Analytica Chimica Acta 898 (2015) 1–18

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Review

Analytical approaches for arsenic determination in air: A critical review

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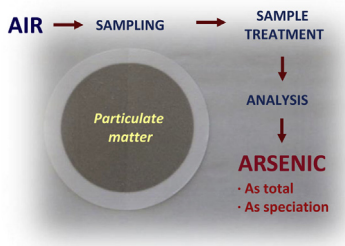
HIGHLIGHTS

- Review about arsenic in the air.
- Sampling, sample treatment and analysis of arsenic in particulate matter and gaseous phase.
- Total arsenic determination and arsenic speciation analysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 May 2015
Received in revised form
15 September 2015
Accepted 17 September 2015
Available online 19 October 2015

Keywords:
Arsenic
Speciation
Air
Sampling
Sample treatment
Analysis

ABSTRACT

This review describes the different steps involved in the determination of arsenic in air, considering the particulate matter (PM) and the gaseous phase. The review focuses on sampling, sample preparation and instrumental analytical techniques for both total arsenic determination and speciation analysis. The origin, concentration and legislation concerning arsenic in ambient air are also considered. The review intends to describe the procedures for sample collection of total suspended particles (TSP) or particles with a certain diameter expressed in microns (e.g. PM10 and PM2.5), or the collection of the gaseous phase containing gaseous arsenic species. Sample digestion of the collecting media for PM is described, indicating proposed and established procedures that use acids or mixtures of acids aided with different heating procedures. The detection techniques are summarized and compared (ICP-MS, ICP-OES and ET-AAS), as well those techniques capable of direct analysis of the solid sample (PIXE, INAA and XRF). The studies about speciation in PM are also discussed, considering the initial works that employed a cold trap in combination with atomic spectroscopy detectors, or the more recent studies based on chromatography

Abbreviations: AAS, atomic absorption spectroscopy; AFS, atomic fluorescence spectroscopy; APDC, ammonium pyrrolidinedithiocarbamate; CRM, certified reference material; CT, cold trap; DMA, dimethyl arsenic; EC, European Commission; EPA, Environmental Protection Agency; ET-AAS, electrothermal atomic absorption spectroscopy; EU, European Union; GC, gas chromatography; GF-AAS, graphite furnace atomic absorption spectroscopy; HPLC, high performance liquid chromatography; HG, hydride generation; IC, ion chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-OES, inductively coupled plasma-optical emission spectroscopy; INAA, induced neutron activation analysis; LA, laser ablation; LOD, limit of detection; LOQ, limit of quantification; MS, mass spectrometry; MMA, monomethyl arsenic; OES, optical emission spectroscopy; PIXE, particle induced X-ray emission; PLE, Pressurised Liquid Extraction; PM, particulate matter; QA/QC, quality assurance/quality control; SFU, stacked filter unit; TMA, trimethyl arsenic; TMAO, trimethylarsine oxide; TSP, total suspended particles; WHO, World Health Organization; XRF, X-ray fluorescence.

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http://dx.doi.org/10.1016/j.aca.2015.09.043

(GC or HPLC) combined with atomic or mass detectors (AFS, ICP-MS and MS). Further trends and challenges about determination of As in air are also addressed.

Contents

1. Introduction

Arsenic is widely distributed in all compartments of the environment, due to natural or anthropogenic sources. It occurs naturally in the Earth's crust, soils, sediments, water, air and living organisms [1]. Natural mineralization, microorganism activity, volatilization and volcanoes represent the main inputs of arsenic into the environment [2]. Human activities have also increased As pollution worldwide, in relation to industrial activities. It is present in over 200 minerals forms, mainly as arsenates, sulfides and sulfosalts. As is obtained either by roasting of arsenopyrite, enargite or realgar, as well as from dust of Cu, Au and Pb smelters. The main uses of As are hardening of alloys, the production semiconductors, pigments, glass manufacturing, pesticides and wood preservatives [3].

The toxicology of As is a complex phenomenon. Although this metalloid is considered an essential element by some authors (e.g. Uthus [4]), it is widely regarded as a toxic element that affects human health. There is abundant literature describing the metabolism, toxicity and carcinogenesis of arsenic [5–8]. The toxicity of As is related to the different chemical forms and oxidation states in which it can be found. The oxidation states of As are −III, 0, III and V, being III and V the most common in environmental samples. Inorganic oxoanions arsenite (As(III)) and arsenate (As(V)) are more toxic than the organic species (e.g. monomethylarsonic acid MMA, dimethylarsinic acid DMA) that are the result of biological activity [9] (Fig. 1). More complex molecules, such as arsenobetaine or arsenocholine, are considered non-toxic. Overall, the oxidation state of As(III) is more toxic than As(V). At the cellular level, trivalent arsenic interacts with proteins and enzymes, causes oxidative stress and alters DNA by methylation [10].

The main concern about the determination of arsenic in environmental samples has been habitually related to its presence in groundwater [11,12], drinking water [9,13], biota [14], soils [15] and food [16]. However, air represents also an important route of dispersion, as it allows As to be transported globally [17,18]. As in the air can affect potentially the health of the population. It has been demonstrated the increase of lung cancer with the presence of As in the air [19], and a correlation between As in the air and the presence of As in the urine of outdoor workers [20]. A recent review about the importance of metals and metalloids in dust and aerosols, indicates that anthropogenic As emissions to the atmosphere represent a pathway for As dispersion underappreciated and potentially understudied [21].

In some of the different specific reviews about As in the environment published since the 1980's to nowadays, the presence of arsenic in the atmosphere is not considered (Duker et al. [7], Singh et al. [9]). In others, it is just mentioned briefly, indicating that As is mainly related to the particulate matter present in the air, as in the review of Mandal and Suzuki [1]. In the comprehensive review of