Review

New procedures for arsenic speciation: A review

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Ming-Li Chen, Lin-Yu Ma, Xu-Wei Chen *

Research Center for Analytical Sciences, College of Sciences, Northeastern University, Box 332, Shenyang 110819, China

ABSTRACT

Considerable analytical methods have been developed for arsenic speciation in the last 5 years, the details of these new arsenic speciation procedures are thus summarized in present mini review. The performances of various sample pretreatment techniques including solid phase extraction, liquid–liquid extraction, hydride generation, liquid chromatography and capillary electrophoresis, which offer effective preconcentration/separation and eventually contribute greatly to excellent sensitivity and selectivity in arsenic speciation when coupling with suitable detection mode, are discussed and compared thoroughly. High-performance liquid chromatography coupling with inductively coupled plasma mass spectrometry and hydride generation atomic spectrometry are proved to be the most powerful hyphenated methodologies for arsenic speciation in environmental and biological matrices.

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1. Introduction

Exposure to arsenic (As) is a global public health concern due to the wide distribution in environment of As and its close association with numerous adverse effects [1]. It has been estimated that about hundred million people in India are at risk of drinking arsenic-contaminated water [2,3]. Total arsenic level of 22 in 23 total water samples from Hungary are confirmed to be higher than the health limit value of European Union (10 µg L^{-1}) [4], the highest total arsenic content is up to 210.3 µg L^{-1}. Serious arsenic pollutions in groundwater are also found in China [5], and arsenic concentration in some water samples are even higher than 500 µg L^{-1}. With the

* Corresponding author. Tel.: +86 24 83687659; fax: +86 24 83676698.
E-mail address: chenxuwei@mail.neu.edu.cn (X.-W. Chen).

deterioration of environment pollutions, humans are at an increasing risk of As exposure. The survey on the water and diet contributions to As exposure in northwest of China reveals that As content in high percentages of water (77% of $n=131$ total samples), vegetables (92%, $n=120$), and cereals (32%, $n=25$) are higher than the acceptable levels [5].

It is well known that the simple knowledge of total arsenic content in real-world samples is far from enough, as the toxicity of As element is predestined by its chemical species presented [6]. For example, inorganic As is the number one toxin in the United States Evninronmental Protection Agency (USEPA) list of prioritized pollutants [2] and classified as Group I carcinogens based on human epidemiological data, while the methylated As species such as monomethylarsonic acid (MMA) and dimethyarsinic acid (DMA) are less toxic, arsenobetaine (AsB), arsenocholine (AsC) and other arsenosugars are even considered to be of non-toxicity [7].

In the past 5 years, various methodologies have been developed to figure out arsenic species in environmental and biological samples including water, plant, sea food, rice, blood, saliva [8], nail, hair and *Euglena gracilis* cells [9]. The construction of new analytical procedures for As speciation not only improve our knowledge on As biogeochemistry, toxicity and metabolism, but also provide abundant information relating to the biomarkers of exposure and As cycling in natural environment. At the same time, the acknowledgment of exact arsenic species in biological and environmental samples facilitates the more accurate assessments of environmental impact and health risks induced by As exposure.

During As speciation, suitable sample pretreatment techniques are usually adopted to eliminate the effect of matrices, to enrich the aimed species and/or to separate the As species for accurate identification. With suitable detection mode, excellent selectivity and sensitivity have been achieved for the newly developed As speciation protocols in last 5 years, which also gain practical demonstration in various environmental and biological assays. In this mini-review, the extraction/separation procedures including solid phase extraction, liquid–liquid extraction, hydride generation, liquid chromatography and capillary electrophoresis, are thus discussed and summarized. Also, the commonly used strategies for arsenic speciation and determination techniques in different samples are also reviewed.

2. Procedures for arsenic extraction/separation

2.1. Solid phase extraction

Solid phase extraction (SPE) is an effective sample pretreatment technique for the extraction/preconcentration of analyte from complex matrices, with the merits of satisfactory recovery and preconcentration efficiency, low cost and reduced reagent consumption as well as environmental friendliness. At the same time, the simple operation offers SPE approach great popularity in on-line or off-line analysis of As species combining with other analytical techniques. In recent years, various materials have been adopted for the extraction/preconcentration of As species from environmental and biological samples, along with improved and satisfied selectivity and preconcentration efficiencies.

2.1.1. Conventional sorbent

Quite a few novel procedures have been developed for arsenic speciation, based on conventional sorbent such as ion exchange resin, glass and modified mesoporous silica.

A simple field separation method is developed for inorganic As speciation, with anion exchange cartridges prior to the inductively coupled plasma sector field mass spectrometric (ICP-SF-MS) detection [4], with the aim to prevent interconversion of arsenic species in the samples. On-site arsenic separation is successfully achieved by SPE cartridges packed with anion exchange resin, in which As(V) is retained on the column, meanwhile As(III) passes through it. The detection limit of As using ICP-SF-MS is $0.06\ \mu g\ L^{-1}$. 23 water samples from public wells in 3 different counties, including a history site of high natural arsenic occurrence in Hungary, and a resort area close to the capital city, are applied for speciation analysis of As(III) and As(V). As(III) and As(V) also can be effectively separated by anion-exchange resin (AG 1-X8) due to the fact that AG 1-X8 shows selective adsorption ability to As(V) in acetate form, while no adsorption to As(V)/As(III) in chloride form [10]. The developed SPE method is suitable for on-site separation and speciation of inorganic arsenic in high arsenic-groundwater, and also could be used for arsenic speciation during arsenic removal by ferrihydrite in the absence of oxygen [10]. A dual-sorbent SPE protocol, in which the sorbent is composed of strong basic anion exchange (SBAE) resin and hydrate iron oxide particles integrated HY resin, has been adopted successfully for the retention of inorganic arsenic species As(V) and As(III) simultaneously [11]. Both SBAE and hydrate iron oxide particles integrated HY resin posses high adsorption capacities toward As species, i.e., more than $370\ \mu g\ g^{-1}$ of As(V) for SBAE resin, more than $4150\ \mu g\ g^{-1}$ of As(III) and $3500\ \mu g\ g^{-1}$ of As(V) for the HY resin. With detection by atomic absorption spectrometry-hydride generation technique, a detection limit of $0.24\ \mu g\ L^{-1}$ is achieved.

Escudero et al. propose a highly efficient separation and preconcentration method for arsenic species determination, based on ionic liquid (IL) dispersive microextraction technique implemented in a flow analysis system. After the selective chelation between As(III) and sodium diethyldithiocarbamate (DDTC), the obtained complex is dispersed IL 1-octyl-3-methylimidazolium hexafluorophosphate ([C(8)mim]PF$_6$) to form a homogeneous solution. The dispersed IL phase is thus on-line retained by a microbore glass column filled with Florisil® resin, followed by the eluting with acidified methanol [12]. As(III) is determined in eluent solution by electrothermal atomic absorption spectrometry (ETAAS), with a detection limit of $0.05\ \mu g\ L^{-1}$. Concentration of As(V) is then deduced by the difference between total inorganic arsenic and As(III).

As As(V) could be selectively adsorbed on the surface of 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) modified ordered mesoporous silica [13], a sensitive quantitative method with inductively coupled plasma optical emission spectrometry (ICP-OES) for the speciation of inorganic arsenic has been developed, along with a detection limit of $0.05\ \mu g\ L^{-1}$. Total inorganic arsenic is determined after the oxidation of As(III) to As(V) with KMnO$_4$ and the As(III) content is obtained by the subtraction As(V) from total As. The adsorption capacity of AAPTS modified ordered mesoporous silica for As(V) is deduced to be $10.3\ mg\ g^{-1}$.

2.1.2. Functional nanomaterials

With the great progress in material science, quite a few functional materials have been emerged, providing excellent sorbent candidate in the field of sample pretreatment. The newly emerged materials, especially nanomaterials such as nanofibers [14], magnetite nanoparticles [15], metal hydroxide precipitate [16,17], and nano-TiO$_2$ colloid [18], usually offer improved separation/extraction efficiency, selectivity and adsorption capacity in As speciation, contributed by the specific functional groups on their surface and their huge surfaces/volume ratio.

Carbon nanofibers (CNFs) modified with ammonium pyrroinedithiocarbarnate (APDC) is demonstrated to own excellent selectivity to As(III), thus a SPE procedure is constructed for arsenic speciation in groundwater samples using microcolumn packed