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Speciation of arsenic in drinking water at Amansie West District

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Abstract

A study of arsenic speciation in drinking water at Amansie West District was conducted. Drinking water samples from boreholes, hand dug wells and streams were taken from 23 communities in the district. Amansie West is a gold mining community with surface mining being the main method used. As (III) and As (V) in the water samples were separated using hydride generation and detection by flame AAS. Drinking water samples collected from boreholes, hand dug wells and streams in Amansie West District was analysed for pH, conductance, DO, Eh. The pH was in the range (6.57 - 7.78 in boreholes, 6.10 - 7.62 in wells, and 6.48 – 8.27 in streams) while conductance was obtained in the range of (74.5 - 313.5 in boreholes, 82.0 – 210.7 in wells, and 152.6 – 563.4 in streams) µS/cm. The results obtained showed that the concentration of arsenic in streams, boreholes and hand dug wells fall between 0.24-37.22 µg/L, 13.49-26.41 µg/L, and 24.11-39.43 µg/L respectively. 74% of surface and ground water samples had arsenic concentrations above 10 µg/L. Correlation between arsenic concentration and some physical parameters (pH, DO, conductivity and redox potential) was done to ascertain any relationship. Speciation results showed that arsenic (III) is the dominant inorganic arsenic species. On average, 64% of all inorganic arsenic species is in the (+3) oxidation state, the rest is in the (+5) oxidation state. There was a strong negative correlation between arsenic speciation and the redox potential.

Keywords: Arsenic; Borehole water; HG-AAS; Speciation; Stream water; Well water

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1. Introduction

Speciation study has shown an increasing interest in the analytical and environmental circles during the last decade. Speciation of an element in a sample, (Ge, 2002), means determination of the concentration of different physicochemical forms of the element that together make up its total concentration in the sample. Some elements can be highly toxic to various life forms while others are considered essential at very small amounts. Inorganic arsenic in the form of As (III) is considered about 10 times more soluble and mobile and more toxic than As (V).

Elemental speciation is a discipline, which is of a great relevance to groups that include chemist, biologist, toxicologist, engineers, etc. In fact this area of chemistry has become one of the most crucial, important and challenging because of its impact on environmental chemistry, nutrition science, pharmacology, toxicology etc.

Arsenic speciation can be explained as the transformation of arsenic species into variety of other forms and derivatives under different environmental condition such as physical, chemical and biological (Ng, 2005). The toxicity of arsenic species varies from virtually nontoxic (e.g. biological derivatives of arsenic such as arsenobetaine (AB) and arsenocholine (AC) to extremely toxic inorganic derivatives (e.g. arsenite, arsenate).

Most research on arsenic pollution in environmental matrices (Golow et al., 1996; Duker et al., 2004; Amonoo Neizer and Amekor, 1993) reports primarily on the extent of total arsenic concentration. However, in order to know toxicity and effectively remove arsenic in ground water, it is not enough to only measure total dissolved concentrations, speciation data are also very important. Knowledge of the speciation of arsenic in surface and ground water is important because the bioavailability, physiological and toxicity of arsenic depends on its chemical form (Bose et al., 2010).

Arsenic undergoes several complex transformations, including oxidation-reduction, precipitation, adsorption-desorption, and biochemical methylation. Aqueous arsenic speciation affects its mobility, bioavailability and toxicity (Penrose, 1974; Cullen and Reimer, 1989; Gao and Burau, 1998). Arsenate [As(V)] and arsenite [As(III)] are the main inorganic forms of arsenic. As (V) is more strongly sorbed onto soil and sediment components than As(III), making it less mobile (Deuel and Swoboda, 1972; Gulens et al., 1979; Holm et al., 1979; Mok and Wai,1994).

High arsenic concentrations have been found in contaminated soils and in bedrocks close to gold mining area. Smedley et al. (1996) found that many of the ground waters of the Obuasi area had low arsenic concentrations, with a median concentration in well waters of just 2 mg/L. Some higher concentrations were observed (up to 64 mg/L) but these were not generally near the mines or related directly to mining activity. Rather, the higher concentrations were found to be present in relatively reducing ground waters (Eh 220 – 250 mV). Oxidizing ground waters, especially from shallow hand-dug wells, had low arsenic concentrations. This was taken to be due to the adsorption onto ferric oxides under the low pH condition of the waters (median pH 5.4 in dug wells; 5.8 in tube wells; Smedley, 1996; Smedley et al., 1996).

Arsenic occurs naturally in the earth's crust and can be released into the aquatic environment by redox processes and also from mine waste. Amansie West is a gold mining town and a study (Duker, 2004) has reported high concentrations of total arsenic in rivers and streams. Buruli ulcer, which has been closely linked to arsenic poisoning, has also been found to be high in the district. Since local inhabitants largely depend on water sources from streams, boreholes and hand dug wells; ingestion of toxic arsenic is most likely and may pose a risk to the health of inhabitants of Amansie West District.

2. Materials and methods

2.1. Study site

Amansie West District is located in the south-western part of the Ashanti Region. Gold deposits have been found in most parts of the district; small scale mining has therefore emerged as the most important economic activity in the district. In Ghana, Biriman rocks of West Africa are mainly volcanic greenstones with intervening sedimentary rocks and granitic intrusions, in places containing deposits composed of pyrite, arsenopyrite, minor chalcopyrite, sphalerite, galena, native gold and secondary hematite (Duker et al., 2004). The people of Amansie West district mainly depend on streams, hand dug well and borehole as a source of drinking water. Pipe borne water, from Ghana Water Company in the District serves only two communities namely, Manso Atwere and Esaase. About 65% of the communities in the District rely on streams and ponds as their major sources of water supply (Ghana districts site).

Figure 1. ***A***: A woman fetching water to drink for the time she will be working in the farm
B: Mining activity that is pumping out polluted water

2.2. Field sampling

About 500 mL of water samples were taken from 15 boreholes at 15 different locations in Amansie West for the determination of total dissolved arsenic, As (III), and As (V). Water samples of 500 mL each were also taken from three hand-dug wells for the determination of total dissolved arsenic, As (III), and As (V). Other 500 mL of water samples were taken from five streams for the determination of total dissolved arsenic, As (III), and As (V). Another 500 mL water samples were collected from boreholes and hand-dug wells at Konongo as control sample. Konongo was chosen because; it has the same geological formations as that of the study area and artisanal mining activities is not as prevalent as compared to that in Amansie West. The water samples were collected using 250 mL opaque plastic containers. The containers were filled to the brim and acidified immediately with 4 % HCl. The sample identification was noted on the container using a permanent marker pen. The samples were transported in ice loaded container on the same day and stored in a refrigerator. The samples were labeled BW, HW and SW corresponding to borehole water, hand-dug well water and stream water respectively.

2.3. Laboratory methods

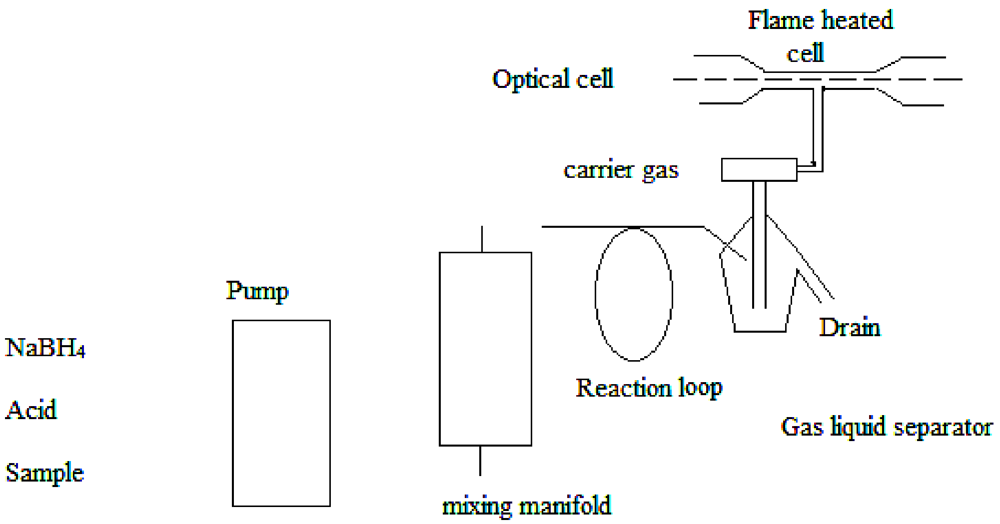

Figure 2. Schematic diagram of hydride generator

The dissolved inorganic arsenic was measured with varian spectra AA 240 FS set to 193.7 nm and equipped with H_2 hollow cathode lamp as background corrector. Hydride generation was performed on a VGA-77 apparatus with a thermally heated cuvette and argon as the inert carrier gas. By the addition of 10% KI (1 ml) to the sample, all arsenic species were reduced to As (V). Approximately 20 ml sample, 0.6% $NaBH_4$, and 6M HCl were taken into the mixing chamber where reduction takes place. Hydrides of the arsenic were then aspirated to the burner head where atomization of arsenic occurs. Atoms of the arsenic absorb radiation to produce signals. The signals or absorbance generated was correlated to the concentration of the arsenic element within the linear calibration curve.

For arsenic in a weak organic acid, hydrides are generated almost exclusively for the As (III) species. As (V) species however, do not react or undergo any reaction. The same setting of the varian spectra AA 240 FS was used but the 6M HCl was replaced with 0.4M citric acid. As (III) is exclusively reduced in the mixing chamber and its hydrides aspirated to the burner head for atomization. The absorbance produced is correlated to the concentration of the arsenic within the linear calibration curve.

The reliability of the instrument was obtained by performing the recovery of 0.02, 0.04, 0.06, and 0.10 mg/L standard arsenic solution. 20 ml of each standard was taken through the process described above.

Table 1. Recovery of total arsenic concentration using 6 M HCl

Reaction medium	Arsenic added (mg/L)	As (total) recovered (mg/L)	% Recovery
Hydrochloric acid 6 mol/L	0.02	0.019	95
	0.04	0.038	95
	0.06	0.06	100
	0.10	0.097	97

Table 2. Recovery of arsenic (III) concentration using 0.4 M Citric acid

Reaction medium	Arsenic added (mg/L)	As (III) recovered (mg/L)	% Recovery
Citric acid 0.4 mol/L	0.02	0.018	90
	0.04	0.038	95
	0.06	0.057	95
	0.10	0.099	99

Average % recovery = 95

3. Results and discussion

Table 3. Results obtained for pH, conductivity, redox potential, total dissolved arsenic and arsenic (III) concentration.

Parameters	**Borehole**		**Well**		**Stream**		**WHO**
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	
pH	6.57 - 7.78	7.19	6.10 - 7.62	6.87	6.48 – 8.27	7.48	6.5 – 8.5
E_h/mV	13 to -36	-4.3	15 to -15	-2.3	0 to -37	-4.9	
Cond/µS/cm	74.5 - 313.5	200.51	82.0 – 210.7	113.88	152.6 – 563.4	287.54	
As (total)/ µg/L	0.18 – 37.22	17.62	15.49 – 26.41	20.03	24.11 – 39.43	32.86	0 – 10
As (III)/µg/L	0.40 – 23.00	10.89	10.00-16.00	12.73	14.00-26.65	22.53	
As (V)/µg/L	0.0 – 21.00	7.30	9.00 – 17.10	8.00	3.99 – 19.00	11.80	

In order to understand arsenic mobilization in ground and surface water, it is important to look into the relationship between the various parameters that influence arsenic concentration. The parameters of the water quality such as pH, conductivity and reduction potential have a significant effect on it. They also influence physiology of organisms in water and may contribute to metal forms in water (Forster et al., 1983). pH, and conductivity were taken on site with a multimeter probe while the Eh was measured in the lab. For each sample, the reading was performed thrice and the mean value taken to represent it.

Correlation between arsenic levels and pH is positive in boreholes, hand-dug wells, and streams with the coefficient of correlation values of (0.0272, 0.531, and 0.657) respectively. The strong correlation between arsenic levels and pH in hand-dug wells and streams show that greater percentage of water samples with high arsenic concentration also has high pH values. Seventy five percent (75%) of water samples with arsenic concentration greater than 10 µg/L had pH values greater than 7 in hand-dug wells and streams. At high pH (6 -9) desorption of arsenic from clay minerals, iron and manganese oxides is promoted (Manning and Goldberg, 1997) which can result in excess concentration of arsenic to be released into water bodies.

There was a slight negative correlation between arsenic concentration and reduction potential. The coefficient of correlation obtained were -0.31, -0.23 and -0.35 for boreholes, hand-dug wells and streams respectively. Water sampled from the streams had the lowest magnitude of redox potential, which can be a reason for the high arsenic level in the stream, followed by water from boreholes and hand-dug wells. The lower redox potential means reduced conditions which is also the reason for the high arsenic content. In an oxidizing environment, solid iron and manganese oxides serve as sorption sites and eventually reduce the concentration of arsenic in natural water (Hundal et al., 2007). Under reduced environments, solid Fe (III) and Mn (IV) oxides also dissolve to soluble Fe (II) and Mn (II) and thus release arsenic from the sorption sites and thereby enhances its concentration in water.

There is a strong positive correlation between arsenic levels and conductivity in the boreholes, wells and streams with coefficient of correlation as 0.416, 0.735, and 0.573 respectively. This result is indicative of high total dissolved ions found in the water.

The average percentage of As (III) in total arsenic in borehole, well and streams are 62%, 67% and 65% respectively. It can be seen that greater percentage of arsenic total occurs in the form of As (III). This is due to the fact that under moderately reduced conditions trivalent arsenite (As^{3+}) is stable and its adsorption is lower compared to pentavalent arsenate (As^{5+}). The high percentage of As (III) as a percentage of total arsenic in the drinking water is a health concern because As (III) is the more toxic form of arsenic compared to arsenic (V). Average percentage of arsenic (V) in total arsenic obtained in boreholes, hand-dug wells, and streams was 38.2%, 35.2%, and 36.7% respectively.

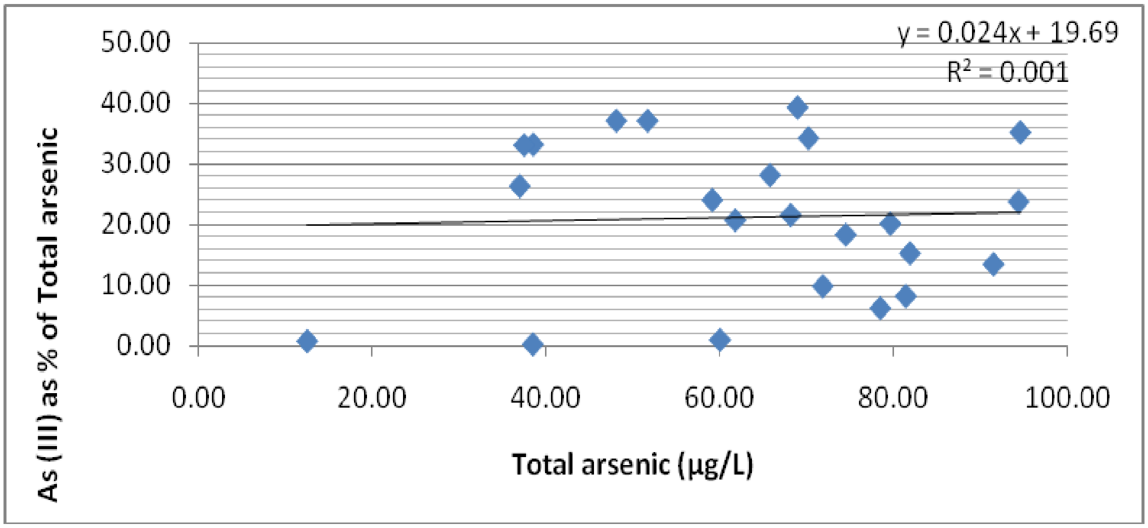

Figure 2. Correlation of As (III) concentration with As total

The comparison between total arsenic and arsenic speciation showed no correlation. The coefficient of correlation was 0.04. This implies that arsenic speciation could not be predicted by total arsenic concentration. In other words, it was impossible to derive any information on speciation using arsenic test methods that measured total arsenic only. An additional technique that separates arsenic (III) from arsenic (V) is necessary to determine speciation.

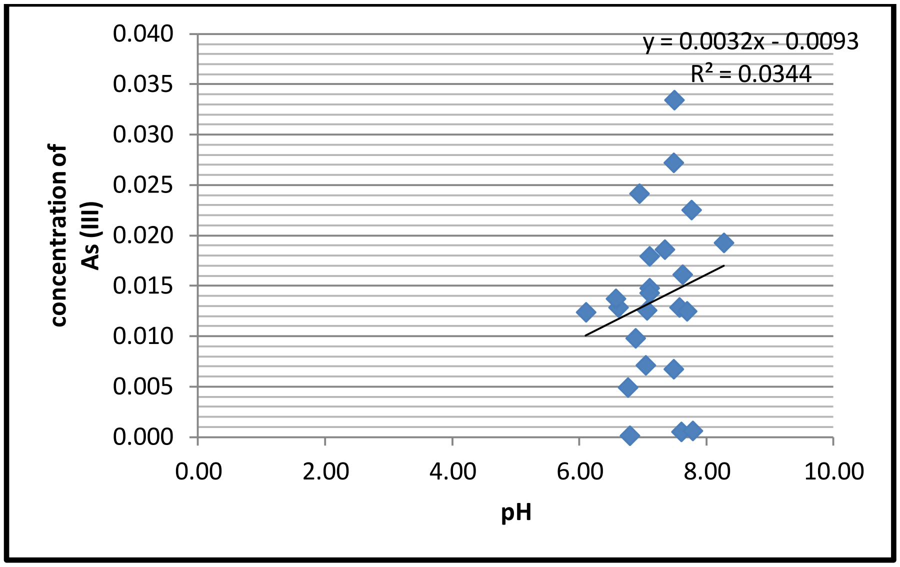

Figure 3. Correlation of As (III) concentration with pH

Arsenic speciation appeared slightly dependent on the water pH. The correlation coefficient was only 0.102 indicating a weak positive correlation. According to literature, (Manning and Goldberg, 1997) pH alone should not have any correlation with speciation.

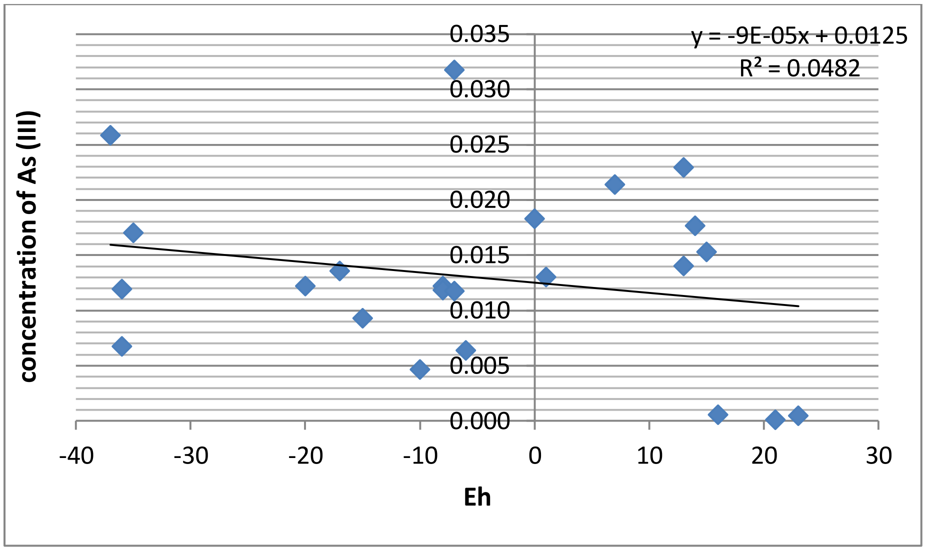

Figure 4. Correlation of As (III) concentration with reduction potential

The observed trend of arsenic (III) concentration decreasing with increasing Eh matched with theoretical prediction (Ngai, 2001). Correlation coefficient between As (III) concentration and reduction potential in boreholes hand-dug wells and stream water are -0.3111, -0.2367, -0.3576 respectively. The lower the Eh, the more reduced the water was. Thus, more arsenic would appear in its reduced form as As (III) than the in its oxidized form of As (V).

4. Conclusions

Reduction of the water sample at 6M HCl and 0.4M citric acid allowed arsenic total and As^{3+} to be selectively reduced respectively. The procedure was precise and low time consuming as just a very simple sample treatment was required.

On the average, 61%, 69% and 68% of the total arsenic was in the more toxic arsenic (III) form in boreholes, hand-dug wells, and streams respectively. The removal of arsenic is therefore highly necessary. There was a strong correlation between reduction potential and arsenic speciation. The lower the reduction potential, the more arsenic are in arsenic (III) form. Concentration levels of arsenic in bore holes, well water and streams were found to exceed WHO and GSB/GWC guidelines for drinking water.

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