Experiment No. 10

Determination of Arsenic in Water

Introduction

Arsenic, the 20th most abundant element in the earth's crust and the 12th most abundant element in the biosphere, is a common trace inorganic contaminant in drinking water and is identified as a significant health risk. Arsenic is known for its high toxicity and its ability to induce cancer after long-term ingestion. Presence of elevated levels of arsenic in groundwater (especially from shallow aquifer) has become a major concern in Bangladesh. Arsenic pollution of groundwater is particularly challenging in Bangladesh since tubewell water extracted from shallow aquifers is the major source of drinking water for most of its population. The rural water supply is almost entirely based on groundwater supply through use of hand pump tubewells; the urban water supply is also heavily dependent on groundwater.

Awareness about the presence of arsenic in groundwater has been growing since late 1993 when arsenic was first detected in the district of Chapai Nawabgonj bordering the West-Bengal district of India. A detail survey carried out by the DPHE and BGS (British Geological Survey) in 1999 identified the presence of arsenic in 268 Upazilas out of 464 in the country (BGS and DPHE, 2001). In 2005, the number of affected Upazilas increased to 270. In 2002 and 2003, 4.7 million tube wells in Bangladesh have been screened for arsenic. Of those, 1.4 million tube wells were found to contain arsenic above the Bangladesh drinking water standard of 50 microgram per liter. According to the Multiple Indicator Cluster Survey (MICS) carried out by GoB and the Unicef in 2012-13, about 24.8 per cent of the population of Bangladesh are drinking water in the household with arsenic above the WHO provisional guideline value of 10 ppb, and 12.4 per cent of the population are exposed to water with arsenic exceeding the Bangladesh standard of 50 ppb (GoB and Unicef, 2015).

In Bangladesh, the arsenic in groundwater is of geologic origin and is probably only apparent now because it is only the last 25 – 35 years that groundwater has been extensively used for drinking in rural areas. Weathering of arsenic-rich base metal sulfides in the upstream of the Ganges basin appears to be a major source of arsenic-rich iron oxyhydroxides in the sediments of Bangladesh. Arsenic-rich iron oxyhydroxides appear to be the major source of arsenic, from which arsenic is released as a result of dissolution and desorption. Reducing environment in the alluvial aquifer, primarily due to the presence of organic matter, promotes dissolution of iron oxyhydroxides and release of arsenic. Use of phosphate fertilizer can potentially enhance release of arsenic as a result of replacement of arsenic by phosphate ions on the adsorption sites of iron oxyhydroxides. Natural and anthropogenic processes that may lead to release/mobilization of arsenic in the subsurface are being investigated.

According to ECR 1997, drinking water standard for arsenic in Bangladesh is 50 μg/L (or 0.05 mg/L). The WHO guideline value for arsenic in drinking water is 10 μg/L and the USEPA is also planning to revise its standard from 50 μg/L to 10 μg/L.

Arsenic Chemistry

Arsenic occurs in water in several different forms, depending upon the pH and the redox potential, E_h. Some of the most important compounds and species are shown in Table 10. 1. In groundwater, arsenic primarily exists as inorganic arsenic. Inorganic trivalent arsenic, [As(III)] or arsenite is the dominant form in reducing environment; while inorganic pentavalent arsenic [As(V)] or arsenate is the dominant form in oxidizing or aerobic environment.

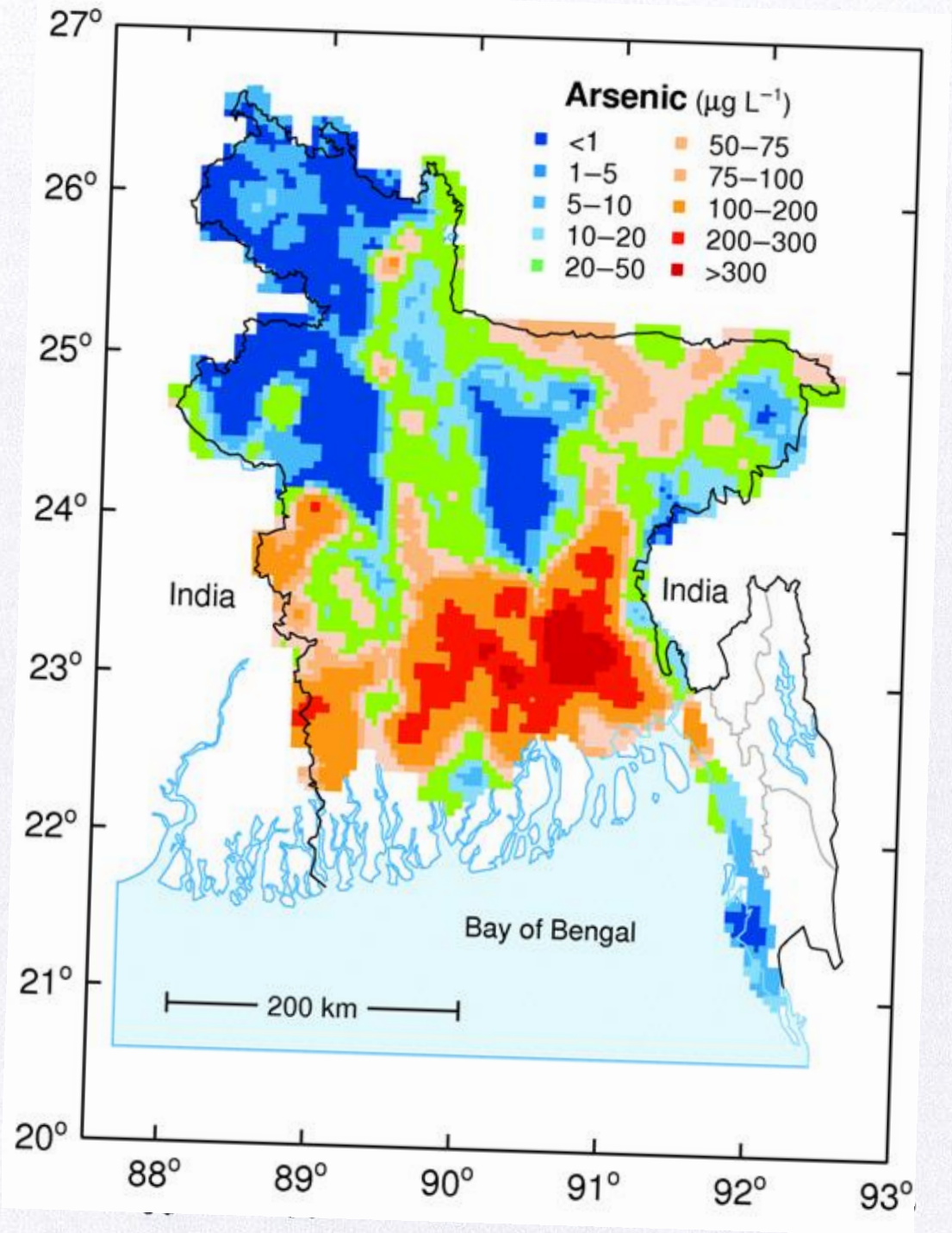


Figure 14.1: Distribution of Arsenic in Groundwater of Bangladesh

In groundwater environment where the conditions are mostly reducing, a significant part of the arsenic exists as As(III). As shown in Table 10.1, in the pH range of most groundwater (i.e., pH 6 – 9), dominant chemical form of As(III) is H_3AsO_3; while dominant chemical forms of As(V) in this pH range are: $H_2AsO_4^-$, $HAsO_4^{2-}$.

Table -10.1: Arsenic compounds and species and their environmental and toxicological importance in water

Compounds	Example	Environmental Significance/ Dominant pH region	Toxicity
Arsine	As^{3-}	Minor importance	Most toxic As species
Elemental Arsenic	As	Minor importance	Least toxic As species
Trivalent Arsenic	As(III)	Anaerobic	10 times more toxic than As(V)
Arsenite, Inorganic	H_3AsO_3, $H_2AsO_3^{1-}$, $HAsO_3^{2-}$, AsO_3^{3-}	pH = 0-9 pH = 10-12 pH = 13 pH = 14	
Methylated As(III) Organo-As(III)		Minor importance	Less toxic than Inorganic As(III)
Pentavalent arsenic	As(V)	Aerobic	10 times less toxic than As(III)
Arsenate, Inorganic	H_3AsO_4, $H_2AsO_4^{1-}$, $HAsO_4^{2-}$, AsO_4^{3-}	pH = 0-2 pH = 3-6 pH = 7-11 pH = 12-14	
Methylated As(V) Organo-As(V)		Minor importance	Less than Inorganic As(V)

Health Effects of Arsenic

In a population drinking arsenic contaminated water, a great variety of specific as well as non-specific symptoms may be observed. Table 2 lists some of the effects of arsenic reported to be due to exposure through drinking water.

In a recent study by the National Institute of Preventive and Social Medicine (NIPSOM), arsenic related diseases (arsenicosis) have been identified in 37 districts (Ahmad et al., 1998). A total of 6000 cases were identified in 162 villages in the 37 districts, mostly in the rural areas. Three stages of manifestations of chronic arsenicosis were observed in the study (Ahmad et al., 1998), but most of the patients were found in the first and second stages.

The most common presentations were melanosis, keratosis, hyperkeratosis and depigmentation. Cancers were found among 0.8% and actinic keratosis and Bowen's diseases were observed among 3.1% of the cases. It is important to note that the study found that the cases at initial and second stages of toxicity showed improvement when patients stopped taking arsenic contaminated water and increased intake of protein rich food, vitamin A, E and C.

Table- 10.2: Toxicological effects due exposure to high arsenic concentration in drinking water (WHO, 1996, Khan, 1997)

Effect	Symptoms	Remarks
Blackfoot Disease Arsenical dermatosis	Dermal lesion, Peripheral neuropathy Keratosis, Hyperkeratosis, Hyperpigmentaion	May necessitate operation
None specific	Nausea, Abdominal Pain, Diarrhoea, Vomiting, Conjunctivitis, Oedema.	Mainly due to acute intoxication
Pregnancy disorders	Spontaneous abortions, miscarriages	-
Heart Disease	Coarctation of aorta, Cardiovascular disturb.	Among children
Cancer	Bladder, Kidney, Skin & Lungs, Liver & Colon	-
Mortality	-	Mainly due to cancer

Analytical Methods for Measuring Arsenic

The most commonly used methods for detection of arsenic in water include:

1. Inductively coupled plasma (ICP) method
2. Hydride generation atomic absorption spectrophotometric method
3. Graphite furnace atomic absorption spectrophotometric method
4. Hydride generation-scraper-spectrophotometric (SDDC) method
5. Hydride generation-scraper-indicator paper-field kit

The first three methods involve high-cost equipment and provide more accuracy and lower detection limit (minimum detection limit, MDL = 1 µg/L). The last two methods are relatively low cost methods but accuracy of determination is less. In our laboratory we have two atomic absorption spectrophotometers and can measure arsenic concentration following methods (2) and (3).

Inductively coupled plasma (ICP) method

An ICP source consists of a flowing stream of argon gas ionized by applied radio frequency field typically oscillating at 27.1 MHz. The water sample is atomized at temperature about 6000 to 8000 ^{0} K. The light emitted from ICP Hydride generation atomic absorption spectrophotometric method is focused on entrance slit and using radio frequency determines absorbance of arsenic.

Hydride generation atomic absorption spectrophotometric method

This method is also known as Flame Atomic Absorption Spectrophotometric (FAAS) method. In this method arsenic is reduced to gaseous arsine in a reaction vessel. The method is two types: i) manual hydride generation and ii) continuous hydride generation. In manual method zinc is added to speed the reaction whereas continuous in continuous hydride generation no zinc is needed. In continues measurement hydride generator a peristaltic pump is used to meter and mix reagents and a gas–liquid separator unit uses flow of argon to strip out hydrogen and arsine gas.

Graphite furnace atomic absorption spectrophotometric method

Also known as Electro thermal atomic absorption spectrophotometric method (ETAAS). This method is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at and intermediate temperature. Finally, a high current heat the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms.

Preparation of Sample for Arsenic Determination:

Preparation of Sample:

Arsenic is often present in very small concentration in water. Therefore, water samples are often *pre-concentrated* in order to increase the quantity of arsenic in a given volume. Pre-concentration is usually done by acidifying 200 to 500 mililiter water sample and then reducing the volume to about 35 mililiter in a water bath.

Precaution:

Arsenic is often found in groundwater with high concentration of iron (Fe). After extraction, Iron present in groundwater in ferrous (Fe^{2+}) form is converted to ferric (Fe^{3+}) form in contact with atmospheric oxygen and forms ferric hydroxide $Fe(OH)_3$ (s) flocs. Arsenic, especially As(V), is strongly adsorbed onto these ferric hydroxide flocs. Therefore, care should be taken while taking water sample from a bottle in which red coloured ferric hydroxide flocs are visible. It is better to acidify the bottle first (thus dissolving the ferric hydroxide flocs) and then take water sample for pre-concentration.

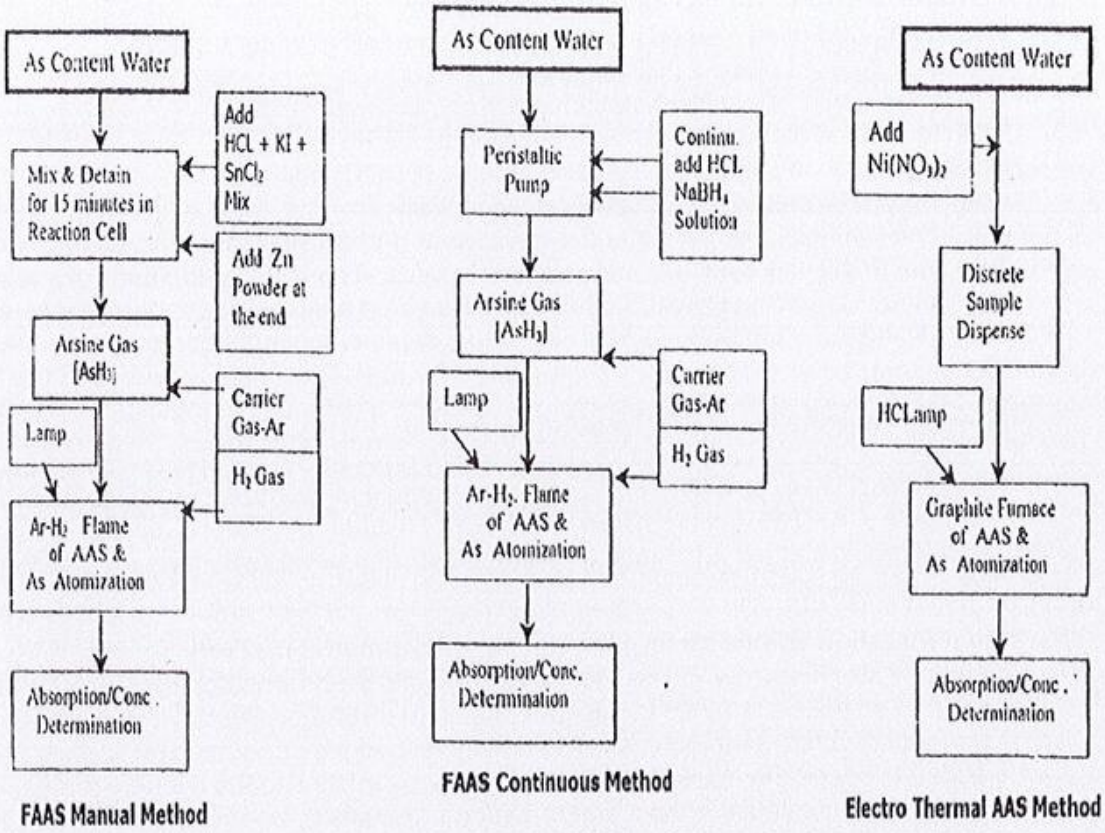


Fig. – 14.2: Different types of Atomic Absorption Spectrophotometric determination of arsenic

Apparatus
- Atomic Absorption Spectrophotometer (AAS)
- Glass tubes, Micro pipette etc.

Reagent
- Nickel nitrate (as matrix modifier)

Procedure
1. Take 9 mL sample and 1 mL nickel nitrate in a container.
2. Draw 20 µL using micro pipette and insert into the hole of graphite tube.
3. A hollow cathode lamp of 193.7 ηm is placed inside the spectrophotometer and switch on the machine. The temperature is raised up to 3000°C to and As atomic cloud is formed (details will be shown in the class).
4. Repeat the procedure and take the average of three measurements.

Calculation
Calculate arsenic concentration using the calibration curve (will be supplied in the class).

Actual As concentration (ppb) = As conc.(ppb) obtained from calibration curve of AAS x D.F.

Where, D.F. = Dilution Factor = $$\frac{\text{volume of sample} + \text{volume of } NiNO_3}{\text{volume of sample(mL)}}$$