
1	Nabagram	14.43 \pm 0.05	24.12 \pm 0.02	9.69
2	Khilinda	9.02 \pm 0.6	16.45 \pm 0.13	7.43
3	Jagir	10.98 \pm 0.82	19.76 \pm 0.09	8.78
4	Macshimul	8.12 \pm 0.7	19.67 \pm 0.41	11.55

No. of Analysis (n=3)

Table 4. Validation of results with HG-AAS with developed anodic stripping voltammetry

HG-AAS	Methods			Variation with HG-AAS			
	SWASV	DPASV	NPASV	SWASV	DPASV	NPASV	Controlled Lab. Standard
	($\mu\text{g/L}$)			($\%$)			
125.0 \pm 1.20	119.90 \pm 0.16	116.54 \pm 0.30	120.78 \pm 0.09	4.08	6.78	4.22	8.25
95.4 \pm 1.50	98.20 \pm 0.12	89.67 \pm 0.50	72.81 \pm 0.80	2.93	6.02	23.68	9.50
120.5 \pm 2.20	118.67 \pm 0.70	123.09 \pm 0.17	115.43 \pm 0.18	1.51	2.14	4.20	8.35

No. of analysis (n=3)

Comparison of the endemic areas with the controlled area

The water samples of Manikgonj which was considered as a controlled area (Free from arsenic contamination) were also analysed with SWASV method as presented in Table 3. The average value of As content in this area was found 20 $\mu\text{g/L}$. On the other hand, the average As contents in different locations of the study areas are about 10 times higher than the average content of the controlled area.

Validation of the results by HG-AAS

To validate the results obtained from the electroanalytical method, Few water samples were analysed by HG-AAS. It was observed that the results obtained by the electroanalytical methods were closed to results obtained by the HG-AAS method. This indicates that the results obtained by the developed electroanalytical methods were effective to analyse arsenic from the groundwater where the variation of results between HG-AAS and electroanalytical method was about 1.5-9.5%.

Conclusion

From the study of the three electroanalytical methods (SWASV, DPASV and NPASV), the SWASV technique is most selective and suitable electroanalytical method. This method could be a better analytical technique for arsenic speciation from water. Moreover this technique is comparatively cheaper than other available methods. The results obtained in this study have been compared with the value of unaffected area (Manikgonj). The observations show that arsenic content of the study area in ground water about 10 times higher than the average content of the controlled area. The total arsenic content and arsenic (III) in water is higher than the WHO guide line value ($50\mu\text{g/L}^{-1}$). So, arsenic contamination in ground water of the study areas is in alarming proportions. Therefore, a proper monitoring process should be evolved along with development of methods to keep the water free from arsenic.

References

1. M. C. Villa-Logo, E. Rodriguez, P. L. Mahia, M. S. Mnuiategui and D. P. Rodriguez, *Talanta*, 57 (2002) 741.

2. S. W. Al Rmalli, P. I. Haris, C. F. Harrington and M. Ayub, *Sci. Total Environ.*, 337 (2005) 23.
3. M. A. Hasan, K. M. Ahmed, O. Sracek, P. Bhattacharya, M. V. Bromssen, S. Broms, J. Fogelstrom, M. L. Mazumder and G. Jacks, *Hydrology J.* (2007), DOI:10.1007/s10040-007-0203-z .
4. M. Ali and S. A. Tarafdar, *J. Radional Nucl Chem.*, 256 (2003) 297.
5. M. G. M. Alam, E. T. Snow and A. Tanaka, *Total Environ.*, 308 (2003) 83.
6. H. K. Das, A. K. Mitra, P. K. Sengupta, A. Hossain, F. Islam and G. H. Rabbani, *Enviro Int.*, 30 (2004) 383.
7. WHO. Vol. 224, Geneva: World Health Organization., (2001).
8. DCHT, Arsenicosis in Bangladesh, Dhaka Community Hospital Trust, February. Dhaka, Bangladesh., (1998).
9. S. B. Rasul, A. K. M. Munir, Z. A. Hossain, A. H. Khan, M. Alauddin and A. Hussam, *Talanta.*, 58 (2002) 33.
10. A. Hussam, M. Habibuddowla, M. Alauddin, Z. A. Hossain, A. K. M. Munir and A. H. Khan, *J Environ Sci Health*, 38 (2003) 71.
11. M. Van Holderbeke, Y. N. Zhao, F. Vanhaeck, L. Moens L, R. Darns and P. Sandra, *J. Anal At Spectrom.*, 14 (1999) 229.
12. J. L. Gomez-Ariza, D. Sanchez-Rodas, R. Beltran, W. Corns and P. Stockwell, *Appl Organonet Chem.*, 12 (1988) 439.
13. C. Soros, E. T. Bodo, P. Fodor and R. Morabito, *Anal. Bioanal Chem.*, 377 (2003) 25.
14. F. T. Henry, T. O. Kirch and T. M. Thorpe, *Anal. Chem.*, 51 (1979) 215.
15. G. C. Barker and I. L. Jenkin, *Analyst.*, 77 (1952) 685.
16. W. H. Horwitz, *Official Methods of Analysis of AOAC International.*, Vol. 1 (2000).