Course Number : CE 332
Course Name : Environmental Engineering Lab
Course Credit : 1.50

Experiment No. 14
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 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 Nawabganj bordering the West-Bengal district of India. Since then higher levels of arsenic (exceeding the WHO standard of 0.01 mg/L and Bangladesh standard of 0.05 mg/L) have been detected in many regions of the country. Affected areas and estimates of affected population are being updated, as more data are becoming available. Out of 64 administrative districts of Bangladesh, arsenic contamination has so far been reported in 61 districts and an estimated 20 million people are at risk of arsenic toxicity. This has lowered the population coverage by safe water supply to an estimated 80 percent from an impressive figure of nearly 98 percent. The southern and northeastern districts are the worst affected by arsenic pollution. Figure 1 shows a distribution of arsenic concentration in groundwater of Bangladesh.

In Bangladesh, the arsenic in groundwater is of geologic origin and is probably only apparent now because it is only the last 20-30 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.

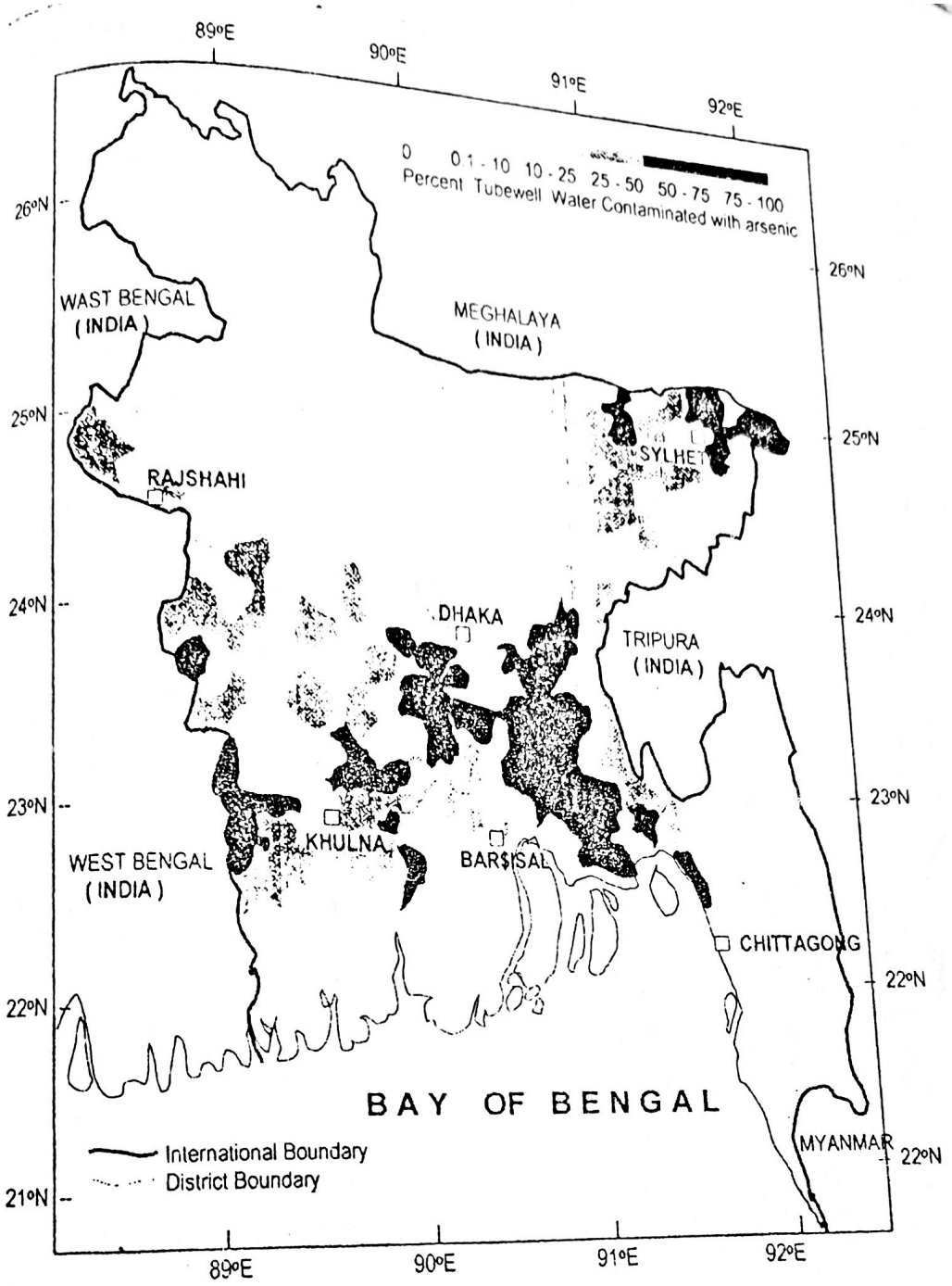


Figure 1. Distribution of Arsenic in Groundwater of Bangladesh

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 compound and species are shown in Table 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. In groundwater environment where the conditions are mostly reducing, a significant part of the arsenic exists as As(III). As shown in Table 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 1: Arsenic compounds and species and their environmental and toxicological importance in water

Compounds	Examples	Environmental Significance/ Dominant pH region	Toxicity
Arsine	As^3	Minor Importance	Most toxic As species
Element 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, $H_2AsO_3^-$, $HAsO_3^{2-}$, 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, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}	pH = 0-2 pH = 3-6 pH = 7-11 pH = 12-14	
Methylated As (V) Oragano-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 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 2: Toxicological effects due to 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 (narrowing) of aorta, cardiovascular disturbance	Among children
Cancer	Bladder, Kidney, Skin & Lungs, Liver & Colon	-
Mortality	-	Mainly due to cancer

ANALYTICAL METHODS FOR MEASURING ARSENIC

Analytical methods for measuring arsenic may be categorized as follows:

(1) Inductively coupled plasma (ICP) method
(2) Graphite furnace atomic absorption spectrophotometry
(3) Hydride generation atomic absorption spectrophotometry
(4) Hydride generation-scraper-spectrophotometry (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 (in the range of 1 µg/L). The last two methods are relatively low cost methods. The principle employed in these two methods is explained Fig. 2.

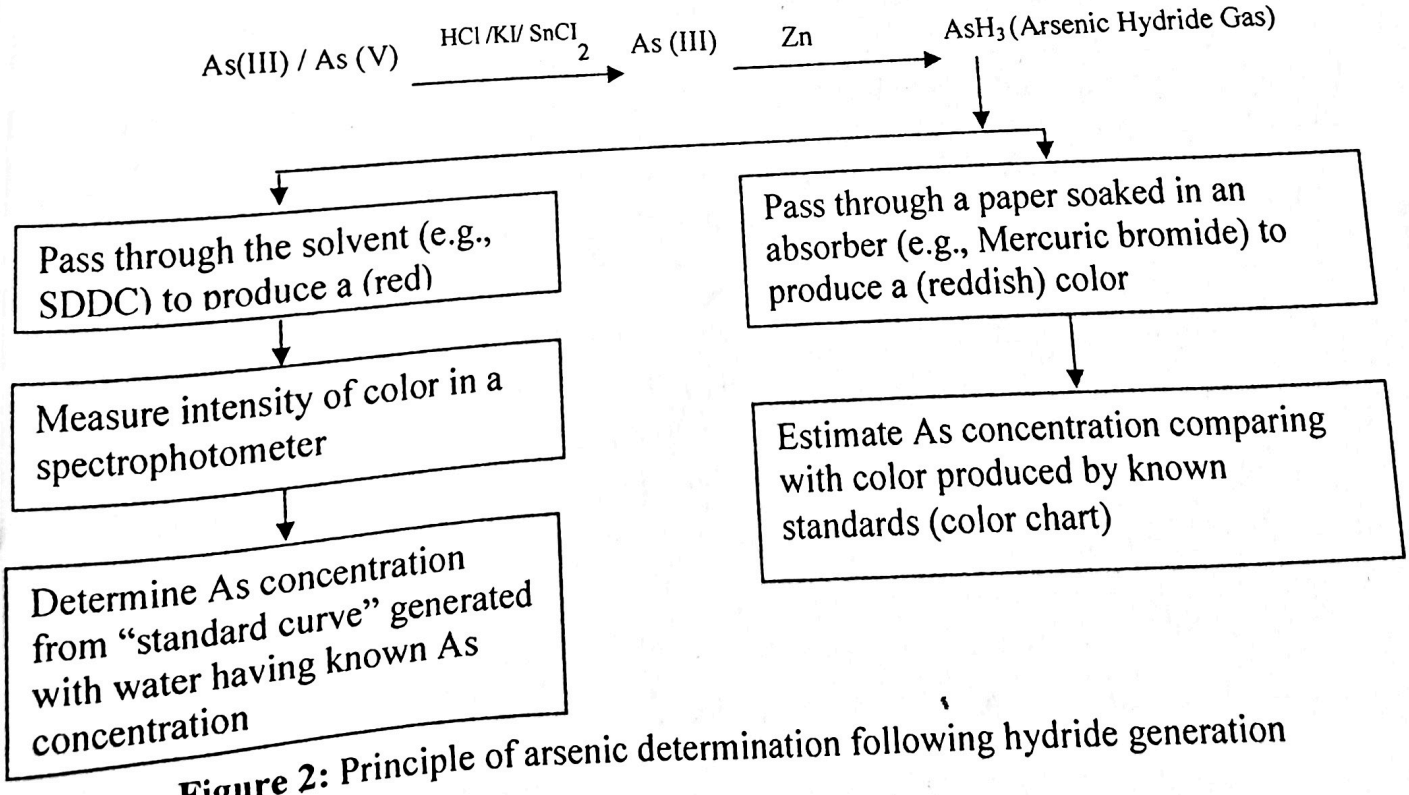


Figure 2: Principle of arsenic determination following hydride generation

quations 1-3 show reactions for arsine generation and formation of colored complex.

$$+ \quad 2H^+ = Zn^2 + 2H \quad (1)$$

$$\text{metal)} + 6H = AsH_3 + 3H_2O \quad (2)$$

$$AsO + \text{SDDC/Bromide} = \text{Colored Complex} \quad (3)$$

AsH_3

RSENIC DETERMINATION

HYDRIDE GENERATION-SCRAPER-SPECTROPHOTOMETRY, *and* HYDRIDE GENERATION-SCRAPER-INDICATOR PAPER METHOD

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

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

) ARSENIC DETERMINATION: *HYDRIDE GENERATION-SCRAPER-SPECTROPHOTOMETRY:* SILVER DIETHYLDTHIOCARBAMATE (SDDC) METHOD

e method followed in the laboratory is commonly referred to a "*Silver elhyldithiocarbamate Method*" (Standard Method, 307B, 1985). Minimum detectable quantity As for this method is 1 µg. This method essentially involves: (i) conversion (reduction) of arsenic in water into As(III), (ii) generation of arsine gas in the form of arsenic hydride sH_3), (iii) passing of arsine gas through a solution of silver diethyl - dithiocarbamate (SDDC) d producing a red-colored complex; (iv) measurement of absorbance of the colored mplex in a spectrophotometer at 535 nm wavelength; (v) determination of arsenic ncentration from a standard curve (As concentration versus Absorbance) developed with own concentration of arsenic following the same procedure.

EAGENTS

) Hydrochloric acid, (2) Potassium Iodide solution,
) Stannous chloride solution, (4) Metallic zinc,
) Silver diethyl-dithiocarbamate solution in pyridine.

PPARATUS

) Assembly for SDDC method
) Spectrophotometer

CEDURE

Take about 35 ml sample in a clean Arsine generator bottle. Add (with constant stirring) 5 ml concentrated hydrochloride acid (HCl), 2 ml potassium iodide (KI) solution, and 0.40 ml stannous chloride ($SnCl_2$) solution. Wait 15 minutes for reduction of arsenic to the trivalent state [As(III)].

) Soak glass wool in lead acetate (PbAc) solution and put in the scrubber. This is done in order to eliminate interference from sulphide gas by absorbing it in the scrubber. Pipette 4- ml silver diethyl-dithiocarbamate reagent in the absorber tube.

) Add 3 g metallic zinc (Zn) in the generator and connect scrubber-absorber assembly immediately. Make certain that all connections are fitted tightly.

) Allow 30 minutes for complete generation of arsine (according to equations 1, 2). Warm the generator slightly to ensure that all arsine is released. Pour solution from absorber in tubes for measurement of absorbance.

5) Measure absorbance of the solution at 535 run in a spectrophotometer, using reagent blank as the reference.

6) *Preparation of Standard Curve*: Treat portions of standard solution containing 0. 1.0, 2.0, 5.0, and 10.0 µg As in the same manner described above. Plot absorbance versus concentration of As in the standard and develop a standard curve.

7) Concentration of Arsenic:

$$\mu g\ As/L = (\mu g\ As \text{ from standard curve}) \times 1000 / (\text{volume of sample})$$

(b) ARSENIC DETERMINATION USING *HYDRIDE GENERATION SCRAPER-INDICATOR PAPER METHOD:* MODIFIED MERCURIC BROMIDE STAIN METHOD *(JALIL , 1998)*

A simple and reasonably accurate method for arsenic measurement has been developed in the Environmental Engineering Laboratory, Department of Civil Engineering. BUET (Jalil. 1998). The measurement using the "BUET Arsenic Kit" follows the principle of Mercuric Bromide Stain Method. It involves: (i) reduction of As(V) in water to As(III); (ii) generation of arsenic hydride (AsH_3); (iii) passing arsine gas through a filter paper soaked in mercuric bromide and producing a yellowish color on the paper, and (iv) determination of arsenic concentration by comparing the produced color with a standard colored chart.

REAGENTS

(1) Hydrochloric acid; (2) Potassium Iodide solution;
(3) Stannous chloride solution; (4) Zinc powder
(5) Filter paper soaked in mercuric bromide solution

APPARATUS

Assembly for "BUET Arsenic Kit"

PROCEDURE

(1) Take 50-ml water sample in the clean arsine generator bottle. Add 5 ml HCl, 1 ml KI and 0.2 ml $SnCl_2$ solution. After each addition, shake the generator for mixing the contents. Wait 15 minutes for reduction of As(V) to As(III).
(2) Take a mercuric bromide soaked filter paper and air-dry it.

Insert the dried paper in its proper position in the rubber-cork assembly.
Add 1 g powder zinc into the generator and immediately close the generator bottle tightly with the rubber-cork assembly.
Allow 30 minutes for complete reaction.
Take the filter paper out from the rubber-cork assembly.
Compare the color of the filter paper with a standard "color chart". The color chart is prepared by treating 5, 10, 20, 30, 50, and 70 µg/L standard arsenic solutions in the same manner described above. If the color produced by the sample does not match any color in the chart, arsenic concentration of the sample is estimated by interpolation between colors in the chart.

SIGNMENT QUESTIONS

In which chemical form arsenic is likely to exist in groundwater? Explain.
In determination of arsenic (following the methods described here), why the water samples are acidified and often pre-concentrated before actual determination of arsenic?
What is the basic difference between the two arsenic determination methods - SDDC method and Mercuric Bromide Stain method, described above?

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