

Speciation and Detection of Arsenic in Groundwater samples: A Review of various analytical methods

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Abstract : It has been found that naturally arsenic exists in many different chemical forms. These forms exist in mainly four oxidation states (As^{3+} , As^{5+} , As^0 and As^{3-}) which exist in organic and inorganic forms. Organic form of arsenic exist as alkyl derivative of arsenic like mono methyl arsenic acid (MMA) and dimethyl arsenic acid (DMA). Soluble forms of arsenic are separated easily by capillary electrophoresis (CE) and high pressure liquid chromatography (HPLC) methods. High pressure liquid chromatography (HPLC) method has more advantage over capillary electrophoresis (CE) because of different mechanism of mobile and stationary phases. For detection of trace elements like As, those techniques are required which are highly sensitive and selective. These techniques are nuclear magnetic resonance (NMR), X-beam photoelectron spectroscopy (XPS), electron spectroscopy for concoction examination (ESCA), X-beam assimilation fine structure spectroscopy (XAFS), electron turn reverberation (ESR), couple mass spectroscopy (TMS) and Mossbauer spectroscopy. Now the sampling problems like loss of analyte or contamination have been understood and solved. These problems with arsenic speciation become more complex and with different forms of arsenic, it has become a long time study. Preservatives have a great significance in maintaining total arsenic content in the samples. Arsenic speciation in a particular water sample cannot be done without maintaining total arsenic content specially in inorganic forms of arsenic As(III) and As (V).

Keywords : nuclear magnetic resonance (NMR), X-beam photoelectron spectroscopy (XPS), electron spectroscopy for concoction examination (ESCA), X-beam assimilation fine structure spectroscopy (XAFS), electron turn reverberation (ESR), couple mass spectroscopy (TMS) and Mossbauer spectroscopy.

1. INTRODUCTION

1.1 ARSENIC CHEMISTRY AND ARSENIC SPECIATION – PREVIOUS REVIEWS

Arsenic has in excess of fifty recognized distinctive normally happening arsenic containing concoction species..Arsenic happens in the earth in four oxidation states (As^{3+} , As^{5+} , As^0 and As^{3-}) in inorganic just as in natural structures, Inorganic arsenic contains two oxy anions, arsenite As(III) and arsenate As(V). Diverse organo arsenic compounds exist however the most well-known in the earth are monomethyl arsenic corrosive (MMA) and dimethylarsenic corrosive (DMA). Furthermore, basic methylated arsenic species are trimethylarsine oxide (TMAO) and the tetramethyl arsonium particle (TETRA). Various organoarsenic mixes are present in natural examples: arsenobetaine (AB) as an overwhelming species in fish, arsenocholine(AC) and trimethyl arsenopropionate (TMAP). Different types of As, such as arseno sugars, happen principally in water life forms. Broad danger investigations of As demonstrated that various structures show various toxicities. Inorganic arsenic species are around multiple times more lethal than natural arsenic mixes. Trivalent arsenic is around multiple times more poisonous than the oxidized pentavalent state. Methylation of inorganic arsenic in the body is a detoxification procedure, which reduces the liking of the compound for tissue as an adsorbent. In common waters, arsenic seems regularly in inorganic structures and to a lesser degree in natural structure, for example, MMA and DMA. As(V), MMA and DMA are steady in oxidized frameworks, while As(III) is shaky under oxidizing conditions and is promptly oxidized. In normal water, As(III) happens at much lower concentrations contrasted with As(V), which makes its immediate recognition troublesome and inevitably pre-focus steps are required.

1.2 ANALYTICAL METHODS FOR SPECIATION ANALYSIS

Late reciprocal surveys on explicit parts of arsenic speciation analysis are recorded in **Fig. 1** of the Supplementary material to this audit. During the most recent decade, a critical number of logical papers reporting the improvement in arsenic speciation have been distributed. The focal point of research was the advancement and improvement of techniques for arsenic extraction, separation and location. The choice of a fitting strategy for the extraction of arsenic species from various frameworks without changing the oxidation state or with insignificant misfortune by volatilization or adsorption is as yet a difficult theme for research. Liquid partition methods, for example, superior fluid chromatography (HPLC) and less prevalent slim electrophoresis (CE) are the most frequently utilized systems for the division of dissolvable types of arsenic species. The bit of leeway of HPLC is the all-encompassing scope of detachment instruments by different portable and stationary stages.

The most connected location strategy is ICP-MS, particularly after HPLC partition. This procedure was connected in many studies for various example types (ecological, organic and sustenance samples).Application of ICP-MS has incredible capacities since it very well may be utilized as a highly sensitive and component explicit finder. Hydride age nuclear absorption spectrometry (HG-AAS) is a generally straightforward and reasonable method but suitable just for hydride dynamic As species. Electrochemical strategies are

suitable only for direct estimations in straightforward solutions. The number of productions on arsenic speciation investigation has increased steadily since 2003. The quantity of distributions, as appeared in **Fig. 1** from Science Direct, has expanded from 32 articles for each year (distributed in 2003)

The perfect answer for direct estimation of species would be in situ analysis. However, not very many systems give the essential selectivity and sensitivity Those are: atomic magnetic resonance (NMR), X-beam photoelectron spectroscopy (XPS), electron spectroscopy for concoction examination (ESCA), X-beam assimilation fine structure spectroscopy(XAFS), electron turn reverberation (ESR), couple mass spectroscopy (TMS) and Mossbauer spectroscopy. required for follow component speciation examination.

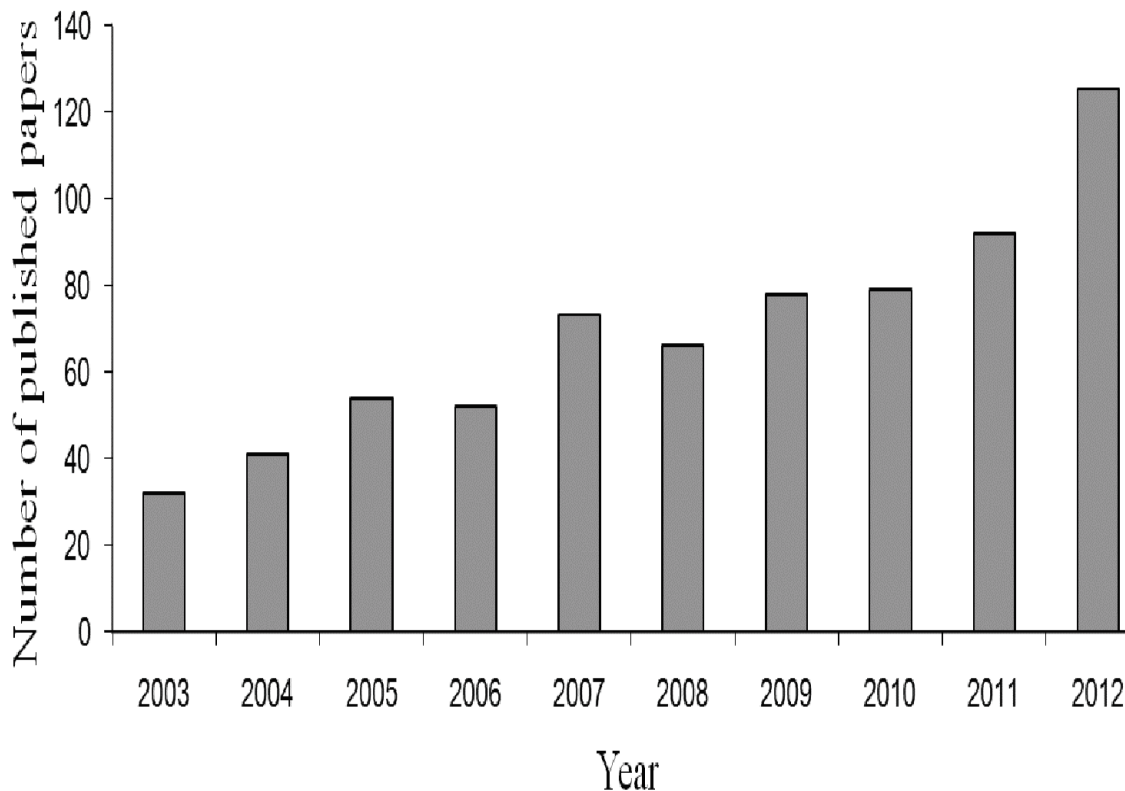


Fig. 1. Development of the quantity of distributed papers on arsenic speciation since 2003.

2. MATERIAL & METHODS

2.1 SAMPLE COLLECTION AND ANALYSIS PROCEDURE FOR As

Tests were gathered in detached mode for example without the utilization of any vitality to cause least deviation from the common conditions. The examining bottles, either glass (borosilicate) or plastic (polyethylene) were already corrosive and cleanser washed, and after that washed with bounteous measure of clean lab water lastly flushed with the refined water. Two sorts of value control tests were gathered I. e. the copy tests and gear spaces. The motivation behind the copy tests was to guarantee the accuracy of inspecting and investigation. The copy tests were gathered for both field screening and for research facility investigation. The motivation behind the hardware spaces was to check that inspecting gadgets were not contributing tainting to the examples. Test filtration, when done, an exchange vessel was utilized to delicately empty the get test into a reusable manual sifting gadget with a dispensable 0.45 μm channel film and separated utilizing a positive weight.

2.2 USE OF PRESERVATIVES FOR SAMPLE COLLECTION

An endeavor was made to see the impacts of different additives on keeping up the absolute arsenic substance of the examples. Speciation of the arsenic was not completed as the insignificant nearness of inorganic arsenic is a potential general wellbeing danger and the redox science of arsenic can cause an adjustment in the speciation rather effectively. Consequently, the two types of As for example M or (III) can experience interconversion, the other way around. In this manner, all out inorganic As alone ought to be principally focused in a territory study for arsenic predominance. Additive utilized in tests were as per the following:

1. HNO_3 : HNO_3 (Concentrated) was included until a $\text{pH} < 2$ checked at the examining site by versatile pH analyzer (Orion). Four primary arrangement of tests were gathered I. e. (1) F, 4C = separated and kept at 4°C (2) F, RT= sifted and kept at room temperature (3) UF, 4C = unfiltered and kept at 4°C (4) UF, RT = unfiltered and kept at room temperature - 35°C).
2. HCl and H_2SO_4 : Concentrated arrangements were utilized as above for keeping up the pH underneath two.

3. NaOH: NaOH (1 M) was included until the pH of 12. Accelerate, assuming any, was separated right away.
4. CHCl₃, CCl₄, HCHO: These were included 10 ml each.

2.3 SOLVENT EXTRACTION

The dissolvable extraction strategy is generally utilized for the assurance of natural arsenic mixes, particularly in organic samples. Methanol/water blends are broadly utilized for removing less polar species. Ciardullo et al. utilized a 1/1 (v/v) methanol/ water blend for the quantification of water-dissolvable As mixes in the muscle tissues of freshwater fish. In addition, extraction with water, or extraction with methanol/ water pursued by centrifugation and filtration, or extraction with chloroform/ methanol/water are ground-breaking extraction media and frequently utilized extraction procedures. The all out arsenic in various examples is normally removed utilizing the microwave extraction technique. So as to maintain a strategic distance from animal groups misfortunes or transformation, parameters, for example, extraction medium, connected microwave influence and exposure time must be cautiously optimized. On the other hand, it has been more than once demonstrated that a basic, inexpensive reagent, for example, tetramethylammonium hydroxide (TMAH) in basic medium, is valuable as a solubilising specialist for a wide assortment of natural frameworks. Speciation analysis of arsenic in fish-based child nourishments by electro thermal atomic absorption spectrometry (ET-AAS) utilizing suspensions arranged in a 0.01 mol L⁻¹ tetra methyl ammonium hydroxide (TMAH) arrangement has points of confinement of discovery for the assurance of AB, DMA and inorganic arsenic 15, 25 and 50 µg g⁻¹ expressed as arsenic, individually. Techniques, for example, these in which methanol/ water is utilized have the component of extracting just a little level of the arsenic in soil and residue samples.

3. RESULT & DISCUSSION

Another important analytical issue dealt in this work, was the type of sample container. Generally, two types of sample container i.e. the glass (borosilicate) or plastic (polyethylene or equivalent) are used. The standard methods for general metal analysis (including arsenic) prescribe the use of either type of container (APHA, 1992; 1995). Bednar et al. (2002) have also reported that storing the samples in opaque polyethylene bottles eliminates the effects of photochemical reactions but they have not presented a comparison with opaque borosilicate glasses. The results produced by them showing the preservation of arsenic species distribution over a 3-month period for a groundwater sample (Colorado well) and an acid mine drainage sample (Koehler Tunnel) shows fluctuations. Hence, an effort was made to test the efficacy of the two sample containers with the nitric acid and EDTA preservation.

To assess the container efficacy, four series of natural samples were taken wherein the arsenic concentration of natural groundwater samples was 0.7, 0.9 1.2 and 1.5 ppm. These samples were preserved with HNO₃ (until the pH 2 with continuous pH monitoring) and EDTA (300 µl of 0.125 M EDTA) to the 30-ml sample obtained from village Chain Chapra (Table 1-4). Results confirm 0% losses of total arsenic in glass bottles preserved with EDTA and HNO₃ up to 336 hours. However when kept up to 672 hours, then a loss of about 6% and 14% was observed with EDTA and HNO₃ respectively.

TABLE 1. ARSENIC LOSSES IN NATURALLY CONTAMINATED WATER SAMPLES PRESERVED WITH EDTA AFTER FILTERATION AND KEPT AT 4°C IN GLASS CONTAINER

Initial As	After 1 Day	After 2 Days	After 3 Days	After 1 week	After 2 weeks	After 4 weeks
0.7	0.7	0.7	0.7	0.7	0.7	0.66
1.2	1.2	1.2	1.2	1.2	1.2	1.12
1.5	1.5	1.5	1.5	1.5	1.5	1.4
0.9	0.9	0.9	0.9	0.9	0.9	0.86

TABLE 2. ARSENIC LOSSES IN NATURALLY CONTAMINATED WATER SAMPLES PRESERVED WITH HNO₃ AFTER FILTERATION AND KEPT AT 4°C IN GLASS CONTAINER

Initial As	After 1 Day	After 2 Days	After 3 Days	After 1 week	After 2 weeks	After 4 weeks
0.7	0.7	0.7	0.7	0.7	0.7	0.57
1.2	1.2	1.2	1.2	1.2	1.2	1.0
1.5	1.5	1.5	1.5	1.5	1.5	1.3
0.9	0.9	0.9	0.9	0.9	0.9	0.82

TABLE 3. ARSENIC LOSSES IN NATURALLY CONTAMINATED WATER SAMPLES PRESERVED WITH EDTA AFTER FILTRATION AND KEPT AT 4°C IN PLASTIC CONTAINER

Initial As	After 1 Day	After 2 Days	After 3 Days	After 1 week	After 2 weeks	After 4 weeks
0.7	0.7	0.69	0.68	0.68	0.66	0.6
1.2	1.19	1.2	1.12	1.15	1.0	.9
1.5	1.49	1.47	1.48	1.3	1.3	1.0
0.9	0.9	0.9	0.84	0.81	0.8	0.73

TABLE 4. ARSENIC LOSSES IN NATURALLY CONTAMINATED WATER SAMPLES PRESERVED WITH HNO₃ AFTER FILTRATION AND KEPT AT 4°C IN PLASTIC CONTAINER (As µg/L)

Initial As	After 1 Day	After 2 Days	After 3 Days	After 1 week	After 2 weeks	After 4 weeks
0.7	0.7	0.68	0.68	0.69	0.65	0.5
1.2	1.19	1.2	1.12	1.18	1.11	1.1
1.5	1.5	1.5	1.3	1.28	1.2	.95
0.9	0.9	0.9	0.84	0.81	0.8	0.73

This result questions the efficacy of plastic container (at least for arsenic) compared to the glass where the losses of trace levels of metals from the glass container have been reported by the sorption mechanism (HMSO, 1980). This study also shows that the glass container is a lesser evil for arsenic sampling. To account for the arsenic loss it is hypothesized that there could be conversion of the arsenic in the natural samples from this location to the volatile phase, which is aggravated by the higher temperature and the diffusion of the gaseous arsenic species is facilitated by the apparent porosity of the plastic container. Roles of the micro organisms need to be investigated which may act as catalysts to speed up otherwise very slow redox reactions.

4. CONCLUSION

The investigation region which is attempted in Eastern U. P. which goes under upper and center Ganga plain is around 238,000 km² and populace 200 millions. Most of living arrangement relies upon cultivating as their preeminent occupation. In U. P. Ballia region has famous instance of Arsenic tainting and speaks to one of dynamic instances of Arsenic harming in U. P. Other than Ballia, Varanasi and Ghazipur likewise indicated expanded breaking point of Arsenic in Groundwater. Arsenic has more than fifty perceived unmistakable regularly happening arsenic containing mixture species. Arsenic occurs in the earth in four oxidation states (As³⁺, As⁵⁺, As⁰ and As³⁻) in inorganic similarly as in characteristic structures, Inorganic arsenic contains two oxyanions, arsenite As(III) and arsenate As(V). Various organo arsenic mixes exist anyway the most outstanding in the earth are monomethyl arsenic destructive (MMA) and dimethylarsenic destructive (DMA). Moreover, essential methylated arsenic species are trimethylarsine oxide (TMAO) and the tetramethyl arsonium molecule (TETRA).

Arsenic research is opening up new consistent focuses, especially in speciation examination. Systems for choosing indications of complete arsenic and unmistakable substance kinds of arsenic have ended up being dynamically noteworthy as a result of the assorted lethality and mixture direct of the various sorts of arsenic. Thusly, extraordinary speciation procedure have been proposed and assessed. For the standard confirmation of a huge number of arsenic tests, settled systems that incorporate the coupling of separation methodology, for instance, molecule chromatography (IC) and predominant liquid chromatography (HPLC), with a tricky ID structure, for instance, inductively-coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry-hydride age (AFS-HG) and atomic ingestion spectrometry-hydride age (AAS-HG) are the procedures for choice.

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