Chemical Toxicology Research Analysis Of Arsenic

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ABSTRACT

It is the study of the sources, reactions transport, effects and fate of chemical species in the air, water and soil and the effect of human activity upon these. There are a number of chemicals in the environment. Some of these are toxic and the rest non-toxic. Chemical toxicology is the science of the study of toxic chemicals and their mods of action. Arsenic commonly occurs insecticides, fungicides and herbicides. Among its compounds, those of As (III) are the toxic.

Arsenic analysis is generally carried out by the silver diethyldithiocarbonate spectrophotometric method. The method was initially use for analysis of bovine urine for inorganic and methylarsenic content. Sodium Borohydride reduction is widely used for total As content using AAS. Arsenic speciation in air samples is carried out using a glass wool filter to trap the particulates, followed by silvered glass beads to trap volatile arsines. The Arsines are removed dil. NaOH wash and analyzed as above, after $NaBH_4$ reduction.

Fig. shows an HPLC-ICP chromatogram indicating the presence of dymethylarsinic acid and a small amount of arsenate in a commercial herbicide. A purified semple of crab met shows the presence of arsenobetaine as compared with a standard solution of sodium arsenite, arsenobetaine and arsenocholine in HPLC-GFAAS chromatogram (fig.)

Introduction:

Environmental Chemistry is multi-disciplinary science involving chemistry, physics, life science, agriculture, medical science, public health, sanitary engineering, etc. In simple terms, it is the science of chemical phenomena in the environment. In broader terms, it is the study of sources, reaction transport, effect and fate of chemical species in the air, water and soil and the effect of human activity upon these.
An understanding of the basic concepts of environmental chemistry is essential not only for all chemists but also for all non-chemists engaged in environmental science, engineering and management. There are a number of chemicals in the environment. Some of these are toxic and the rest non-toxic. The toxic chemicals are discharged by industries into air, water and soil. They gate into the human food chain from the environment. Once they inter our biological system they disturb the biochemical process, leading in some cases to fatal result. Chemical toxicology is the science of the study of toxic chemical and their modes of action.

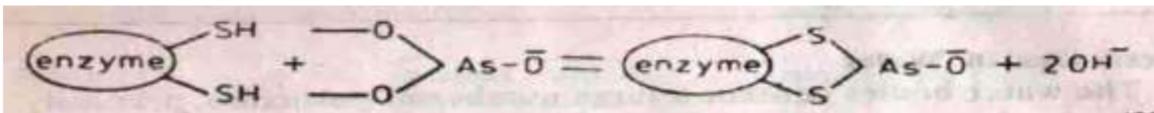
Toxic chemical in Air:

As a matter of fact, thousand of chemicals presumably pose the problems of health hazards so that it is necessary to exercise strict control on those which offer the most serious threats during manufacture and handling . In 1978 the U.S. environmental protection agency , occupational safety and health Administration , and consumer product safety commission listed 24 extremely haxardous substances in the atmosphere :

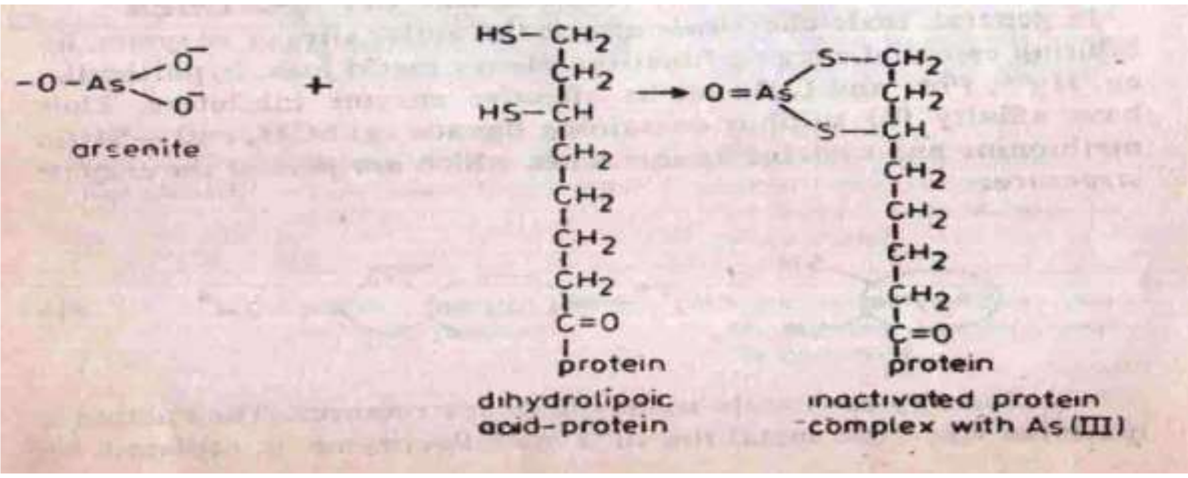
Biochemical effect of arsenic:

Arsenic commonly occurs in insecticides, fungicides and herbicides. Among its compounds, those of As(III) are the most toxic.

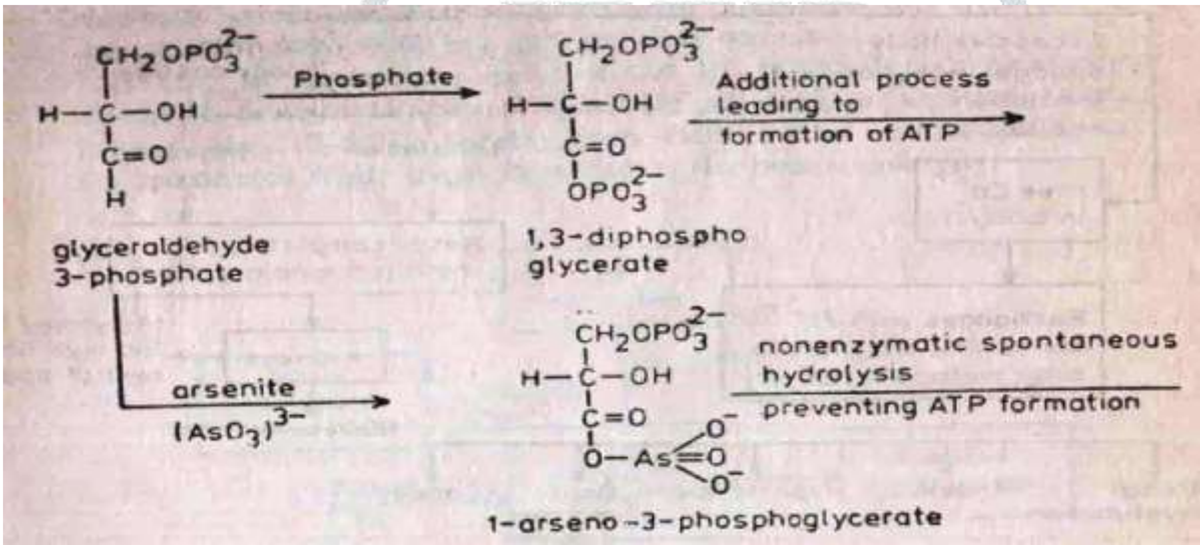
As(III) exerts its toxic action by attacking-SH groups of an enzymes, thereby inhibiting enzyme action.



The enzymes which generate cellular energy in the citric acid cycle are adversely affected. The inhibitory action is based on inactivation of pyruvate dehydrogenase by complexation with As(III), whereby the generation of ATP is prevented.



By virtue of its chemical similarity to P, As interferes with some biochemical processes involving P. this is observed in the biochemical generation of the key energy-yielding substance, ATP (adenosine triphosphate). An important step in ATP generation is the enzymatic synthesis of 1,3-diphosphoglycerate from glyceraldehydes 3-phosphate. Arsenite interferes by producing 1-arseno-3-phosphoglycerate instead of 1,3-diphosphoglycerate. Phosphorylation is replaced by arsenolysis which consists of spontaneous hydrolysis to 3-phosphoglycerate and arsenate.



Arsenic (III) compounds at high concentrations coagulate proteins, possibly by attacking the sulphur bonds maintaining the secondary and tertiary structures of proteins.

The three major biochemical actions of As are coagulation of proteins, complexation with coenzymes and uncoupling of phosphorylation.

The general antidotes for As poisoning are chemicals having-SH groups capable of bonding to As(III), e.g. 2, 3-dimercaptopropano (BAL)

$$HSCH_2 - \underset{\displaystyle SH}{\underset{|}{CH}} \quad CH_2OH$$

Analysis of Arsenic :

Biomethylation of As has been studied in detail . Arsenic analysis is generally carried out by the silver diethyldithiocarbonate spectro- photometric method. The methyl and dimethyl arsenic acid compounds do not give the same absorption curves . Although convenient for speciation in the 10^{-6} g As or greater sample-size range , the method was initially used for analysis of bovine urine or inorganic and methylarsenic content . sum borohydride reduction is widely used for total As content using AAS . $NaBH_4$ may also be used for reduction of alkyl and arylarsenic compounds. As(iii) is reduced to AsH_3 above pH 4, while As(v) is reduced at pH 1.5 . AsH_3 generated in reaction chambers is trapped in cold toluene and then analyzed by GC-AES . Alternatively, AsH_3 is cold trapped on a short column and separated by warming with AES detection . methyl arsenic compounds are found in several water bodies in substantial percentages . But these are a small percentage of total As in sea water . some typical environmental data for As are tabulated in Table.Arsenic speciation in air samples is carried out using a glass-wool filter to trap the particulates, followed by silvered glass beads to trap volatile arsines. The arsines are removed by dil.

NaOH wash and analyzed as above, after $NaBH_4$ reduction. Ambient air appears to contain As mostly as the inorganic species, some $(CH_3)_3As$ in vapour form, and some methyl arsenic compounds as particulates.

Table Environment analysis for Arsenic (ug/L)

I Natural Water bodies

Location	As(III)	As(V)	Methyle Arsenic acid	Dimethyle arsenic acid	Total
Fresh water					
Withlacooche River	<0.02	0.16	0.06	0.30	0.42
Lake Carroll	0.89	0.49	0.22	0.15	1.75
Pond	<0.02	0.32	0.12	0.62	1.06
Saline water					
Tampa Bay	0.12	1.45	<0.02	0.20	1.77
Sea water					
San Diego					
Surface	0.017	1.49	0.005	0.21	1.72
25m	0.016	1.32	0.003	0.14	1.48
100m	0.06	1.59	0.003	0.002	1.66
Rain					
La Jolla, Callifornia	<0.002	0.18	<0.002	0.024	0.204

II Air: Particulate and vapour, ng/m^3

	As(III)+As(V)	$(CH_3)_2AsOOH$	$(CH_3)_3As$
Suburban lawn	4.1	- 0 90-	
Urban air	3.6	1.0	0.4
Rural air	0.4	0.3	0
Green house	1.7	0.4	20.5

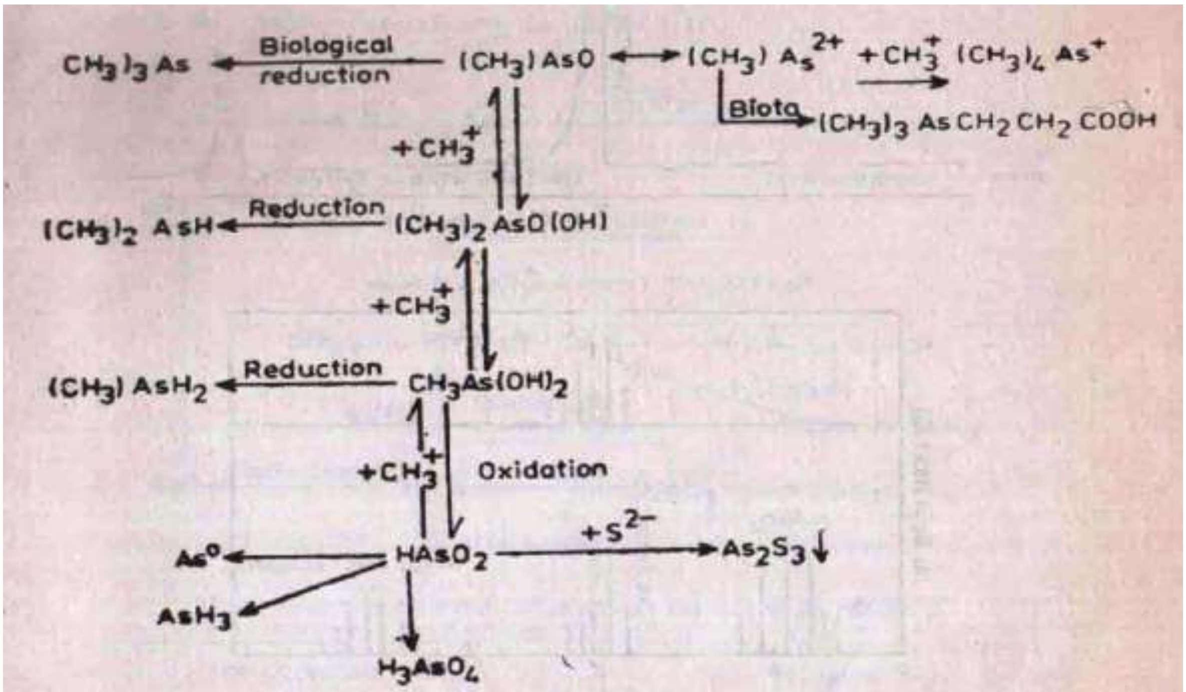
Table Arsenic speciation in human urine

Species	Average values	ug/L
As(III)	1.3	1.9
As(V)	1.3	3.9
Methylarsonic acid	3.4	1.8
Dimethyle arsenic acid	11.5	15.0
Tatal As	21.2±2.04	22.5±8.5

Speciation of As in water, urine and biological samples has been conducted by I-reduction instead of $NaBH_4$ reduction. As(V) compounds are converted to iodides in the presence of I^-, which are then allowed to react with diethylammonium diethyl dithiocarbamate to form the As-complexes of diethyldithiocarbamate:

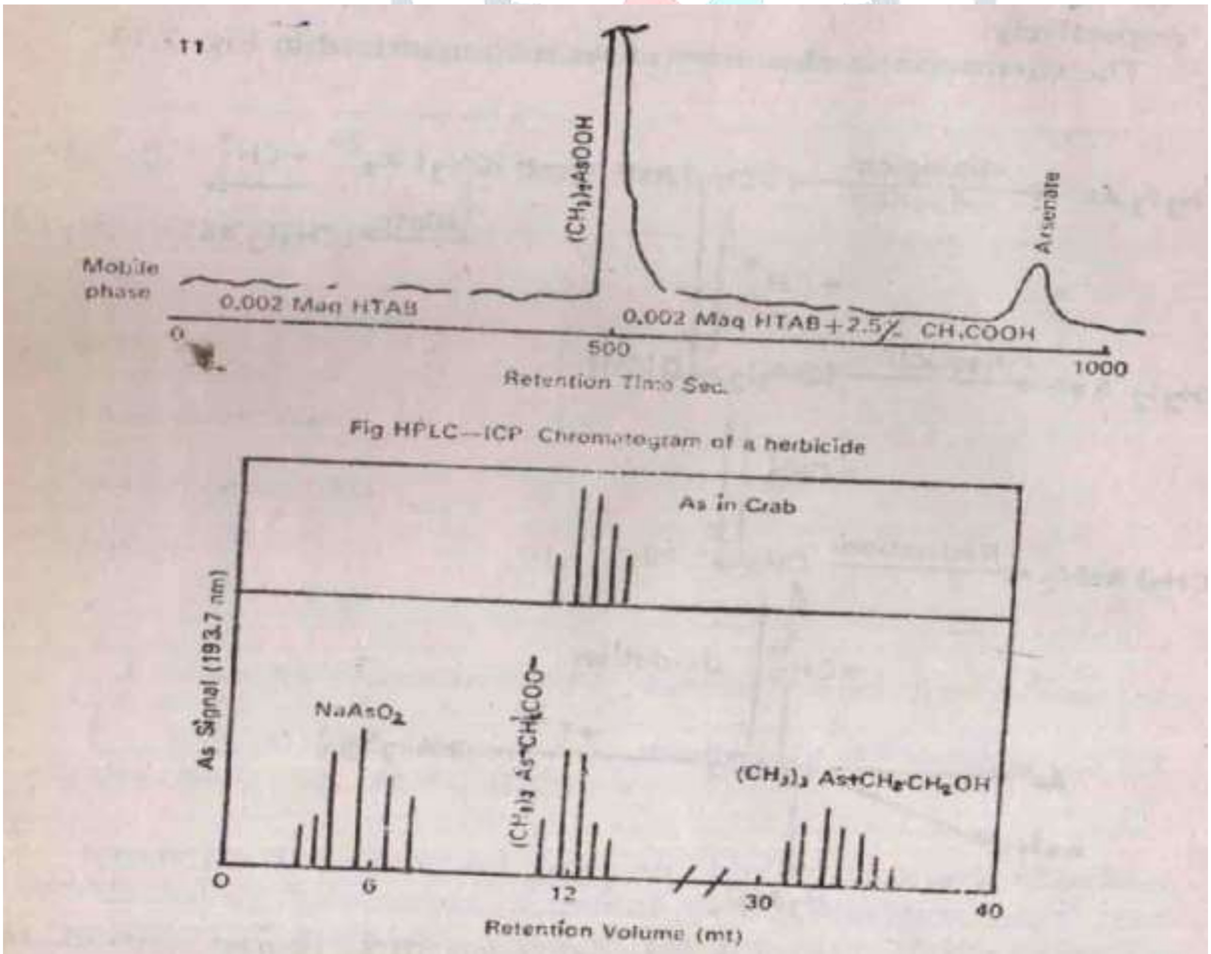
$$As[(C_2H_5)_2\ N\ C\ S_2]_3$$
$$CH_3\text{-}As[C_2H_5)_2N\text{-}CS_2]$$
$$(CH_3)_2\text{-}As[(C_2H_5)_2N\text{-}CS_2]$$

These complexes are then separated by GC with an electron capture detector. The detection limits are 73, 40 and 15 ng/ml for inorganic As, methyl-arsenic compounds and dimethyl arsenic compounds, respectively.



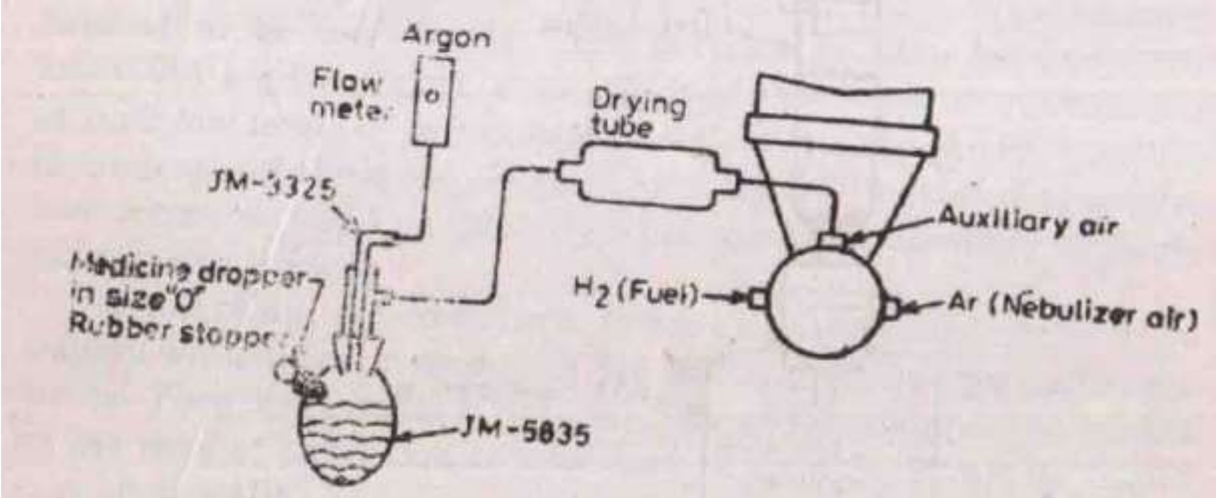
The environment chemistry of As is summarized in Fig.

Fig. shows an HPLC-ICP chromatogram indicating the presence of dimethylarsinic acid and a small amount of arsenate in a commercial herbicide. A purified sample of crab meat shows the presence of arsenobetaine as compared with a standard solution of sodium arsenite, arsenobetaine and arsenocholine in HPLC-GFAAS chromatograms (Fig.)



Atomic Absorption Spectrophotometric Method

Arsenic is reducted to the + 3 state and converted to AsH_3 which is directly aspirated into Ar-H_2 flame and measured in an atomic absorption spectrophotometer at 193.7 nm. As can be estimated down to 2.5 ppb.



The apparatus set up for As estimation is shown in Fig.

Procedure

1. ***Inorganic As:*** Take a 25 mL sample in a 50 mL volumetric flask. Add 20 mL conc. HCl and 5 mL 18 N H_2SO_4.
2. ***Total As:*** (a) To a 50 mL sample in a 150 mL beaker, add 10 mL conc. HNO_3 and 12 mL 18 N H_2SO_4. (b) Evaporate to SO_3 fumes (volume about 20 ml.) Add small amounts of conc. HNO_3 from time to time whenever the red-brown fumes of NO_2 disappear in order to avoid loss of As and maintain the oxidizing conditions. (c) Cool slightly, add 25 mL deionized distilled water, 1 mL$HClO_4$ and again evaporate to SO_3 fumes. (d) Cool, add 40 mL conc. HCl and make up to 100 mL with deionized disttled water.

Transfer 25 mL aliquot of sample prepared under (1) or (2) above into the reaction vessel and proceed as follows: (a) Add 1 mL of 20% KI Solution and 0.5 mL $SnCl_2$ solution (100 g $SnCl_2$ dissolved in 100 mL conc. HCl). Allow the mixture to stand for 10 mins. As(V) is reduced to As(III). (b) Fill the medicine dropper with 1.5 mL Zn-slurry (50 g Zn dust (200 mesh) in 100 mL deionized distilled water) which has been kept in suspension with a magnetic stirrer. Insert the stopper containing the medicine dropper into the side neck of the reaction vessel. (c) Squeeze the bulb to introduce the Zn-slurry into the sample. (d) Measure the AsH_3 peack at 193.7 nm. (e) Prepare a standard curve under identical conditions with 0.5 to 20 ppb As.

Conclusion:

- Environmental Chemistry is multi-disciplinary science involving chemistry, physics, life science, agriculture, medical science, public health, sanitary engineering, etc.
- Chemical toxicology is the science of the study of toxic chemical and their modes of action.
- Arsenic commonly occurs in insecticides, fungicides and herbicides. Among its compounds, those of As(III) are the most toxic. As(III) exerts its toxic action by attacking-SH groups of an enzymes, thereby inhibiting enzyme action.
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