

POINT OF VIEW

Toward Fast and Simple yet Reliable Alternative Arsenic Speciation Methods

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Arsenic (As) can occur in many chemical forms, from harmless to toxic compounds. Its toxicity depends on valence and the chemical environment. Small amounts of toxic forms can even have therapeutic and fortifying effects. The use of As was practiced for hundreds of years, leading to accidental or deliberate poisoning. Waters with high As concentrations (up to 5000 $\mu\text{g/L}$) adversely affect the drinking water supply of about 200 million people worldwide mainly in Argentina, Chile, Mexico, China, West Bengal (India), Bangladesh, Vietnam and Hungary [1]. In Hungary, the As exposure of the population has been significantly reduced since 2017 by drilling new wells with lower As content and setting up new waterworks in the settlements affected, with financial help from the European Commission. Arsenic possesses a complex water chemistry and occurs in several inorganic and organic species in water depending on pH, salinity, acid dissociation constants of its oxyacids, and the As(V)/As(III) redox potential. The possible technological solution for As removal from water is definitely governed by the species concerned. Chemical oxidation, co-precipitation, adsorption, ion exchange, reverse osmosis and membrane filtration are used to remove As from water. From the technological point of view, As removal processes can be divided into three major groups: i) conventional technologies (coagulation, iron–manganese removal, lime softening); ii) sorption processes (ion exchange, activated aluminum); and iii) membrane technologies (reverse osmosis, nano-, micro- or ultrafiltration). Each of the aforementioned technologies is more efficient for As(V). Therefore, an oxidation step is often needed. Oxidation by simple direct aeration is slow, but there are a number of chemicals that can accelerate the process, such as chlorine gas, sodium hypochlorite, ozone, potassium permanganate, hydrogen peroxide and manganese oxides, and ultraviolet radiation may also be suitable for oxidizing As(III) [2].

Given the lack of a definitive solution for As removal from drinking water, it is important to estimate the exposure of the population in large areas affected by As contamination. For estimation of the As(III)/As(V) ratios, conventional As speciation analysis generally consists of on-line hyphenation of a chromatographic separation technique to an atomic spectrometric detector. Replacement of either the high-performance liquid chromatograph or the atomic spectrometer (e.g. inductively coupled plasma mass spectrometer) – or both – may lead to cost-effective solutions enabling extension of our knowledge with respect to As speciation. Besides its cost-effectiveness, the advantage of the use of solid phase extraction (SPE) microcartridges filled with ion-exchange resins consists of preventing interconversion of As species during sampling and analysis. Recently, significant efforts in this direction can be seen, mainly in the As speciation of water matrixes. Various SPE cartridges enabling on-site separation have been investigated for the speciation of inorganic As(III), As(V) and methylated forms of As(V) [3–5]. In-situ separation of As species in water with a strong anion exchange SPE can easily be accomplished from water matrixes of pH < 9 and/or of higher salinity and temperature (e.g., geothermal water) by applying preconcentration of iAs(V) followed by laboratory analysis of acid-preserved samples [6]. Mono-elemental graphite furnace atomic absorption-based techniques can be recommended for routine measurements. Among multi-elemental techniques,

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total-reflection X-ray spectrometry allows the simultaneous determination of several other trace elements in drinking water [7]. Some new solid-phase sorbents employed for separation and preconcentration of As include nanometer-sized titanium dioxide particles immobilized on silica gel, octadecyl silica, yeast immobilized on controlled-pore glass, PTFE turnings, cetyltrimethylammonium bromide-modified alkyl silica, [3-(2-aminoethylamino)propyl]trimethoxysilane-modified mesoporous silica, macrocyclic materials, hybrid resins based on the activity of hydrated iron oxides and silver chloride, carbon nanofibers and nanotubes, and eggshell membrane [6].

In brief, the pace of development of analytical measurement techniques is extremely rapid, and advances in speciation analysis are also helped by the knowledge acquired in many other scientific fields. In addition to the hyphenation of the chromatographic separation and atomic spectrometric techniques, speciation analysis procedures include a number of sample preparation procedures that can be separate sources of error. These may have already occurred at the time of sampling in the form of unwanted species interconversion, and the interference of the sample matrix constituents may also be significant. Therefore, it would be useful to develop alternative, cost-effective yet reliable analytical methods extensible to as many As species in different matrixes as possible, which could be widely used in routine analysis.

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