CHAPTER-I

INTRODUCTION
ARSENIC
Symbol = As

Chemical properties of arsenic [1]

Atomic number 33
Atomic mass 74.9216 g.mol$^{-1}$
Electronegativity according to Pauling 2.0
Density 5.7 g.cm$^{-3}$ at 14°C
Melting point 814 °C (36 atm)
Boiling point 615 °C (sublimation)
Vanderwaals radius 0.139 nm
Ionic radius 0.222 nm (-2) 0.047 nm (+5) 0.058 (+3)
Isotopes 8
Electronic shell [Ar] 3d$^{10}$ 4s$^{2}$ 4p$^{3}$
Energy of first ionisation 947 kJ.mol$^{-1}$
Energy of second ionisation 1798 kJ.mol$^{-1}$
Energy of third ionisation 2736 kJ.mol$^{-1}$
Standard potential - 0.3 V (As$^{3+}$/ As)
Discovered by The ancients
Arsenic was one of the most famous poisons in former times starting with Nero’s poisoning of Britannicus to secure his Roman throne in 55 A.D. and becoming very popular especially in the Middle Ages due to its easy availability, low cost and the fact, that it is taste- and colorless and was not detectable in bodies until 1836 when Marsh found a possibility to determine it as arsine (AsH₃) [2].

Arsenic was also used for more than 2000 years as remedy to cure anorexia and other nutritional disturbances, neuralgia, rheumatism, asthma, tuberculosis, diabetes, intermittent fever, skin disorders, hematologic abnormalities, for embalming corpses, for the treatment of malaria and sleeping sickness and since 1909 until its replacement by penicillin as principal drug for the treatment of syphilis [2].

Arsenic is stable in dry air, but the surface oxidizes slowly in moist air to give a bronze tarnish and finally a black covering to the element. When heated in oxygen, arsenic ignites in oxygen to form "arsenic pentoxide" - actually tetraarsenic decaoxide, As₄O₁₆, and As₄O₆ [3].

\[
4\text{As}(s) + 5\text{O}_2(g) \rightarrow \text{As}_4\text{O}_{16}(s)
\]

\[
4\text{As}(s) + 3\text{O}_2(g) \rightarrow \text{As}_4\text{O}_6(s)
\]

Arsenic belongs to the same group of the periodic table as both nitrogen and phosphorus and is often described as a metalloid element. In most situations, however, its chemical behavior can be considered that of a non-metal. Arsenic exhibits two common oxidation states when in aqueous form; arsenic(III) and arsenic(V). In solution, they are usually present as the oxyanions arsenite (AsO₃³⁻) and arsenate (AsO₄³⁻) respectively. These oxyanions can exhibit various degrees of protonation depending on the solution pH [4].
Arsenate is isoelectric with phosphate (PO₄³⁻) and there are many similarities between the behaviour of arsenic and phosphorus in natural waters when arsenic present as arsenate. This is partly illustrated by comparing dissociation constants for arsenic and phosphoric acid.

**Phosphoric Acid**

\[
\begin{align*}
H_3PO_4 + H_2O &\leftrightarrow H_2PO_4^- + H_3O^+ & K_a & = 2.15 \\
H_2PO_4^- + H_2O &\leftrightarrow HP0_3^{2-} + H_3O^+ & K_a & = 7.20 \\
HP0_3^{2-} + H_2O &\leftrightarrow PO_4^{3-} + H_3O^+ & K_a & = 12.36
\end{align*}
\]

**Arsenic Acid (Arsenate Anion)**

\[
\begin{align*}
H_3AsO_4 + H_2O &\leftrightarrow H_2AsO_4^- + H_3O^+ & K_a & = 2.20 \\
H_2AsO_4^- + H_2O &\leftrightarrow HAS0_3^{3-} + H_3O^+ & K_a & = 6.97 \\
HAS0_3^{3-} + H_2O &\leftrightarrow AsO_4^{4-} + H_3O^+ & K_a & = 11.53
\end{align*}
\]

Arsenic (As) a toxic, ubiquitous element with metalloid properties, presents in environmental samples i.e. soil, sediment, water, aerosol, rain, aquatics, vegetations, milk, etc. [5 - 6]. It is found naturally in metal ore deposits, mainly as arsenides of Cu, Ni and Fe [7]. The most important compound, arsenic oxide, is produced as a by-product in the smelting of copper, lead and iron ores. Arsenic chemistry is complex, and exists in the form of both organic and inorganic compounds in four oxidation states i.e. -3, 0, +3 and +5. Arsenic compounds are used mainly in agriculture and forestry as pesticides and herbicides and in the glass and ceramic industries, etc. Arsenic compounds are also used as alloying agents and in the manufacture of semiconductors, lasers, transistors, metal adhesives, explosives and pharmaceutical products. Arsenic accumulation in the environment has been found to be hazardous to ecosystem and human health. Arsenic enters the human and animal food chain mainly either by drinking contaminated water or by the consumption of plants commonly grown food.
The natural and anthropogenic sources (i.e. industries, mining, farming, rock weathering, atmospheric deposition, etc.) have added to the arsenic contents in the ecosystem i.e. soil, water. Atmospheric arsenic presents within troposphere, and its > 90% content is in particulate form with a diameter < 3.5 μm.

Toxicity, biological availability and transport mechanism of arsenic highly depend on its physico-chemical form. Inorganic As-species are known to be more toxic than organic As-species. In turn, As (III) is more toxic than As (V). The toxicity decreases with increasing methylation. Monomethylarsenic acid (MMA) is more toxic than dimethylarsenic acid (DMA). However, arsenobetaine (AsB), arseneocholine (AsC), arsenic sugars (AsS), etc. are believed to be non-toxic [9 - 10]. The common arsenic species reported are summarized in Table 1.1.

Table 1.1. Common inorganic, methylated and organic species:

<table>
<thead>
<tr>
<th>Species</th>
<th>Acronyms</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenous acid</td>
<td>As(III)</td>
<td>H₃AsO₃</td>
</tr>
<tr>
<td>Arsenic acid</td>
<td>As(V)</td>
<td>H₃AsO₃</td>
</tr>
<tr>
<td>Monomethylarsonic acid</td>
<td>MMA</td>
<td>CH₃AsO₃</td>
</tr>
<tr>
<td>Dimethylarsinic acid</td>
<td>DMA</td>
<td>C₂H₃AsO₂</td>
</tr>
<tr>
<td>Trimethylarsine oxide</td>
<td>TMAO</td>
<td>C₃H₇AsO</td>
</tr>
<tr>
<td>Methylarsine</td>
<td>-</td>
<td>CH₃As</td>
</tr>
<tr>
<td>Dimethylarsine</td>
<td>-</td>
<td>C₂H₇As</td>
</tr>
<tr>
<td>Trimethylarsine</td>
<td>-</td>
<td>C₃H₇As</td>
</tr>
<tr>
<td>Arsenobetaine</td>
<td>AB</td>
<td>(CH₃)₂As(CH₂)COOH</td>
</tr>
<tr>
<td>Arsenocholine</td>
<td>AC</td>
<td>[(CH₃)₂As'CH₂OH]X</td>
</tr>
<tr>
<td>Arseno</td>
<td>AS</td>
<td>(CH₃)₃AsO-sugar</td>
</tr>
</tbody>
</table>
Speciation of arsenic in the various environmental compartments is still an analytical challenge especially for soils, sediments, biological and medical samples. Water is the major means of transport for arsenic in the environment and uses of the contaminated drinking water represents so far the greatest hazard. In living organisms, soluble pentavalent inorganic arsenicals can compete with phosphate and lead to the formation of 1-arseno-3-phosphoglycerate, which is spontaneously hydrolyzed without ATP production. In addition, they are easily reduced into arsenite, which rapidly binds to biological thiol groups, inhibiting many important enzymes among which pyruvate dehydrogenase, a multi subunit complex requiring the dithiol cofactor lipoic acid for enzymatic activity. An impairment of energy production coupled with the inhibition of many other thiol enzymes can affect virtually all cellular functions. Hyper pigmentation, depigmentation, keratosis, peripheral vascular disorder, etc. are the most commonly reported symptoms of chronic exposures of arsenic. Skin cancer and a number of internal cancers can also result. Cardiovascular and neurological diseases have been linked to arsenic indigestion and exposure. In the population chronically exposed to inorganic arsenic, the respiratory, cardiovascular, gastrointestinal, hematological hepatic, skin, neurological and genotoxic effects have been reported [11 - 13].

**SCOPE OF THE PROPOSED WORK**

A number of large aquifers in various parts of the world have been identified containing arsenic at concentration > 10 μg l<sup>-1</sup>. The most noteworthy occurrence is in parts of west Bengal and Bangladesh, Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of USA [14 -19]. Occurrence of mining related As problems also have been recorded in many parts of the world, including Thailand, Ghana, Greece, Austria and parts of the USA. Arsenic associated with geothermal waters has also been reported in
several areas, including hot springs from parts of the USA, Japan, Chile, Argentina, France, Dominica, and New Zealand [20 - 24].

Arsenic poisoning in West Bengal, India, and Bangladesh is now one of the biggest pollution calamities in the world. Drinking water is naturally contaminated by arsenic in most of the districts of West Bengal and Bangladesh. Arsenic concentration in tube-well water in the affected districts exceeds the World Health Organization (WHO) guidelines for drinking water (10 μg/l). More than million of people are suffering from arsenical skin lesions in West Bengal alone. Cases of melanosis, keratosis, hyperkeratosis, cancer, gangrene, and early death cases related to arsenic have been reported in West Bengal and Bangladesh. Although the cases of arsenic contamination of tube-well water in West Bengal and Bangladesh could be geological, exact explanation as to how this is happening is still lacking [25 - 42].

The arsenic exists in several forms: As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), tetramethylarsenium ion (TETRA), trimethylarsine oxide (TMAO), arsenochloline (AC), arsenobetaine(AsB), arsenosugar(AsS), etc. in environmental samples [43 - 44].

Elemental speciation involves the separation and quantification of the different oxidation states (i.e. As (III), As (V)) or chemical form (e.g. MMA, DMA, TETRA, TMAO, AsB, AsC, AsS, etc.) of arsenic. The elemental speciation at sub-microgram levels could be achieved by coupling two powerful techniques: one, which provides separation of the various forms of the element of interest and another, which gives the low detection limits. Chromatography techniques i.e. HPLC, GC, SFC, CE, etc. provides the separation methods necessary for the elemental speciation. Technique i.e. Induced coupled plasma mass spectrophotometry (ICP-MS) is considered the method of choice for elemental analysis at sub-nanogram to picogram levels. Alternatively, other techniques i.e. hydride generation-atomic fluorescence spectrometry (HG-AFS), hydride generation-atomic absorption spectrometry (HG & GF-AAS), voltammetry, capillary electrophoresis, etc. are used for the
determination of arsenic at trace levels [45 -92].

Spectrophotometry is a versatile technique for the field detection of pollutants in spite of poor sensitivity. Several inorganic and organic reagents i.e. molybdenum blue, diethyldithiocarbamate, dyes, chlorpromazine, gibberellin, N,N'-diphenylbenzamidine, etc. were reported for the spectrophotometric determination of arsenic but they involve poor selectivity or / and sensitivity. The molybdenum blue and diethyldithiocarbamate are widely used for determination of arsenic but require a prior separation to overcome interferences. The cationic dyes and organic bases i.e. chlorpromazine were reported to enhance the sensitivity of the heteropoly acid, however, suffer from serious interferences of phosphate and silicate. Some dyes i.e. rhodamine-B, methylene blue were reported for the indirect determination of arsenic but many chemical species present in situ may interfere [93 – 98].

Arsenic contaminated area, Ambagarh Chauki block (area \( \approx 2.0 \times 10^3 \text{ km}^2 \)) lie in Chhattisgarh (CG) state of the country. It is situated in peninsular plateau, between \( 20^\circ 33' - 20^\circ 51' \) N latitudes and \( 80^\circ 33' - 80^\circ 47' \) longitudes at altitudes of \( \geq 430 \) meters from sea level, Figures 1-3. It lies at the highest summer temperature profiles. It is based on the igneous and metamorphic rocks. The soil is brown in color with low silica and high iron and aluminium contents. The area is very rich in the biological diversity. Both, tropical moist and dry deciduous forests are present in this region. The total population of the district is about 1.5 million. The Asia biggest steel plant (5 MT iron ore/year) is in operation \( \approx 100 \) km away from the study area. About 5 MT iron ore every year is smelted to produce 3.153 MT iron.

In the present work, a new, simple and selective method for the sensitive spectrophotometric determination of arsenic in the environmental samples (i.e. water) is described. The distribution of total As in the water, soil and sediment of the Ambagarh Chauki area is investigated. The content of other trace elements i.e. Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Sn, Sb, Pb, and U in the soil, and their correlation with As are described.
The accumulation of metals i.e. As, Cu and Pb in main food (i.e. rice grain), and effect of the arsenic content in the water and soil as well as the rice morphology (i.e. cultivation period, height, grain size, husk percentage, etc.) are discussed. The quantification of accumulated arsenic in human samples (i.e. hair, nail, skin and urine) is described.
Figure 1: Representation of Chhattisgarh State in India
Figure 2: Representation of Ambagarh Chauki in Chhattisgarh
Figure 3: Representation of the study area
OBJECTIVE OF THE PROPOSED WORK

1. To develop new and simple method for detection of arsenic.
2. Investigation of arsenic contaminated environment in the Ambagarh Chauki area.
3. To investigate accumulation of arsenic, copper and lead in main food i.e. rice.
4. Speciation of arsenic in human samples i.e. hair, nail, skin and urine.
SUMMARY OF THE PROPOSED WORK

The work content of the proposed thesis has been divided into five chapters as under

Chapter-I: Introduction part of the proposed thesis

Chapter-II: Spectrophotometric determination of arsenic with iodide and amide

A new, simple and selective spectrophotometric method for the determination of arsenic in the contaminated water samples is described. The method is based on the complexation of As (III) with I⁻ ions in strong HCl medium, and extraction of the yellow colored complex with N-octylacetamide (OAA) into chloroform solution. The optimum acidity range is 4.5 - 6.0 M HCl / 2.5 - 3.5 M H₂SO₄. The apparent value of molar absorptivity in the terms of arsenic is \((5.00) \times 10^4\) l mol⁻¹ cm⁻¹ at \(\lambda_{max}, 420\) nm. The calibration curve is linear upto 1200 µg l⁻¹ As with slope, intercept and correlation coefficient of \(6.52 \times 10^{-4}\), 0.005 and + 0.99, respectively. The rel. std. dev. of the method for 6 replicate measurements was found to be ± 1.3%. The detection limit (i.e. more absorbance than 3 std. dev.) of the method is 10 µg l⁻¹ As. The method is free from interference of the ions commonly found to be associated with arsenic in environmental samples. The method has been tested for the field determination of arsenic in contaminated water of the Ambagarh Chauki.
Chapter-III: Arsenic contamination in water, soil and sediment

The situation of arsenic contamination levels in the environment (i.e. water, soil and sediment) of Ambagarh Chauki area is described. The concentration ranges of the total arsenic in water $(n=64)$, soil $(n=30)$ and sediment $(n=27)$ found were $15 - 825 \, \mu g \, l^{-1}$, $9 - 390 \, mg \, kg^{-1}$ and $19 - 489 \, mg \, kg^{-1}$, respectively. The predominant species present in water are inorganic arsenic i.e. As(III) and As(V). The depth profile distribution of As in soil, correlation with other elements and sources are discussed.

Chapter-IV: Accumulation of arsenic, copper and lead in rice

The accumulation of heavy metals i.e. As, Cu and Pb in ten different rice species (i.e. Culture, G. Gurmatia, IR-64, Kalinga, Luchai, Mahamaya, Masuri, Purnima, Safari, Shyamla) is described. The concentration of As, Cu and Pb in the field water, soil, rice and husk are also discussed. The concentration of As, Cu and Pb in the field water, soil, rice and husk was ranged $47 - 180$, $78 - 131$ and $7.0 - 19.0 \, \mu g \, l^{-1}$; $8.8 - 252$, $23.9 - 80.9$ and $13.3 - 45.5$; $0.018 - 0.446$, $4.3 - 10.32$ and $0.21 - 1.51$; and $0.194 - 1.048$, $5.3 - 16.3$ and $0.56 - 6.28 \, mg \, kg^{-1}$ with mean value of $108$, $102$ and $11.0 \, \mu g \, l^{-1}$; $71$, $49$ and $25$; $0.27$, $6.6$ and $0.64$; and $0.50$, $9.4$ and $1.5 \, mg \, kg^{-1}$, respectively. The effect of variables i.e. metal content in the water and soil, grain mass, cultivation period, plant height, yield, etc. in the accumulation of the metals in rice and husk are discussed.
Chapter-V: Speciation of arsenic in hair, nail, skin and urine

The speciation of As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), etc., in the human samples i.e. hair, nail, skin and urine is described. The concentration levels of total arsenic (AsT) in the hair, nail, skin and urine samples were ranged 338 - 2047, 1529 - 7614, 820 - 6988, and 22 - 148 with mean value of 918, 3525, 2875 and 65 \( \mu g \text{ kg}^{-1} \) respectively. The speciation pattern of arsenic i.e. As(III), As(V), MMA and DMA in the hair, nail, skin and urine are described. The main arsenic exposures involved in the arsenic accumulation are discussed.
OUTCOMES OF THE WORK

1. A new, simple, selective and sensitive method for spectrophotometric determination of arsenic in the contaminated water samples has been developed.

2. Situation of arsenic contamination in the environment of the Ambagarh Chauki area has been investigated.

3. Accumulation pattern of heavy metals arsenic, copper and lead in main food i.e. rice has been evaluated.

4. Quantification of arsenic species i.e. As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), etc in human samples i.e. hair, nail, skin and urine has been carried out.
REFERENCES


