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Arsenic in Water: Determination and Removal

Ljubinka Rajakovic and Vladana Rajakovic-Ognjanovic

Abstract

Depending on the physical, chemical and biogeochemical processes and condition of the environment, various arsenic species can be present in water. Water soluble arsenic species existing in natural water are inorganic arsenic (iAs) and organic arsenic (oAs) species. All acidic species, according to the chemical equilibrium, have well-recognized molecular and ionic forms in water. The distribution of iAs and oAs species is a function of pH value of water traces of arsenic that are found in groundwater, lakes, rivers and ocean. The WHO provisional guideline value for arsenic in drinking water is 10 μg L⁻¹. The most selective and sensitive methods for determination of total arsenic and its species in water are coupled techniques including chromatography, optical methods and mass spectrometry. Determination of arsenic species is of crucial importance for selection of arsenic removal technology. Best available technologies are based on absorption, precipitation, membrane and hybrid membrane processes. Adsorption is considered to be relatively simple, efficient and low-cost removal technique, especially convenient for application in rural areas. Sorbents for arsenic removal are biological materials, mineral oxides, activated carbons and polymer resins.

Keywords: arsenic, water, traces, species, toxicity, determination, removal, purification

1. Introduction

Arsenic, As, belongs to the group of elements that are called metalloids. A metalloid is a chemical element that has properties of both metals and nonmetals. Arsenic is from all its features mostly recognized as a poison. Arsenic has a complex chemical behavior since it exists in four different oxidative states [1]. Depending on oxidative state and presence in environment, arsenic species exhibit different toxicity [2]. Arsenic species can be present in all types of
environment and can originate from natural and anthropogenic sources [3]. Natural sources of arsenic are: rocks with incorporated arsenic compounds, activity of volcanoes and some biological processes. Anthropogenic sources are numerous, from mining to different types of production (pesticides, wood preservatives, and pigments). When the arsenic compounds reach groundwater, it is hard to distinguish the origin, both natural and anthropogenic arsenic species are released [3].

According to Science Direct, during the last decade, a significant number of scientific papers reporting the results from arsenic investigations are presented in Figure 1. The focus of these researches was the development and improvement of methods for arsenic detection, extraction, separation and removal.

The investigation of arsenic species and their behavior in various samples, especially in natural waters and environment is important for chemistry and environmental protection. The most common arsenic species are presented in Table 1

![Figure 1](image_url). The number of publications with keyword arsenic, according to Science Direct.

Depending on the oxido-reduction conditions, microbiological environment, arsenic species can be present in water in solution or in a precipitated form, and they can also adsorb or desorb from the existing precipitates [1, 2]. When arsenic species are soluble in water, they can be present in both inorganic and organic forms. For iAs species both As(III), arsenite, and As(V), arsenate, can be present. For oAs species, MMA and DMA are soluble forms of organic arsenic species. From the value of the chemical equilibrium constants for each molecular or ionic form of arsenic in water, the present species can be recognized [3]. When choosing and
analyzing the most dominant form of arsenic in water, the most present is inorganic arsenic as As(V). If As(III) is present, there are two important things that need to be taken into account. As(III) is more poisonous (even at low concentrations) than As(V). Beside the severe toxic effect, As(III) is easily oxidized. In oxidized conditions, stable forms of arsenic are As(V), and MMA and DMA, from oAs species. Many water sources in the world containing high concentration of arsenic cause health problems or diseases such as cancer. The WHO provisional guideline value for arsenic in drinking water is 10 μg L$^{-1}$ [4]. Water quality analysis usually do not include test on arsenic. Arsenic compounds are colorless and odorless. Once the presence of arsenic is determined in water, the separation and removal is obligatory. Removal technologies that are efficient, but still need improvement include absorption, precipitation, different electrochemical processes, membrane and hybrid membrane processes [6–9].

### 2. Arsenic in water

Arsenic enters the water through the dissolution of minerals, ores, soil, sediments, water, living organisms and rocks containing high concentrations of arsenic. Drinking water from surface water bodies usually does not contain high concentrations of arsenic. Higher concentrations have only been found in the groundwater. Human activities influence and change the content of arsenic in nature. When using arsenic compounds for different purposes, there is a direct influence. There is also indirect influence that affects the mobility of arsenic from different natural sources. Organic arsenic compounds such as AsB, AsC, TETRA, TMAO, arsenosugars and arsenic-containing lipids are mainly found in marine organisms although some of these compounds have also been found in terrestrial species.

Despite the fact that iAs species are predominant in natural waters, the presence of oAs has also been reported. Even though the main analytical interest is to determine total arsenic in water, it is also important to develop the procedures for As species determination, separation, and removal. The distribution of iAs and oAs species is a function of pH value of water [2].

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>Oxidation state</th>
<th>Chemical formula</th>
<th>Group</th>
<th>Presence in the environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>+5</td>
<td>AsO$_4^{3-}$</td>
<td>iAs</td>
<td>Water</td>
</tr>
<tr>
<td>As(III)</td>
<td>+3</td>
<td>AsO$_3^{3-}$</td>
<td>iAs</td>
<td></td>
</tr>
<tr>
<td>MMA</td>
<td>+5</td>
<td>CH$_3$AsO(OH)$_2$</td>
<td>oAs</td>
<td></td>
</tr>
<tr>
<td>DMA</td>
<td>+5</td>
<td>(CH$_3$)$_2$AsO(OH)</td>
<td>oAs</td>
<td></td>
</tr>
<tr>
<td>TMAO</td>
<td>+5</td>
<td>(CH$_3$)$_3$AsO</td>
<td>oAs</td>
<td>Seafood (fish, mussels)</td>
</tr>
<tr>
<td>TETRA</td>
<td>+3</td>
<td>(CH$_3$)$_3$As</td>
<td>oAs</td>
<td></td>
</tr>
<tr>
<td>AsB</td>
<td>+3</td>
<td>(CH$_3$)$_3$As$^+$(CH$_2$COO)$^-$</td>
<td>oAs</td>
<td></td>
</tr>
<tr>
<td>AsC</td>
<td>+3</td>
<td>(CH$_3$)$_3$As$^+(CH_2CH_2)OH$</td>
<td>oAs</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Common inorganic and organic arsenic species [5].
The distribution of arsenic species vs. pH values of water is presented in Figure 2 [2].

As(III) species: $\text{H}_3\text{AsO}_3$, $\text{H}_2\text{AsO}_3^-$, $\text{HAsO}_3^{2-}$ and $\text{AsO}_3^{3-}$, are stable under slightly reducing aqueous conditions. As(V) species: $\text{H}_3\text{AsO}_4$, $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$, are stable in oxygenated waters [6]. Two valences of the same element, molecular (ortho, $\text{H}_3\text{AsO}_3$ and $\text{HAsO}_2$) and ionic forms with different charges make the research of arsenic removal from water more challenging and indivisible of arsenic chemistry knowledge. Any arsenic removal technology strongly depends on the water conditions and the stability of arsenic forms in the water.

Bearing in mind the fact that arsenic occurs in water in molecular and ionic form depending on water pH, the main goal of many investigations is to select the most efficient exchanger, not only in terms of efficiency, but also in terms of applicability in the wide range of water pH values in real and environmentally friendly water treatment systems. In neutral conditions, As(V) species are completely in ionic form ($\text{H}_2\text{AsO}_4^-$ and $\text{HAsO}_4^{2-}$), while As(III) is in molecular ($\text{H}_3\text{AsO}_3$ or $\text{HAsO}_2$), as shown in Figure 2 [2].

**Figure 2.** The distribution of iAs and oAs species as a function of pH values of water [2]. Copyright approved by publisher.
3. Determination of arsenic and arsenic species in water

There are a variety of chemical methods from classical to contemporary analytical techniques that are used for determination of arsenic and arsenic species in water.

There has been several review articles on the speciation of arsenic in a variety of samples [10–14]. These reviews focus on (1) determination of total content of arsenic and (2) speciation analysis.

A review of contemporary methods for arsenic and arsenic species in water is presented in Table 2. The parameters, as detection limit, advantages and disadvantages are pointed out in order to have an insight into ability and application of available techniques.

The total concentration of arsenic in drinking water (mostly traces of arsenic, level of μg L\(^{-1}\) or less) can be detected only by sophisticated analytical techniques as ICP-MS, GF-AAS and HG-AAS [3, 14]. For As speciation analysis, well-established methods that involve the coupling of separation techniques, such as HPLC with a sensitive detection system, that is, ICP-MS, are recommended, and they are mostly used [13].

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Detection</th>
<th>Detection limit (µg L(^{-1}))</th>
<th>Advantages</th>
<th>Disadvantage</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-AES</td>
<td>Total arsenic</td>
<td>~30</td>
<td>Minimal sample volume; no sample pretreatment and short measurement time</td>
<td>Expensive; needs lot of knowledge for operating and interpretation of data</td>
<td>[14]</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Total arsenic</td>
<td>~0.1</td>
<td>Approved by US EPA</td>
<td>Spectral and matrix interferences</td>
<td>[11, 13, 19]</td>
</tr>
<tr>
<td>GF-AAS</td>
<td>Total arsenic</td>
<td>~0.025</td>
<td>Approved by US EPA</td>
<td>–</td>
<td>[3, 14]</td>
</tr>
<tr>
<td>HG-AAS</td>
<td>Total arsenic and arsenic speciation</td>
<td>0.6–6.0</td>
<td>Approved by US EPA</td>
<td>–</td>
<td>[14]</td>
</tr>
<tr>
<td>HPLC-HG-AAS</td>
<td>Total arsenic and arsenic speciation</td>
<td>1–47</td>
<td>No need for sample pretreatment</td>
<td>–</td>
<td>[3, 14]</td>
</tr>
<tr>
<td>HPLC-HF-AAS</td>
<td>Arsenic speciation</td>
<td>0.05–0.8</td>
<td>Rapid, inexpensive. No need for sample pretreatment</td>
<td>–</td>
<td>[3, 14]</td>
</tr>
<tr>
<td>IC-ICP-MS</td>
<td>Arsenic speciation</td>
<td>0.01</td>
<td>No need for sample pretreatment</td>
<td>–</td>
<td>[19]</td>
</tr>
<tr>
<td>HPLC-ICP-MS</td>
<td>Total arsenic</td>
<td>0.01</td>
<td>No need for sample pretreatment</td>
<td>–</td>
<td>[13]</td>
</tr>
</tbody>
</table>

Table 2. A review of contemporary methods for arsenic and arsenic species determination in water.
Historically, colorimetric/spectrophotometric methods have been used to determine total arsenic concentration. Several commercial field kits have been based on Marsh and Gutzeit reaction. All As species in a sample reduce to As (arsenic mirror) or arsine, AsH$_3$, (it passes on to an HgBr$_2$-impregnated filter, turning it to yellow to brown color, depending on the amount of arsenic present). These tests are obvious, visible proofs for arsenic detection, and they are popular and useful in the field of forensic toxicology. The colorimetric methods are easy to use and inexpensive in terms of equipment and operator cost. They are useful for the semi-quantitative determination of high concentrations of arsenic in water. Spectrophotometric methods are based on conversion of arsenic to the colored compound such as molybdenum blue, or silver diethylidithiocarbamate [15, 16].

Electrochemical methods, particularly voltammetric methods, are affordable, sensitive and ease of fabrication, and they are noteworthy for arsenic determination. Much work has been done in this area [12]. The ASV methods using platinum and gold electrodes, and CSV method using a glassy-carbon electrode have very low detection limit for arsenic determination. Determination of total As is performed by reducing As(V) to As(III) using various chemicals, and the limits of detection achieved were in vicinity of 0.02 μg L$^{-1}$. Also, arsenic in drinking water can be measured with Cu(II) by differential pulse cathodic stripping voltammetry (DPCSV) using hanging mercury drop electrode (HMDE) as working electrode and Ag/AgCl as reference electrode [12, 17, 18].

At present, for total As concentration determination, laboratories often prefer more sensitive methods such as AAS, AES, MS or AFS. Usually, the total concentration of arsenic needs to be determined, then the speciation analysis follows.

To perform speciation analysis properly, the best option is coupling of two analytical techniques. One technique is used for the separation of all chemical forms of arsenic that are present in water, and the other is used for the detection of these species. Besides coupling analytical techniques, there are necessary steps for complete analysis of arsenic. The first one is the extraction of arsenic, which has to be both mild and effective, at the same time. The second step is separation of various forms of arsenic species. The final step is the measuring step which gives the answer to the quantification of each present arsenic compound.

3.1. Sophisticated coupling technique

Analytical methods for determining different arsenic species have become increasingly important due to different toxicity and chemical behavior of various arsenic forms. Methods that involve the coupling of separation techniques, such as IC and HPLC with a sensitive detection system, such as ICP-MS, HG-AFS, HG-AAS and GF-AAS [3, 11, 13, 14, 19]. HPLC has been a preferred technique used for separation of arsenic compounds. Coupled with ICP-MS for determination, as HPLC-ICP-MS system it is a method of choice for separation and measurements all arsenic species in water. In addition, applying IC coupled with ICP-MS, it is possible to separate and estimate arsenic species in water: iAs(III), iAs(V), DMA, MMA, AsBet. A representative result is presented in Figure 3 [19].

The evaluation of analytical method is based on defining: selectivity, repeatability, accuracy, specific features of the method and defining the limits of detection and quantification (LoD
and LoQ). These limits, these numbers give the information on the smallest concentration that can be detected and quantified with certain accuracy that has been defined [10]. The LoD was discussed and determined for the induced coupled plasma-mass spectrometry (ICP-MS) measurements of arsenic [11]. Thorough analysis has shown that the best option for LoD would be experiments, which would include the repetition many times. If experiments would be repeated 100 times, it is expected that only five measurements would be inadequate. Although this is ideal, the time consumption for the repetitive measurements is not acceptable. The most important conclusions were that LoD is not permanent and constant value, and it has to be verified and adopted for each new case. LoD is a basic parameter for estimation of the LoQ. It was concluded in [11] that the traditional (IUPAC) method is the one that could be applied.

4. Removal of arsenic and arsenic species from water

Different methods can be applied for arsenic removal from water. Arsenic (V) is more effectively removed than As(III) by both conventional and nonconventional methods. Pretreatment (preoxidation) of As(III) to As(V) is an essential step for better removal [2]. Methods that have been successfully applied in water treatment plants are: precipitation and coprecipitation, electrochemical (such as electrocoagulation), ion exchange and MST (reverse osmosis, ultrafiltration and other membrane techniques) [6–9, 20, 21].

Figure 3. Determination of five arsenic species by IC-ICP-MS. Mobile phase: NaOH [19].
4.1. Sorption processes for arsenic separation and removal

A wide range of sorbent materials for aqueous arsenic removal has been tested and used: biological materials, mineral oxides, activated carbons and polymer resins. Even some agricultural and industrial by-products such as red mud, fly ash, waste iron slag from steel production plant and waste filter sand from water treatment plant, have proved to be good and inexpensive arsenic sorbents [6, 7]. The potential use and application of industrial wastes in water treatment is in favor of the eco-friendly concept that preserves natural resources and supports the reuse-recycle concept. The technology of arsenic adsorption is based on materials which have a high affinity for dissolved arsenic. Adsorption of arsenic by iron modified sorbents has been established by several authors [6, 7]. There are numerous scientific and professional investigations with intention to develop a small and efficient system for arsenic removal based on natural and artificial sorption materials [20, 21]. Large amount of chemicals used for precipitation and coprecipitation processes (alum sulfate or ferric chloride) produce sludge, which needs treatment before disposal. If not treated properly, leachate with high concentration of arsenic is emitted to soil, threatening to contaminate the aquifers.

A step forward has been made by investigations that were devoted to the evaluation of selective multifunctional sorbents including ion-exchange resins for SPE and chromatographic columns connected with a sensitive measurements system [2]. The need to determine As species in water resulted in developing new materials for arsenic separation and removal. A simple procedure for selective separation (in pretreatment) of arsenic species in water using chemically modified and unmodified ion-exchange resins is presented in Figure 4 [2].

For separation of As species in water, two types of resins, strong base anion exchange resin (SBAE), hybrid resins (HY) and hybrid resin chemically modified (HY-Fe and HY-AgCl), were tested and used. The HY-Fe resin retained all arsenic species except DMAs(V). This is recognized as an advantage because this makes direct measurement of this species in the effluent possible. The HY-AgCl resin retained all iAs, which was convenient for direct determination of oAs species in the effluent. The selective bonding of arsenic species on three types of resins, as shown in Figure 4, has been established as the procedure which enables the separation and calculation of all arsenic species in water [2].

EC comprises complex chemical and physical processes involving many surface and interfacial phenomena. Very effective and perspective EC process consists of three processes: electrochemical reactions (simultaneous anodic oxidation and cathodic reduction), flotation and coagulation [9, 20]. The EC process relies on the generation of metal ions from electrodes. The electrodes can be made of iron, aluminum or zinc, depending on the most favorable reactions for arsenic removal. The reaction in reaction chamber starts after the application of direct current. The electrode (metallic anode) dissociates into valent metallic ions. The metallic ions migrate to oppositely charged ions and the precipitation of different insoluble salts occur (different sulfides, oxides, hydroxides, chromates or phosphates, depending on the presence of ions in water). EC has several advantages when compared to other methods. The construction of reaction chamber is compact, control of the process is simple, no additional chemicals are required, and the result is reduced amount of sludge. If the electrode is made of iron, ferric hydroxide is one of the main solid products, as shown in Eq. (1) [9]:
$\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe}(	ext{OH})_3(s). \quad (1)$

Arsenate co-precipitates or adsorbs to Fe(OH)$_3$(s), as shown in Eq. (2).

$\text{Fe}(	ext{OH})_3(s) + \text{AsO}_4^{3-}(\text{aq}) \rightleftharpoons [\text{Fe}(	ext{OH})_3 \cdot \text{AsO}_4^{3-}](s). \quad (2)$

The potential of EC as an alternative water treatment technique to remove arsenic from water needs to be realized [8, 9, 20].

Ion-exchange, IE, processes with regeneration capability is a proven, efficient and low-cost treatment method for the exchange of arsenic in the As(V) form [1, 2]. The ion-exchange reaction between As(V) and a bed of chloride-form SBAE resin (designated as R-Cl resin) occurs as presented by Eq. (3):

$2 \text{R}^+ + \text{HAsO}_4^{2-} \rightleftharpoons \text{R}_2^+ - \text{HAsO}_4^2 + 2\text{Cl}^-. \quad (3)$

When the regeneration of resins is needed, both HCl and NaCl can be applied. Still, with HCl solution, more efficient regeneration occurs because the ionic forms of arsenic (anions)
<table>
<thead>
<tr>
<th>Technology for arsenic removal</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Some specific feature</th>
<th>Future perspective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Cheap materials, effective and efficient removal</td>
<td>Further treatment for regeneration and consumption of chemicals</td>
<td>Additional filter for removal of fine particles is required</td>
<td>Still attractive as an efficient and cheap technology for As removal. Finding new, environmentally friendly sorbent is still a challenging task.</td>
</tr>
<tr>
<td>Chemical coagulation</td>
<td>Effective for industrial wastewater treatment plants and efficient for As(V) removal</td>
<td>Chemical required. pH adjustment needed. Large volumes of sludge that needs further treatment</td>
<td>Arsenic leaching out from sludge</td>
<td>Not attractive as a solution, only if it coupled with electrochemical techniques</td>
</tr>
<tr>
<td>Electrocoagulation</td>
<td>Efficient for arsenic removal. Low maintenance costs. No chemicals or pH adjustment. Low operating costs</td>
<td>Applicable only on batch scale. Passive oxide films for on the electrode. High energy consumption</td>
<td>No generation of secondary pollutants</td>
<td>Attractive for future investigations. Need to overcome the lack of application on a large scale</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Efficient for As(V) removal. Exchange resins are available; the selective resins for removing arsenic are one of the most important requirements to provide high removal. Together with hybrid solution is an excellent technology</td>
<td>Interference with other ions. Easily blocked. Huge amount of chemicals</td>
<td>Using this kind of technique depends on the pH values of water</td>
<td>Attractive only if selective and sensitive chemical agents are included in ion-exchange process</td>
</tr>
<tr>
<td>Membrane technologies</td>
<td>Efficient in arsenic removal. No chemical reagents. No sludge. Small dimensions for membrane treatment plant. Easy automation and control</td>
<td>Removal of arsenic depends on the pressure, pH value, solute concentration, temperature of feed solution</td>
<td>Arsenic is concentrated in the retentate</td>
<td>Attractive in future perspective. With decrease of investment the MST will prevail in arsenic removal technologies. Different membrane materials and processes need to be evaluated to select the optimum for each situation</td>
</tr>
</tbody>
</table>

Table 3. The comparison and future perspective of different technologies for arsenic removal.
transform to molecular form ($H_3AsO_4$). Molecular forms do not affect the equilibrium of ion-exchange processes as illustrated by Eq. (4):

$$R_2–HAsO_4 + 2Cl^- + 2H^+ \rightleftharpoons 2RCl^- + H_3AsO_4.$$  (4)

Different sorption processes, from adsorption, to chemisorption and ion-exchange, have shown a potential being efficient and cheap (depending on the selected sorbent). With improved, more selective and chemically modified sorbents, the extraction technique can be replaced [17–19]. What has been specifically used as an advantage for arsenic species separation is different behavior of arsenic species at various pH values [3, 22].

The hybrid resin (HY) that has successfully been applied uses the activity of the hydrated iron oxides (HFO) and anion exchange for selective separation of arsenic [2]. With integrated use of anion exchange and sorption, the separation of As(III) and As(V) species and removal of all species of arsenic can be accomplished. With application of HY resin, two separate things can be accomplished: the collection and preconcentration of low concentrated $iAs$ or the removal of $iAs$ species, if it is interfering the determination.

Membrane separation technologies, such as RO, NF, UF, MF, can be employed in the removal of arsenic from water. Depending on the removal efficiency, RO and NF are more efficient than UF and MF. Operating conditions, membrane material, water quality, temperature, pressure, pH value and chemical compatibility have to be considered during operation of a membrane plant. When MF and UF are applied, less amounts of chemicals are used, and therefore, less sludge is produced. When RO and NF are used, no chemicals are needed and the amount of sludge is negligible [8].

The comparison and future perspective of different technologies for arsenic removal are presented in Table 3.

5. Conclusion

Arsenic contamination of water has been reported as a critical issue in many articles, which reflects the latest state-of-the-art understanding of the behavior and toxicity of various arsenic species. Many water sources in the world contain low concentration of arsenic (mostly traces of arsenic, level of $\mu g \ L^{-1}$ or less). If the concentration of arsenic in drinking water is higher than 10 $\mu g \ L^{-1}$, which is the WHO provisional guideline value for arsenic, it causes various health problems. All arsenic compounds dissolved in water are toxic. In natural waters, arsenic appears most often in inorganic forms and to a lesser extent in organic form. Inorganic species, arsenic acids ($H_3AsO_3$ and $H_3AsO_4$) and their ions are more toxic than organic forms. In addition, As(III) species are more toxic than As(V) ones. The valence (+III and +V), the type of arsenic species, ionic or molecular forms are dependent on the oxidation–reduction condition and pH of the water. Arsenic in water occurs in both inorganic and organic forms, but inorganic
species are predominant in natural waters. In neutral conditions, As(V) species are completely in ionic form \( \text{H}_3\text{AsO}_4^- \) and \( \text{HAsO}_4^{3-} \), while As(III) is in molecular form \( \text{H}_3\text{AsO}_3 \text{ or HAsO}_2 \).

Arsenic compounds are colorless and odorless, and testing water for arsenic is an important strategy for the health and well-being of people. Working with a water professional to monitor and maintain the quality of the well and water supply is an important responsibility.

In this work, methods for arsenic and arsenic speciation separation, determination and removal were reviewed. There are numerous methods for separation and determination of arsenic species in water. It is very important to recognize easy, simple and inexpensive methods to estimate the very low concentrations of arsenic.

The total concentration of arsenic in drinking water can be detected by simple Gutzeit method, and some similar colorimetric methods of comparing stains produced on treated paper strips. Although its minimum detectable concentration is 1.0·μ L\(^{-1}\), these tests should be used when only a qualitative or semiquantitative detection is needed.

For precise, and reliable determination of arsenic in water, only sophisticated analytical techniques as ICP-MS, GF-AAS and HG-AAS can be applied. These methods are approved by US EPA. The features of these methods are high sensitivity, high accuracy, minimal sample volume; no sample pretreatment and short measurement time with minimum detectable concentration of 0.1 μ L\(^{-1}\). They are expensive, need lot of knowledge for operating and interpretation of data.

For As speciation analysis, well-established methods that involve the coupling of separation techniques, such as HPLC with a sensitive detection system, that is, ICP-MS, are recommended, and they are mostly used. Through the limits, it is possible to define the smallest concentration of analyte that can be reliably detected and quantified. Limit of detection for the HPLC-ICP-MS system is 0.001 μ L\(^{-1}\). This system is also expensive and needs lot of knowledge for operating and interpretation of data.

In all works, a special attention is paid to the preservation of arsenic species in environmental water samples for reliable speciation analysis. An appropriate procedure for the extraction of arsenic species from water should be accomplished without changing any original state of arsenic. This is still a challenging topic for research. The proposed system showed themselves to be accurate, precise and time efficient, as just a very simple sample treatment is required. Successful application of all methods required considerable practice.

Sorption processes (ion exchange, adsorption, chemisorption) with regeneration capability are proven as efficient and low-cost treatment methods for the removal of arsenic species from water. Separation of arsenic species using these new selective and chemically active sorbents recognize as a cost- and time-saving alternative to the traditional extraction techniques. The major drawback of all these techniques is that they are unable to remove As(III) efficiently.

Membrane separation technologies, such as RO, NF, UF, MF, are recommended for the removal of arsenic from water in water treatment plants.

Although there are numerous research papers focused on extraction techniques, yet it is not possible to set universal extraction procedures. These procedures depend on the presence of...
different species as well as on the type of matrices. For arsenic speciation, the choice of the most appropriate method is of great importance for obtaining reliable and accurate results.

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**Abbreviations**

**Arsenic compounds**

- **As** arsenic
- **iAs** inorganic arsenic
- **oAs** organic arsenic
- **As(III)** arsenite ion
- **As(V)** arsenate ions
- **MMA** monomethylarsenic acid
- **DMA** dimethylarsenic acid
- **TMAO** trimethylarsine oxide
- **TETRA** tetramethylarsonium ion
- **AsB** arsenobetaine
- **AsC** arsenocholine

**Methods and techniques for arsenic determination**

- **IC** ion chromatography
- **HPLC** high-performance liquid chromatography
- **MS** mass spectrometry
- **AES** atomic emission spectrometry
- **ICP-MS** inductively coupled plasma-mass spectrometry
- **ASV** anodic stripping voltammetry
- **CSV** cathodic stripping voltammetry
DPCSV  differential pulse cathodic stripping voltammetry
GF-AAS  graphite furnace absorption spectrometry
HG-AAS  hydride generation atomic absorption spectrometry
HPLC-HG-AAS  high-performance liquid chromatography-hydride generation-atomic absorption spectrometry
HPLC-HG-AFS  high-performance liquid chromatography or solid-phase cartridge separation combined with hydride generation-atomic fluorescence spectrometry
HPLC-ICP-MS  high-performance liquid chromatography-inductively coupled plasma-mass spectrometry

Methods and techniques for arsenic removal
SPE  solid phase extraction
IE  ion exchange
SBAE  strong base anion exchange resin
HY  hybrid resin
EC  electrocoagulation
RO  reverse osmosis
NF  nanofiltration
UF  ultrafiltration
MF  microfiltration
MST  membrane separation technologies

Author details
Ljubinka Rajakovic* and Vladana Rajakovic-Ognjanovic*
*Address all correspondence to: ljubinka@tmf.bg.ac.rs
1 Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia
2 Faculty of Civil Engineering, University of Belgrade, Belgrade, Serbia

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