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Review

Sample preparation for arsenic speciation in terrestrial plants—A review

Clarice D.B. Amaral [a,b], Joaquim A. Nóbrega [a], Ana R.A. Nogueira [b,*]

[a] Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, PO Box 676, 13560-970 São Carlos, SP, Brazil
[b] Embrapa Southeast Livestock, PO Box 339, 13560-970 São Carlos, SP, Brazil

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ABSTRACT

Arsenic is an element widely present in nature. Additionally, it may be found as different species in several matrices and therefore it is one of the target elements in chemical speciation. Although the number of studies in terrestrial plants is low, compared to matrices such as fish or urine, this number is raising due to the fact that this type of matrix are closely related to the human food chain. In speciation analysis, sample preparation is a critical step and several extraction procedures present drawbacks. In this review, papers dealing with extraction procedures, analytical methods, and studies of species conservation in plants cultivated in terrestrial environment are critically discussed. Analytical procedures based on extractions using water or diluted acid solutions associated with HPLC–ICP–MS are good alternatives, owing to their versatility and sensitivity, even though less expensive strategies are shown as feasible choices.

Contents

Abbreviations: AAS, atomic absorption spectrometry; AFS, atomic florescence spectrometry; As, arsenic; AsB, arsenobetaine; AsC, arsenocholine; CRM, certified reference material; DMA, dimethylarsinic acid; ESI–MS, electrospray ionization mass spectrometry; ESI-MS/MS, electrospray ionization tandem mass spectrometry; ESI–TOF–MS, electrospray time-of-flight mass spectrometry; ETAAS, electrothermal atomic absorption spectrometry; FAAS, flame atomic absorption spectrometry; GFAAS, graphite furnace atomic absorption spectrometry; HG, hydride generation; HPLC, high-performance liquid chromatography; HR, high resolution; IC, ion chromatography; ICP–MS, inductively coupled plasma mass spectrometry; ICP–OES, inductively coupled plasma optical emission spectrometry; LA, laser ablation; LC, liquid chromatography; LOD, limit of detection; MAE, microwave-assisted extraction; MMA, monomethylarsonic acid; MPE, modified protein extraction; *o*-APAA, *o*-aminophenylarsonic acid; *p*-APAA, *p*-aminophenylarsonic acid; PAA, phenylarsonic acid; PAO, phenylarsine oxide; PCs, phytochelatins; PCn, (γ-Glu-Cys)*n*-Gly ($n=2$–11); PLE, pressurized liquid extraction; RT, room temperature; SON, sonication solvent extraction; SEC, size exclusion chromatography; TFA, trifluoroacetic acid; TMA, tetramethylarsonium ion; TMAO, trimethylarsine oxide; UV, ultraviolet; XANES, X-ray absorption near edge structure spectroscopy; XRF, X-ray fluorescence.

* Corresponding author at: Embrapa Southeast Livestock, PO Box 339, 13560-970, São Carlos, SP, Brazil. Tel.: +55 16 34115600; fax: +55 16 33615754.
E-mail address: ana.nogueira@embrapa.br (A.R.A. Nogueira).

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1. Introduction

Arsenic is an abundant element in Earth's crust, mainly as arsenopyrite mineral (FeAsS), its most important ore, and the natural occurrence of As is associated with volcanic deposit and geochemical environment [1–3]. On the other hand, anthropogenic sources of contamination are mostly due to mining activity, burning coal, copper smelting and the use of fertilizers and herbicides [4–7]. The most common forms of As in nature are arsenite (As_2O_3) and arsenate ($H_2AsO_4^-$ and $HAsSO_4$), i.e. As(III) and As(V), respectively, which lead to the presence of these species in plant tissues [8]. Consequently, the determination of As in terrestrial plants plays an important role because As occurs in some areas in high concentrations, either naturally or as a consequence of human activities.

Some plants have potential for phytoremediation, which is the property of absorbing elements present in soil. It can be easily seen as an advantage if they are essential elements or even if they are used in metals phytoremediation experiments [9,10]. However, if the absorption takes place in an excessive or accidental condition, the situation can easily turns into a dangerous health issue, if the contaminated plant is ingested by a human or inserted in the food chain. Thus, rice is the most intensively studied plant organism in As speciation, because of its high consumption by humans and also its great ability to accumulate arsenic in higher amounts than other grains. Additionally, the soil used for rice cultivation can also increase the concentration of As [11]. Although it is known that As is mainly found in plant tissues in its inorganic form, therefore toxic form, further researches are necessary to evaluate the response of the matrix for different extraction procedures.

Several extraction procedures are usually employed for As speciation in plants with particularities in solvent extractors, extraction devices, and instrumentation used for analysis [12–14]. Arsenic speciation studies become more attractive if they involve the mechanism of translocation of the analyte up to plant parts, since this is an aspect that adds important information[15]. The studies of As bound to phytochelatins (As–S) are mostly made on plants roots, once such binding occurs mainly in this part of the plant. The formation of this tripeptide is a defense mechanism of the plant organism, in order to avoid poisoning and translocation of the metal to the aerial parts of the plant [16,17]. Another crucial point in speciation analysis, is the conservation of species in order to ensure that the analytes obtained after extraction are as representative as possible of species present in the sample.

Although many studies on As speciation have been devoted to marine tissue samples, there is an increasing number of works evaluating the several species of this element present in earth-grown plants [18–22]. In this paper, a review on sample preparation for As speciation in terrestrial plants is presented by discussing previous studies that dealt with sample pretreatment, extraction procedure of analyte species, as well as separation and determination methods. Several procedures are employed for this sort of samples without establishing a standard procedure or protocol; therefore it is important to systematize this information and to look for general and simple analytical procedures. Furthermore, some adopted strategies have failures which often compromise the quality of the analysis; moreover, the most suitable procedure can be tailored to the type of sample.

2. Uptake and metabolism of arsenic in plant tissues

The main species monitored in studies of As speciation in plant are As(III), As(V), DMA and MMA [22,23], although there are studies that monitor the organic species of TMA, TMAO, AsB, AsC, and phenylarsenic compounds [24–27]. The major species present in plants are As(III) and As(V). However, in some sorts of plants or habitats traces of MMA and DMA can be found [28]. It is not well understood if all types of plants are able to methylate inorganic arsenic species, or even whether these organic species are taken up from soil by plants, already in the methylated form [29,30].

The plant capacity to absorb the elements present in the soil, for instance As, and the transport to the aerial parts like leaves and fruits depends on the properties of the soil, such as organic matter content, pH, ion competition, redox potential [31,32], microbiological activity [27], As species [33], presence of iron oxides [34], and also the sort of plant will affect the transport and accumulation of As [35].

In studies of As speciation in plant tissues, possibly the greatest goal is to understand how As is metabolized in plant cells, and not only to determine the concentration of each species. For complex matrices, many doubts are not well clarified, which show that despite previous works, new studies are always relevant to elucidate processes related to As metabolism. Several As species are found in plant samples, the presence of more than 14 species of complexed arsenic in sunflower samples were reported by Raab et al. [36].

According to Bergqvist and Greger [22], As accumulation in plants is determined by the habitat whereupon the plant was grown; plants cultivated in an environment that contains more water have higher accumulation power than those cultivated in dry soil. Algae, for instance, accumulates more As than terrestrial plants [37]. The uptake of As from soil to plant is associated with the sort of plant and how the element is available in soil [38]. Accumulation in terrestrial plants is very dependent on the As concentration in soil. Paradoxically, a study had shown that an increase in As concentration in soil caused a reduction of its accumulation in plant tissues [22].

Lomax et al. [39] have studied three plants (rice, tomato and red clover) aiming to investigate whether plants are able to synthesize methylated As species or if they just taken up these species produced by microorganisms [40]. When plants were cultivated in a habitat with MMA and DMA, they hold methylated species in their tissues. When exposed to an environment without methylated species, the three plants analyzed showed no MMA and DMA in their tissues and arsenite was the predominant species, although the plants were exposed to arsenate. It also became clear that the evaluated plants did not have the ability to transform methylated species in arsenite and that the methylation of As in soil does not depend on the plant presence.

On the other hand, Raab et al. [41] and Xu et al. [42] found traces of MMA and/or DMA in plants that were grown in a hydroponic solution without methylated arsenic species. It was shown the ability of some plants to perform the detox mechanism of methylation. These studies emphasize that the ability of As methylation can be associated to each particular plant organism. The plant tissue that is absorbing As will always play a role in the mechanism of translocation of As and interactions between element and matrix. Some seaweeds e.g. *Fucus spiralis* and *Hizikia fusiforme*, were not able to form complexes As–PC, unlike what happens in most terrestrial plants, although these seaweeds contain As(III) and As(V) in their tissues, which are known as strong inducers of phytochelatins formation [43].

Raab et al. [44] presented the first work detecting and quantifying complexes of As bound to phytochelatins in plant tissues, without changes of original species and involving HPLC–(ICP–MS)–(ESI–MS) instrumentation. In this procedure, organic and metal specific detector was used after extraction with 1% vv^{-1} formic acid. It is emphasized that the analysis should be performed within a short period of time to achieve complex preservation.