Analytical approaches for arsenic determination in air: a critical review

Daniel Sánchez-Rodas[1,2,*], Ana Sánchez de la Campa[1,3], Louay Alsioufi[1]

[1] Centre for Research in Sustainable Chemistry-CIQSO. Associated unit CSIC-University of Huelva "Atmospheric Pollution". Campus El Carmen, University of Huelva 21071-Huelva, Spain.
[2] Department of Chemistry and Materials Science. University of Huelva. 21071-Huelva, Spain.
[3] Department of Mining, Mechanic and Energetic Engineering. ETSI. University of Huelva. 21071-Huelva, Spain.

* corresponding author

e-mail: rodas@uhu.es

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, INA 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 (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.

Key words: arsenic, speciation, air, sampling, sample treatment, analysis

Abbreviations: AFS, atomic fluorescence spectroscopy; AAS, atomic absorption 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.

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] (Figure 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 Cullen and Reimer [22] about As speciation in the environment, it is indicated that there are few studies about arsenic speciation in the atmosphere. A more detailed description of the global arsenic cycle that includes the atmosphere has been reviewed by Matschullat in 2000 [23], although it does not contain information regarding As speciation. A review of arsenic in ambient air in the United Kingdom consider both particulate and vapour phases [24]. The different As species that has been identified in atmospheric samples are mainly As(III) and Av(V), and to a minor extend MMA and DMA, whereas methylated arsines correspond to the gaseous phase. Also, a review about As concentrations in particulate matter in certain locations around the world has been published recently by Fang et al. [25].

From an analytical point of view, the different steps involved in the determination of arsenic in the atmosphere are not usually explained in detailed or justified in many of the scientific works. A recent extensive and complete review by Tyson [26] about the determination of As compounds in environmental samples, does not contain specific references about atmospheric samples. Also, two reviews about analytical methods and new procedures for arsenic speciation (Chen et al. [27]), or the specific use of X-ray absorption spectroscopy for As speciation (Gräfe et al. [28]) do not consider atmospheric samples. The exception to the above references, is the valuable information regarding As species in the air can be found in a recent article published by Lewis et al. [29], which contemplates measurement methodology and risk assessment considerations.

The purpose of this review is to provide an overview of the analytical approaches for As determination in atmospheric samples. First, the origin, concentration and legislation in relation to As in the air have been considered. The different steps of the analytical procedure are described and discussed: sampling, sample treatment and the different methods for analysis. The present work evaluates the As presence in the particulate matter and the gaseous phase, as well as the total As determination and As speciation analysis.

2. Origin, concentration and legislation about As in the air

As in the air originates from natural and anthropogenic sources. It can be released from soils into the atmosphere due to microbial metabolism, in addition to volcanoes, low temperature volatilization, wind erosion, forest fires and sea spray. Of the human activities, the most important ones that emits arsenic are metal production and burning of fossil fuels. It has been estimated that close to two thirds of the As emissions to the atmosphere are related to anthropogenic sources [2].

Cu production is the main important anthropogenic emission source of As, due to mining activities and the posterior transformation of the metallic sulphides (pyrites) by Cu-smelting and refining. Pyrites can contain up to a 10% in weight of arsenic [30] that can be released during roasting. The production of other metals (Pb, Zn and steel) results also in the emission of As. Coal burning is the second main source of As emission. The world average As content in coals has been estimated in 9.0 ± 0.8 mg As kg^{-1} for bituminous coals [31], although some coals in China can contain up to several hundreds or thousands of mg As kg^{-1} [11, 32]. Petroleum represents a minor emission source, as its As estimated average concentration is 0.26 mg As kg^{-1} [33]. The sum of Cu-smelting and coal burning stand for a 60% of the anthropogenic As emission to the atmosphere worldwide [23]. A detailed inventory of anthropogenic As emissions in the European Union (EU) can be found in Zevenhoven et al. [34].

The presence of As in the atmosphere was estimated in the 1980's between 0.8-1.74 $x10^6$ kg, with a distribution of 85% in the north hemisphere and 15% in the south hemisphere. The mean worldwide concentration was estimated in 2.8 ng m^{-3} [2]. This data should be handled with care and may be obsolete, due to the increasing industrial activity in the world in relation to global As production since the industrial age to recent times [33], specially due to the fast development of the countries of South-East Asia. In this sense, China is becoming one the most important emitters of As into the atmosphere. The inventories of atmospheric emission from coal combustion in China has been described, with data corresponding to 2005 [35]. Also, a recent review of Duan et al. [36] has reported a mean value of 51 ng As m^{-3}

corresponding to the ambient air of 44 main Chinese cities. For comparison, in urban areas of the EU, the background values range from 0.5 to 3 ng m^{-3}, with the exception observed in the of the vicinity of Cu or Pb smelters [34].

In spite of the toxicity of arsenic, there was no formal regulation of its concentration in ambient air until recent times, and only in some countries. In 2000, the World Health Organization (WHO) performed a health risk evaluation for As, based on the information of previous studies about the relation between As and lung cancer. In view of the results, the WHO Air Guideline for Europe established that a safety level for inhalation cannot be recommended [37]. The first regulation concerning As in ambient air was established by the EU in 2005 (Directive 2004/107/EC), indicating a target value of 6 ng As m^{-3} in PM10 to be accomplished by beginning of 2013 [38]. In this sense, China has adopted a National Ambient Quality Standard (NAAQS) (GB 3095-2012) with a similar value of 6 ng As m^{-3} [36]. Other regulations establish values of 5.5 ng As m^{-3} (New Zealand) or 10 ng As m^{-3} (Ontario, Canada) [39]. However, most of the countries do not have specific national legislation about arsenic in ambient air, although permissible exposure limits are usually established (e.g. 10 µg m^{-3} of inorganic arsenic and 0.05 ppm of arsine for occupational workers in the United States [40]). One of the lacks of the actual legislation regarding ambient air, is that it referees just to the total arsenic content, not considering the different species with distinct toxicity.

3. Sampling of particulate matter and the gaseous phase

The different sampling procedures depend on the purpose of the analysis, either the determination of As bound to particulate matter or if it is present in the gaseous phase. Nowadays, almost the totality of the sampling procedures are focused on particulate matter.

3.1 Sampling of particulate matter

Particulate matter (PM), also referred as aerosol, represents the solid or liquid suspended particles present in the atmosphere [41]. PM is complex, regarding particle size and composition, as it may contain metals, metalloids, inorganic ions, organic compounds, black carbon and biogenic material (e.g. algae, pollen, bacteria or fungi), affecting human health through inhalation. It has been established a correlation between particle size of PM and mortality [42-44]. In this sense, the different studies about As in the air consider total suspended particles (TSP), or particles with a certain aerodynamic diameter, expressed in microns (e.g. PM10 and PM2.5, usually designed as “coarse” an “fine” particles). The smaller the diameter of the particles, the higher their capacity to penetrate into the respiratory system: PM10 particles can reach the larynx, PM2.5 the bronchi, and PM1 the alveoli [45]. The chemical composition is also important, as PM can contain metals [46] and metalloids, As among them [21, 47].

The PM sampling procedures employ air captors (flow rate rates 1-68 $m^3\ h^{-1}$), equipped with a vacuum pump that forces ambient air to pass through a filter in which particulate matter is collected. The sampling time of PM differs in the numerous studies, ranging from a few hours [48, 49] to several days [50]. This difference of time can be due several circumstances. A short period of 8 hours can be selected to distinguish between day and night samples, as indicated by Hu et al. [48]. 12 h sampling has been employed by Alastuey et al. [49] to register a meteorological event, such a Saharan Dust Episode, in the Canary Islands. In other cases, long periods of several days are selected in those areas where low amount of PM is like to be found, such as mountains slopes, as reported by Romo-Kröger et al. in Chile [50]. But these are exceptions to the common practice, which is to perform 24 h sampling periods, due to established norms that regulate the gravimetric determination of PM10 or PM2.5 in the EU (e.g. EN 12341) [51], or TSP and PM10 in the United States [52, 53]. The collection of particles of a certain diameter, such as PM10 or PM2.5, is accomplished with air captors equipped with a specific head at the air inlet, which allows to discriminate the desired particle sizes that are going to be retained on the filter. On the other hand, the use of a cascade impactor, also referred as stacked filter unit (SFU) sampler, allows the apportioning of particles with different diameters. Using SFU samplers, Romo-Kröger et al. [50] and Freitas et al. [54] collected simultaneously coarse (PM10) and fine particles (PM2.5). Onat and Sahin [55] used an air captor with several stages, and were able classified atmospheric particles into eight different sizes, with diameters ranging from >8 µm to <0.45 µm. These studies help to know the distribution of As among the different grain sizes.

The surface of exposed area of the filters is ca. 100-500 cm^2, with rectangular or circular shapes, depending of the equipment employed. The selection of the material of the filters is an important matter, because in most cases the filter has to be acid digested or extracted with a suitable solution for posterior analysis of As present in the PM. Most of the studies employ quartz fibre filters, following the method of the European norm EN 12341 for PM10 gravimetric determination [48, 49, 55-59]. A previous European norm (EN 14907) allowed the use of other types of materials in addition to quartz for PM2.5 determination [52]. Also, the U.S. EPA indicated the use of glass or quartz fibre filters for PM collection [44]. In this sense, there are some studies that employ filters made of polycarbonate [50, 54, 60], PTFE (Teflon) [61-63] or glass fibre [46, 64, 65], although in none of these references a justification is given for the selection of a particular type of material. The properties and blank values for As with different filter media have been reviewed by Maggs [24]. According to this author, of the different materials available, quartz is usually preferred to glass fibre, as it provides lower blank values and it is easier to digest. The blanks of glass fibre filters can be variable and can have a low flow resistance. Teflon filters also provide low blank values, similar to quartz, and a high flow resistance, but are relatively expensive. Also, the amount of PM retained on its surface can be influenced by ambient water, resulting in biased data, as it has been evaluated by Perrino et al. [66]. On the other hand, cellulose filters are prone to electrostatic charge.

The material of the filter has to be free of impurities, and filters blanks has to be performed along with sample measurements. A standard pre-treatment procedure to remove impurities is to heat the filters before their use during several hours at few hundred degrees. However, there is not agreement in an established procedure, although they are rather similar. Hu et al. [48] heated the filters for 6 h at 500 ºC, whereas Wang et al. [67]) heated at the same temperature for 2h, and Hueglin et al. [68] heated them for 2 h at 600ºC. In most articles, nothing is said if the filters are heated or not to remove the impurities. In a few of them, the authors indicate that the do not pre-treat the filters by heating, as mentioned by Querol et al. [69] and in a study of Onat and Sahin [55], who indicate that blank corrections have to be done.

After sampling, the filters are conditioned in most cases for 24-48 h in a desiccator at room temperature (20-22ºC) and a relative humidity 30-50 % [48, 66, 68] before weighing to determine their PM content. An exception to this procedure is described by Halek et al. [70], who indicates that filters are heated 2-3 h at 105 ºC after sampling and then placed in a desiccator. No indication of possible loses during heating are given, or any reference linked to this procedure. After sampling, filters are usually refrigerated at 4 ºC [55, 63] until analysis, although conservation at -18ºC or -20ºC is also reported in the literature [48, 66, 68].

3.2 Sampling of the gaseous phase.

In addition to PM, volatile As compounds may be found in the gaseous phase. Along with arsine (AsH_3), other organic arsines, such as mono, di and trimethyl arsines ($MeAsH_2$, Me_2AsH, Me_3As) can be produced as the result of microbiological activity and released to the atmosphere. The review of Cullen and Reimer [22], indicated in the 1980’s that there are few studies considering these volatile compounds. More than two decades afterwards, the situation remains very similar, due to the cumbersome procedures to collect the volatile As species.

Johnson and Braman [71] indicated in the 1970’s that methylated volatile arsines in the air could be trapped in a pyrex tube containing a 3 cm bed of 60/80 mesh silver plated pyrex beads. The removal of the arsines can be done afterwards by a mild, warm alkaline wash and the solution is submitted to direct currrent emission spectroscopy detection. However, this methodology do not allow to distinguish between the arsines and the organic acid forms of As.

The use of trapping media for gaseous and particulate As has been reviewed by Helsen [72], considering air pollution control. The sampling procedures for AsH_3 or vapour As_2O_3 described in the literature employ adsorption on active carbon, impingers with different solutions ($NaOH$, H_2O, HNO_3, NH_3), or cellulose membranes impregnated in Na_2CO_3. If the As is retained upon a solid sorbent, the posterior dissolution can be achieved by wet digestion (ultrasonic agitation, hotplate digestion or microwave assisted). The analysis of the extract can be performed by a large set of analytical techniques: atomic spectroscopy (e.g. AAS, ICP-MS, ICP-AES). Also, the consecutive use of series of impingers (a first one with a NaOH solution and a second one with $KMnO_4$ solution) allows to retain AsH_3, MMA and DMA [73]. This methodology was used only at a lab scale, but not with real samples. A main drawback of the trapping media described in the review of Helsen [72] or in the work of Spini et al. [21] is that they do not contain information regarding methylated volatile arsines. Only recently Jakob et al. [74] has proposed the use of Tedlar bags from trapping methylated arsines. The procedure involves the use of a U-shaped cryotrap with liquid N_2, connected to a capillary GC column, which is equipped with a cryofocusing unit before GC-ICP-MS. After removing the liquid N_2, the GC column is heated from 50 ºC with a ramp of 10 ºC min^{-1}. The authors have employed this procedure for lab experiments, but application to real samples is not yet provided. The same authors also propose an indirect approach to estimate the volatile arsines, considering the presence of MMA, DMA and TMAO in the solid PM as a result of the oxidation of the corresponding arsines in the atmosphere.

4. Sample treatment for total As determination in PM

After PM sampling, the filters containing As are summited in most case to a chemical treatment, depending on the analytical technique employed for As determination, usually atomic spectroscopy (e.g. AAS, ICP-MS or ICP-OES). No chemical treatment is necessary for analysis based on non-destructive techniques (e.g. PIXE, INAA or XRF).

Sample chemical treatment employs acids, either to extract the PM from the filters or to dissolve the whole sample. Table 1 includes information about chemical treatment for different types of filters, as well as the analytical technique and the concentration of As found in sampling locations around the world. As it can be observed in Table 1, high As concentrations in PM correspond to urban areas (big cities, waste incinerator) or places with industrial activity (e.g. copper mining, copper smelters or ceramic industry).

4.1 Sample digestion

For the digestion of the filters, a portion is cut and placed in a reaction vessel (Teflon is preferred in most studies) and acids are added, assisted by some thermal treatment. The reaction vessel should be closed, in order to avoid possible losses due to the formation of As halides. The variety of digestion procedures is high, and almost each research group uses its own. The digestion of glass filters has been performed with HNO_3, heating in a sand bath (Šerbula et al. [75]) or a heating block (Pandey et al. [64]). For PTFE filters Thomaidis et al. [62] employed $HClO_4$ at room temperature in an ultrasonic bath during 30 min, whereas Acevedo Figueroa et al. [63] just indicates acid digestion in a hot plate, without specifying the acid or the time. Also, Kovaćević et al. [76] performed digestion of PTFE filters with a HNO_3:H_2O_2 mixture in closed reactors placed in a microwave oven.

In the case of quartz fibre filters, HF is commonly added to HNO_3, HCl or HNO_3:$HClO_4$ mixtures. Richter et al. [57] performed digestion of PTFE filters with a mixture of HNO_3:HF:H_2O_2 for complete digestion in a microwave oven, evaporation on a hot plate and dilution to 25 ml. Other authors employ mixtures of HNO_3:$HClO_4$:HF on a heating plate for complete digestion, a process that is time consuming, as the digestion lasts 2-3 days [49, 56, 58, 77]. However, the use of HF is discouraged, due to its hazardous handling. Instead, a mixture of HNO_3:H_2O_2 is recommended by the actual legislation in the EU (EN 14902:2005) for As determination in PM10, aided by microwave radiation [48, 78, 79]. Fang et al. [84] employed the same mixture and heating instead of microwave. Similarly, for cellulose filters, a better digestion is described using a mixture of HNO_3:H_2O_2 than just HNO_3 [80].

In view of the above digestion procedures, it seems that there is not an established approach to select the best mixture of acids for sample digestion, and that each research group uses the one following their own experience. Almost none of them comment possible losses during the digestion process due to volatilization, or the possible interferences that the acids may produce in the posterior analysis. Also, the digestion time is usually obviated and may be time consuming (hours or days) if the acid digestion is evaporated to dryness and then re-dissolved in diluted acid before analysis. An exception is a systematic study of Wang et al. [81], which proposed an optimized digestion of two steps, with HNO_3-$HClO_4$ followed by $HClO_4$-HF, using either microwave or a high pressure bomb digestion. However, in a posterior article [82], this author tried different mixtures of HNO_3, $HClO_4$, H_2O_2 and HF with certified reference materials SRM1648 “Urban particulate matter” and SRM 1633b “coal fly ash”. Their results clearly indicate that As concentration was best estimated by an HNO_3:H_2O_2:HF mixture, and that $HClO_4$ should be avoided for ICP-MS detection, due to the possible $Ar^{40}Cl^{35}$ interference with the same m/z 75 as As.

4.2 Sample single step extraction

As an alternative to sample digestion, As can be extracted from the filters with acids, in order to reduce the time of sample treatment to few hours or minutes. For glass fibre filters, Halek et al. [70] followed the EPA 3051A method, which consists of acid leaching of the sample with a HNO_3:HCl mixture assisted by microwave radiation. Pasias et al. [65] followed the EPA 600/4-77-027a method, which also employs a HNO_3:HCl mixture and an ultrasonic bath at 50 ºC during 50 min. For the same type of filters, Šerbula et al. [75] extracted PM samples only with HNO_3 and sand bath heating. Also, for PTFE filters, an extraction procedure has been proposed at room temperature with a mixture of HF:HNO_3 [61, 83], although the extraction time is long (4 days), in comparison to the few hours employed with methodologies that heat the sample (e.g. extraction with HNO_3 on a heating plate for 2 h, as described by Gioda et al. [85]. A faster extraction procedure for quartz fibre filters has been employed by Yadav and Turner [86] which consists of the extraction with a mixture of HNO_3:HCl in a heating block at 90 ºC for 90 min. For cellulose filters, extraction of As is accomplished with HNO_3 assisted by microwave, as reported by Tsai et al. [87]. As these extraction procedures do not dissolve the filter that retains the PM, recoveries tests have to be performed to guarantee of the extraction process, as commented in the last section 8. about QA/QC.

As it happens with digestion procedures, in the existing literature no rationale is given for the selection of a certain procedure of extraction. A possibility to obtain results that are comparable is to follow an established extraction method. In this sense, Morales-García [88] and Huang et al. [89] employed the US EPA 3051A for PM samples, although this method refers to soil and sediments. In this case, acid leaching is done with a HNO_3:HCl mixture in a microwave oven.

In addition to the total As content (either by acid digestion or acid extraction), some studies focuses on the bio-accessible fractions of As. The purpose of this approach is to assess human health risks associated to As in PM. In this sense, extractions are performed with water, although the procedures change among the authors: Karthikeyan et al. [90] performed aqueous extraction of PM samples from Singapore at room assisted by microwave, whereas Qureshi et al. [91] employed ultrasound at 70 ºC for PM samples of New York (USA), and Wang et al. [67] also applied ultrasound without heating to samples from Nanjing (China). The different extractions conditions makes difficult to compare the data, as they provide different extraction results (0.6-1.5 ng m^{-3} [90], 2 ng m^{-3} [91] and 11.99-23.44 ng m^{-3} [67]). In the case of [67], no total content is determined, so percentage of extraction cannot be calculated. In reference [91], the authors indicate that a 84% of the As is water soluble, contrary to the results of Karthikeyan et al. [90], who indicated a low extraction of As, as the their samples contained total As concentrations in the 12.4-35.5 ng m^{-3} range.

In addition to water, other selective extraction methods have been proposed. Hu et al. [48] consider a Simple Bioaccessibility Extraction Test (SBET) based on glycine at pH 1.5, indicating that mean As extractions of 47.5% and 48.2% for TSP and PM2.5, respectively. The recent developments in the assessment of bio-accessible trace metal fractions, including As, has been recently reviewed by Mukhtar and Limbeck [92], indicating leaching, procedures and analysis in relation to the fractioning according to particle size, rather than speciation of As.

4.3 Sample sequential extraction for total As

Originally, sequential extraction procedures aim to distinguish the distribution of elements among the different mineral fractions of soils. These procedures have been extended to other types of samples, such as PM. The successive application of the extractants allows to estimate the mobility of the metals, considering to which fraction they are bound. There are few articles that deal with this topic. Richter et al. [57] followed the extraction procedure of Chester consisting of four extracting solutions for the following fractions: water soluble fraction (water), environmental mobile fraction (ammonium acetate solution), bound to carbonate and oxides fraction ($NH_2OH{\cdot}HCl$ solution) an organic and refractory-associated fraction (HNO_3:HF:H_2O_2 solution). Their results applied to PM10 samples from Chile indicated that As is rather mobile, as a 70% of the As was found mainly in the first and second fractions. Another sequential extraction procedure for PM samples is the one of the BCR (Bureau of Certificate and Reference), which considers also four fractions: acid soluble (acetic acid solution), reducible fraction ($NH_2OH{\cdot}HCl$ solution), oxidable fraction (H_2O_2 solution followed by CH_3COONH_4), and residual (aqua regia digestion). Sun et al. [93] and Li et al. [94] applied the BCR procedure to TSP and PM2.5 samples of Nanjing (China). Their finding agree with the results of [57], as a 70-80% of the As was found in the first and second fractions. Similarly, Feng et al. [95] found also that ca. 70% of the As was associated to the first and the second fractions for PM2.5 of Guangzhou (China). These results indicate the mobile and bioavailable character of As, and therefore more studies in this sense should be advisable.

5. Analytical techniques for total As determination in PM

There are numerous analytical techniques employed along the last four decades for As determination in atmospheric samples, most of them based on different types of atomic spectroscopy and also mass spectrometry. Each technique is summarised and discussed separately in the following sections.

5.1 Colorimetry

As early as 1969, a tentative method for As content in PM was proposed by Tabor et al. [96], based on the As reduction to arsine with $SnCl_2$ and Zn, which reacts with a pyridine solution containing silver diethyldithiocarbamate. The resulting red complex was measured by photometry at 536 nm. As the minimum As that could be measured was 0.1 µg m^{-3}, the applicability of this method was not effective to real air samples, with typical concentrations of As in the ng m^{-3} range.

5.2 Hydride generation – atomic absorption spectroscopy

Braman [97] indicated in the 1970’s that hydride generation (HG) with sodium borohydride ($NaBH_4$) for arsine evolution was faster and less prone to interferences than the classical approaches using zinc or magnesium. The arsine detection by flame or flameless atomic absorption spectroscopy (AAS), gave better detection limits than colorimetry by a factor of two. In this work, Braman already indicated the suitability of HG in combination with atomic absorption or emission spectroscopy for the determination of total As and its species in atmospheric samples.

In HG-AAS, the sample is acidified (e.g. HCl) and a $NaBH_4$ or KBH_4 solution is added. The arsine is transported by an inert gas carrier (e.g. N_2 or Ar) to the atomizer, a T-shape quartz tube. The atomization of the arsine is achieved by heating the quartz tube either electrically or by an air/acetylene flame. HG-AAS has been applied to PM samples from urban sites: Beceiro-González et al. [98] found up to 2.49 ng m^{-3} in La Coruña (Spain), Vassilakos et al. [99] found a maximum of 14.7 ng m^{-3} in Athens (Greece). In India, Singh et al. [80, 100] reported a maximum of 5.58 ng m^{-3} in Delhi, whereas Tripathi et al. [101] indicated a maximum of 13.5 ng m^{-3} in Bombay. When measuring As by HG, it should be bared in mind that inorganic As may be present as As(III) or As(V). In order to obtain reliable results, care must be taken that all the As is in the same oxidation state. To achieve this, the usual procedure is to perform a reduction to As(III) adding KI and ascorbic solutions prior to HG [80, 100]. The LOD for HG-AAS indicated by these authors are between 0.17-1 µg l^{-1} (in the PM extract solution), which corresponds to 0.02 ng As m^{-3} in the air. No indication is usually given in these articles about possible interferences (e.g. transition metals) during the HG step or the use of any reagents to mask them. Tripahi et al. [101] performed and interference study with synthetic samples spiked with Pb, Cd, Cu, Zn, Co, Ni, Mn, Mg, Se, Fe, In, Tl, Cr, Sn, Co and Ni (0.5-10 ppm) and did not find significant interferences (percentage of error <6%). However, there is no indication that spiking experiments were performed with real PM samples. Overall, the number of studies by HG-AAS is reduced and its use is nowadays scarce. The main reason is that other techniques are preferred because they can provide better sensitivity consuming a lower volume of sample (e.g. ET-AAS) or are capable of multielemental analysis (e.g. ICP).

5.3 Electro thermal- atomic absorption spectroscopy (ET-AAS)

ET-AAS, also referred as graphite furnace atomic absorption spectroscopy (GF-AAS), is an alternative to HG-AAS for total As determination in PM. Its use is more extended than HG-AAS, as it is included as one of the detection techniques recommended in the European Standard for As in PM10 (EN 14902:2005) [102]. This technique has been employed by several authors: Chakraborti et al. [103] measured concentrations of As ranging 9-512 ng m^{-3} in Dehli (India). Acevedo-Figueroa et al. [63] and Gioda et al. [85] found low As concentrations below 0.5 ng m^{-3} in PM2.5 and PM10 samples from Puerto Rico. Tsai et al. [87] analysed different PM fractions in Taiwan (PM2.5-PM10), finding As concentrations between 0.18 and 12.4 ng m^{-3}. Higher As concentrations (maximum of 95.4 - 149 ng m^{-3}) were reported by Šerbula et al. [75] and Kovaćević et al. [76] for PM10 samples taken at Bor (Serbia), nearby a copper smelter. Also, Thomaidis et al. [62] found 29.3 ng m^{-3} in Athens (Greece), whereas Onat and Sahin [55] found 171.8 ng m^{-3} in industrial areas of Istanbul (Turkey).

When employing ET-AAS for As determination, molecular interferences from the PM matrix should be taken into account. The common procedure is to work with Zeeman background correction and to add $Pd(NO_3)_2$ [55] or a mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ [62, 104] as matrix modifier. More recently, Pasias et al. [67] has proposed a zirconium-iridium permanent modifier for simultaneous determination of As, Pb, Cd and Ni. Some authors follow an established method for As determination by ET-AAS, corresponding to US EPA 7060A [64, 73]. There are some discrepancies between the LOD described in the literature, as they ranged from as low as 0.05 ng As m^{-3} [55] to 2 ng As m^{-3} [75]. In this later case, no indication is given if a matrix modifier is employed for analysis, and the amount of sample employed for the digestion is not indicated, parameters that can affect the LOD.

5.4 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS has the capability of multielemental analysis, providing at the same time low detection limits (e.g. LOD 0.05 ng m^{-3} [68]). It is nowadays the most employed technique for total As determination in PM. As it happens with ET-AAS, ICP-MS is also a recommended analytical technique, as indicated in the European Standard for As in PM10 (EN 14902:2005) [102], and therefore its use is more extended than other techniques. The As content in atmospheric samples has been evaluated in several countries around the world by ICP-MS analysis: Gidhagen et al. [61], Richter et al. [57] and Hedberg et al. [83] analysed PM10 samples in several areas of Chile, some of them near copper mines and smelters, with maximum As concentrations between 30.7 and 190 ng m^{-3}. Extensive work has been performed in several locations of Spain by Querol et al. [105], and at industrialized areas, e.g. near a ceramic cluster [59, 79, 106], with reported As concentrations of 11.7-16.0 ng m^{-3}, or near a copper smelter in Huelva [56, 58] in which As mean values of 5.4-9 ng m^{-3} were found, with a maximum of 96 ng m^{-3}. Other studies conducted in Taiwan by Fang et al. [84] indicated mean As concentrations between 2.81 and 4.11 ng m^{-3}. In urban and rural areas of Switzerland the As concentrations reported by Hueglin et al. [68] lay below 1 ng $m^{-3.}$ Emerging large cities, like Wuhan in China, showed high mean As values of 18-70 ng m^{-3}, with a recorded peak of 298 ng m^{-3} [69]. Also, high As concentrations have been determined by ICP-MS in PM samples from Oruro, a mining area of Bolivia, in which Goix et al. [107] reported mean As concentrations of 24 and 45 ng m^{-3} in PM2.5 and PM10, respectively.

When determining As by ICP-MS in PM, possible interferences may arise from polyatomic ions. In this sense Wang et al. [82] discourage the use of $HClO_4$ for PM sample digestion. Their results with reference materials SRM 1648 and 1633b showed recoveries 500-600%

higher than the certified As values. This difference was attributed to $[Ar^{40}Cl^{35}]^{+}$, with the same m/z 75 as As. However, other authors indicate that the sample matrix effect and the instrumental parameters can be more important that just that polyatomic ion interference. In this sense, Brown et al. [108] indicate the correction based on the use an arithmetic operation that includes the m/z 77 of $[Ar^{40}Cl^{37}]$ can remove the interference from the calibration solutions, but not from analysing the reference material. The authors point out that by adjusting the flow of the nebulized to a low value, As concentrations in agreement with the certified values were found, possible to the diminution of other possible interferences, such as $[Co^{59}O^{16}]^{+}$.

In relation to ICP-MS, there is the possibility to use Laser Ablation (LA) for sample introduction in the plasma, as it has been proposed by Wang et al. [81] for PM samples collected on PTFE filters, with promising results, although no more references were published afterwards with LA. Laser instability and inhomogeneous composition of the filters are parameters that have to be considered in order to have reproducible results.

5.5 Inductively coupled plasma- optical emission spectroscopy (ICP-OES)

In addition to ICP-MS, the literature cites few other plasma applications, such as ICP-OES. Halek et al. [70] applied this technique for As determination in atmospheric samples of Teheran (Iran), where low As concentrations were found, with average means of 0.20-0.27 ng m^{-3}, with a rather high LOD referred to the analysed solution (50 µg l^{-1}). The poor sensitivity of ICP-OES makes this technique only suitable for samples with extremely high As concentration, like the ones analysed by Querol et. al. [77] in the Guadiamar Valley (Spain) after a severe spill of heavy metals waste, in which concentrations up to 2681 ng m^{-3} of As were found in TSP. Also, Morales-García et al. [88] found mean concentrations of 424.4 ng m^{-3} in Puebla City (Mexico), with a maximum of 4877 ng m^{-3}, due to the proximity of the active volcano Popocatépel. When HG is employed in combination with ICP-OES, the LOD is improved (e.g. 1 µg l^{-1}), as reported by Pandey at al. [64], who found a mean As concentration of 7.85 ng m^{-3} in Bhilai (India) with HG-ICP-OES.

5.6 Direct techniques

The term “direct techniques” is used in this context for those one that do not precise a chemical treatment, and analysis is performed directly on the PM retained onto the filters. In this sense, the literature describes As determination by PIXE, INAA and XRF.

PIXE has been one of the first techniques that was reported for analysis of As in PM. Already in the 1980’s it was employed by Winchester and Bi [109] for PM analysis in samples of Beijing (China), finding As concentration between <0.28-10.3 ng m^{-3}. Also, Romo-Kröger et al. [50] found high As concentration (23-241 ng m^{-3} in fine particles) with PIXE, near a copper smelter in Chile. However, its use is scarce due to the fact that it is a technique not available for most researchers. In spite of it, PIXE presents as an advantage the capacity to analyse samples on an hourly basis, using a “streaker” sampler, thus providing more detailed information in comparison to most of the studies in which the samples correspond to a 24 hour sampling period, as it has been described by D’Alessandro et al. [110] and Fernández-Camacho et al. [111]. In this sense, PIXE analyses with a streaker sampler will help to identify peaks of pollutants in ambient air coming from anthropogenic or natural sources.

There are also few references about As determination in PM by INAA. Freitas et al. [54, 60] measured As in PM10 and PM2.5 of Lisbon and other locations in mainland Portugal, with mean As concentrations of 3.6 and 2.8 ng m^{-3}, respectively. Also Šlejkovec et al. [123] determined total As concentrations by INAA in urban samples from Budapest (Hungary), with concentrations ranging from <0.30 to 5.3 ng m^{-3}. XRF has also been proposed for multielemental determination in PM10, although there are few references for As with this technique: Waldman et al. [112] determined As concentrations up to 64 ng m^{-3} in Wuhan (China), Vercauteren et al. [113] found a mean of 3.8 ng m^{-3} in Flanders (Belgium). In spite of that, an interlaboratory comparison exercise of As, Cd, Ni and Pb in PM10 conducted in Europe has demonstrated that XRF can provides similar reliable results as those obtained by ICP-MS or ET-AAS [78]. Recently Godelitsas et al. [114] has described the use of Synchrotron-radiation µ-XRF for As determination in PM samples from Athens (Greece).

In spite of the reliable results obtained with these direct techniques, their use is not extended by several reasons. The first one is the need of specialized laboratories and facilities, such as an isochronous cyclotron for PIXE, or a nuclear reactor for INAA. In the case of INAA, its good sensitivity is hindered by the high cost of the analysis and the time of irradiation, which is of several days. For XRF, its main drawback is its rather poor sensitivity, as it has been summarized by Wang et al. [81].

6. Sampling and sample treatment for As speciation in air samples

The term "speciation" in analytical chemistry, as defined by IUPAC, is referred to the distribution on an element in different species according to its molecular structure or oxidation state [115]. Sometimes it is also described as "chemical speciation" to distinguish it from "physical speciation", this latter indicating the distribution among different particle sizes [116], thus generating some confusion. In this latter case, the IUPAC recommends to use the term "Fractionation" instead of "Physical speciation". At present, the number of As speciation studies in ambient air (Table 2) is less numerous than the ones about total As determination. Most of the speciation studies pretended to determine the total As content of the samples, performing an extraction step in the case of PM samples, as described in the following section 6.1. Selective extractions procedures (bioaccessible As and sequential extraction schemes) are described in section 6.2.

6.1. Sampling and extraction for As speciation

The first speciation studies go as early as the decade of 1970's, with the initial work of Johnson and Braman [71] in urban and suburban samples in the Tampa Bay (Florida). These authors employed a two stage collector to distinguish between PM >0.3 µm retained onto glass fibre filters, and the combined gaseous and PM <0.3 µm fraction retained onto silver plated pyrex beds placed in a pyrex tube. As species were extracted using an alkaline warm solution and submitted to direct current discharge-OES. This procedure allowed to distinguish between inorganic As and methylated arsines (methyl, dimethyl and trimethyl arsines). The most relevant result of this early study is that it indicated the minor presence of methylated As species in outdoor and indoor samples, although a great variability of the percentage of the organic compounds was reported. A handicap of this initial work is its inability to distinguish between the oxidation states of inorganic As.

More studies regarding methylated As were performed by Mukai and Ambe [117, 118] in the 1980's, concerning the use of organic As pesticide in rural areas of Japan. PM containing As species was collected using glass or quartz fibre filters and extracted with a similar procedure as described in [71], by sonication with either a NaOH or HCl solutions. The extract was then submitted to hydride generation with a $NaBH_4$ for posterior analysis. The authors performed an optimization of the extraction process, comparing NaOH and HCl with or without EDTA, concluding that the best extraction and reproducible results were achieved by HCl with

EDTA. The results indicated again the presence of methylated arsenic at low concentrations, in the pg m^{-3} level.

In a similar way, Nakamura et al. [119] also performed the extraction of MMA and DMA from PM samples taken in the marine atmosphere, with an HCl solution by sonication during 30 min. They also attempt inorganic As analysis, using for the extraction HNO_3 and H_2O_2, followed by HG, a cold trap and atomic absorption detection.

In the same period, Rabano et al. [120] reported a first study about inorganic As speciation in coarse (TSP) and fine (PM2.5) particles, conducted in Los Angeles (California). The authors described the use of PTFE to collect PM with high volume air captors. The filters were then treated with a diluted ethanol solution to reduce the hydrophobic nature of the collecting material. As in previous cited works, the extraction was done with a diluted HCl solution in a Teflon vial, heating during one hour at 85-90 ºC. Hydride generation was performed afterwards in the extracts prior to the analysis by AAS. The authors checked the extraction efficiency, spiking unexposed filters with As(III) and As(V), obtaining close to 100% recovery for both As species. However, when the same procedure was applied to filters exposed to PM, a 79% recovery was obtained for As(III). This indicated the complex nature of the PM matrix, which could be overcome by quantification by standard addition calibration method. No comments were made about possible methylated arsenic species in the air samples.

Other limited studies about inorganic As speciation were performed in the 1990's at a Geysers Geothermal area in California by Solomon et al. [121], and by Talebi at the city of Isfahan (Iran) [122]. In the first case, PM was collected upon quartz filters and extracted with diluted HCl in a similar way as in [120], whereas in the second case quartz filters were employed and digested with H_2SO_4 and HNO_3 for posterior analysis by HG-AAS. Again, no methylated arsenic species were considered in both studies. The authors indicated the effect of the matrix of PM on the extraction of the As species [121]. They found a recovery of 60% for As (III) and 120% for As(V). Although a partial oxidation of the arsenite during sample extraction was observed, the results were not corrected for this possible matrix effect. In this sense, other authors [120] estimated that the possible matrix represented less than a 20% of difference in their samples.

In 2000 and the following years, liquid chromatography (HPLC) was combined with hydride generation and atomic fluorescence spectroscopy (AFS) for As speciation in PM samples. Several authors employed this hyphenated technique to attempt the study of inorganic and organic As speciation. This involves always an extraction process that has to fulfil some basic premises, as providing a quantitative extraction without altering the distribution of the species using an extraction media compatible with the posterior analysis. Šlejkovec et al. [123] sampled coarse (PM2-10) and fine (PM2) particles in filters at urban sites of Budapest (Hungary), using water or 0.1 M phosphate solutions as extractant and sonication during 3 h. Their results indicated low extractability of As with water (mean extraction 12% and 45% in coarse and fine particles, respectively) and even lower with phosphate (mean extraction 10% and 15% in coarse and fine particles, respectively). Also, Oliveira et al. [124] described the analysis of TSP samples collected in Huelva (Spain) near a copper smelter, trying water, 0.1 M $NH_2OH \cdot HCl$ and 0.01 M H_3PO_4 extracting solutions, with the aid of microwave (4 min) or sonication (15 min). The selected extraction method in this study was a 0.1 M $NH_2OH \cdot HCl$ solution plus microwave oven extraction, with a percentage recovery of 94%. The same extraction procedure was applied afterwards by these authors in the same study area to PM10 [125] and PM2.5 samples [126], in which only inorganic As species were found after analysis by HPLC-HG-AFS. In a similar way, Yang et al. [127] employed sonication with H_3PO_4 to achieve As(III) and As(V) speciation in PM10 samples of Beijing (China). The extraction efficiency was found to be ca. 92%, a little better than the 86% reported by Oliveira et al. [123] when using H_3PO_4 assisted by microwave radiation. Tsopelas et al. [128] collected coarse PM and fine particles (PM2.5) at Aspropygos (Greece), an industrial site with a refinery and close to a highway, using glass or polycarbonate filters. The authors performed the extraction at room temperature by stirring with concentrated acids, 9.5 M HCl giving better extraction efficiency than 6M H_3PO_4. One drawback of the proposed method is the relative long time of the extraction (2h), compared to others based on microwave or sonication in which the extraction time is of few minutes. A comparison of the extraction efficiency of the different extraction procedures is commented in section 8 about QA/QC procedures.

An alternative to sonication and microwave extraction, is the use of Pressurised Liquid Extraction (PLE). Moscoso et al. [128] tried PLE using an EDTA solution as extracting media at 100 ºC and a pressure of 1000 psi, during 5 min, with satisfactory results for inorganic As species. In spite of that, there are not more publications about the use of PLE for As studies. A second alternative is the technique of slurry sampling, as proposed by Macedo et al. [129], mixing the sample containing PM with 4M HCl and sonication during 30 min. Again, no more studies have considered this possibility.

Jakob et al. [74] have reported more recently an extraction method for methylated arsenic species from PM samples. These authors submitted PM10 samples from urban sites of Argentina to extraction with H_2O_2 (30%), heating in a microwave oven. The resulting solution was freeze-dried to remove the solvent, and 1 ml of H_2O was added allowing the posterior determination of methylated arsenic species by HPLC-ICP-MS. They results indicated the presence of MMA, DMA and TMAO at the pg m^{-3}. However, inorganic As(III) and As(V) were not quantified in the samples. Also, no direct evaluation of the efficiency of the extraction procedure is given, as the authors employ the whole filters for the extraction, and no portion was saved for total As determination.

6.2 Selective extraction for As speciation

In some studies, the authors do not aim to extract all the As species in a single extraction step. This is the case of bioaccessible fractions, as described by Huang et al. [89], who employed a physiological based extraction test (PBET) with PM2.5 samples, consisting of a gastric solution simulating the chemical conditions of the gastrointestinal tract. This study evaluated the possible presence of inorganic As(III) and As(V), as well as MMA and DMA. However, their results indicate that only the presence of inorganic As, As(V) being the major species (15. 53 ng m^{-3} As(V), 4 ng m^{-3} of As(III)). When compared to the total As content of the sample, the bioaccessible fraction represented a 32.76%. This percentage is lower than other experiments performed for total As content in PM2.5 samples, as described previously by Hu et al. [48], who reported a 35-58.6% employing a Simple Bioaccessibility Extraction Test (SBET) based on glycine at pH 1.5. The difference can be attributed to the different extraction media of each experiment. At present there are still few studies about bioaccessibility of As in air samples. Therefore, more research is advisable in this sense, considering more study areas and comparable extraction procedures.

In relation to sequential extraction schemes for As speciation in PM, there is little information available. Farinha et al. [131] employed a three step scheme using Milli-Q water, $CaCl_2$ and H_3PO_4 solutions and posterior analysis of the extracts by HPLC-HG-AFS. In this study, a low extractability for inorganic As species was described for water (6-11%) and higher for $CaCl_2$ + H_3PO_4 (13.8-68.5%). These authors did not reported methylated species in coarse or fine particles of PM samples. Likewise, Šlejkovec et al. [123] employed a two steps extraction procedure for coarse (PM2-10) and fine (PM2) particle, with water and a phosphate solution (pH 6). In this case, only As(V) was found in the samples. The extraction was always low with water (45% in fine particles, 12% in coarse particles), but results were poorer with phosphate (10%-15%). As in the case of bioavailability of As, it may be interesting to perform more studies regarding As speciation by sequential extraction schemes that could be serve as comparison for bioaccessible As in PM.

7. Analytical techniques for As speciation

Almost the totality of the published studies is focused on As speciation in PM. The next sections deal with the analysis of the corresponding aqueous extracts of PM samples, based on hydride generation, liquid or gas chromatography combined with atomic spectroscopy or mass spectrometry. Only the last section describes a tentative method for the analysis of collected methylated arsines.

7.1. Hydride generation and/or cold trap-spectroscopy

The initial work of Johnson and Braman [71] employed HG with a cold trap and direct current discharge-emission spectroscopy (precision ±10%, detection limits 0.1-0.2 ng m^{-3}) to the aqueous extracts of PM, a technique that has not been applied to posterior studies. Although they were able to quantify organic arsenic in both PM and the gaseous phase, their method was not able to distinguish between the methylated arsines and the corresponding organic acids. Therefore, the comparability to other studies is limited.

The speciation of inorganic As(III) and As(V) undertook by Rabano et al. [120] and Solomon et al. [121] in 1980's was based in the different response of inorganic As(III) and As(V) to HG, without chromatographic separation of the As species. As(III) can be converted into AsH_3 with a Zn slurry, and As(V) is reduced afterwards in the same sample with $NaBH_4$. The hydrides are transported and detected by AAS in an N_2-H_2-air-entrained flame. This method provided LOD of 20-25 ng for each As species, with an accuracy of 9-11% [120]. If expressed as concentration, according to [121], the LOD is 0.23 ng m^{-3}, with a similar accuracy of 12-13%.

Another possibility with HG-AAS proposed by Macedo et al. [130] is to analyse two aliquots of the extracted PM solution, adjusting the chemical conditions of hydride generation to determine separately the total As and As(III). In this case, total As in the extract is measured reducing its As(V) content to As(III) with a KI/ascorbic acid mixture, whereas As(III) is measured masking the As(V) with a buffer of citric acid/sodium citrate. As(V) is estimated as the difference between total As and As(III). The hydrides are transported to a T-shape tube heated by an air/acetylene flame for AAS analysis. The LOQ are 0.6 and 1.0 ng m^{-3} for total As and As(III), respectively. Although the authors indicate a good match between the total As in the extract and the total As content by acid digestion, the results indicated the most of the As of the three studied samples is present as As(III) (58-74%), which is opposite to most speciation studies, in which As(III) is a minor constituent compared to As(V). No spiking experiments are presented or an explanation is given for this high As(III) concentration.

Of the two articles published by Mukai et al. in the 1980's, the first one [117], employed a reaction vessel where the PM extract was submitted to HG, and the volatile arsines were trapped in a U-shape tube half packed with glass beds, dipped in liquid N_2. The methylated arsines were desorbed afterwards by a N_2 carrier, mixed with H_2 and transported to the alumina tube heated by an air-acetylene flame. With this instrumentation, the authors separated and detected monomethyl and dimethyl As, whereas trimethyl As overlapped with dimethyl, so they had to be quantified as the sum of both species. The LOD (in mass) reported was 0.5 ng for the organic arsenic compounds. No information was provided regarding the possible presence of inorganic As species in the studied samples. In their second article [118], the same authors improved the separation of the three methylated by heating the U-shape tube with a nichrome wire heater, and transporting the arsines with a stainless steel capillary to the inlet of a gas chromatographic column. The chromatographic separation was performed by a programme of temperature from 25 ºC to 180 ºC, and the detection by AAS was performed in a similar way as their previous work. It is worth to mention that these authors conducted an extensive interference study of metals and anions referred to the HG step in relation to the response of the methylated arsines. Their finding showed that the main interferences were Fe, NO_3^- and NO_2^-, and that adding an EDTA solution during HG could avoid them. However, as in the previous cited works, the need of a careful manual manipulation of the reaction vessel for HG and the cold trap for the arsines represents a drawback. In a similar way, Nakamura et al. [119] also collected the arsines that evolve after HG into a U-shaped tube with liquid N_2. In this case the trap was filled with a chromatographic packing, which allowed the separation of MMA, DMA and TMA after heating with a nichrome wire and their detection by AAS. These authors also considered possible interferences during the HG step, and sulphanilamide was added as masking agent to prevent the NO_3^- interference.

7.2. High performance liquid chromatography-hydride generation-atomic/mass spectrometry

More recent speciation analysis of PM, focused mainly on inorganic As speciation, have been performed combining HPLC with atomic or mass spectrometry detection (AFS, ICP-OES, ICP-MS and MS), with or without and intermediate HG step (Table 2). Of the different atomic detectors, AFS is the most employed for As speciation analysis in PM samples.

The initial study of Šlejkovec et al. [123] employed an anion exchange guard column for the separation of As(III), DMA, MMA and As(V) in PM extracts of samples from Budapest, using a potassium phosphate solution (pH 6) as mobile phase. After HG with HCl and $NaBH_4$ solutions, the arsines were transported to a glass gas-liquid separator and an Ar flow transported them to the H_2 diffusion flame of an AFS detector. The LODs (referred to the injected solution) reported were 0.12, 0.04, 0.63 and 0.08 µg l^{-1}, respectively, for the four above mentioned As species. They are in the same range of the LOD values reported by other authors for those As species with AFS detection (0.1 to 0.2 µg l^{-1}) [132]. Of the four studied species, only As(V) was detected in all the PM2 and PM2-10 samples from Budapest. HPLC-HG-AFS with the same anion exchange guard column was employed by Farinha et al. [131] with PM2.5 and PM10 samples of Portugal, finding both As(III) and As(V). The authors also tried a cation exchange column with a pyridine mobile phase (pH 2.65), but no results were obtained corresponding to cationic As species. Again, no MMA or DMA were found in the samples.

The use HPLC-HG-AFS, using an anion exchange column with a phosphate buffer has also been employed for As(III) and As(V) speciation in samples of TSP [124], PM10 [125] and PM 2.5[126] near a copper smelter in Huelva (Spain). Reported LODs for inorganic As(III) and As(V) were 0.1 and 0.4 ng m^{-3}, for a volume of injection of 200 µl. Again, no organic arsenic were found, and As(V) represented ca. 80-90% of the As content of the samples. In a similar way, Yang et al. [127] considered HPLC-HG-AFS with similar chromatographic conditions as in [124-126] for As speciation in TSP samples from Beijing (China). The method LODs were higher than in other similar works, 1.45, 1.16, 1.97 and 1.26 ng m^{-3}, for As(III), DMA, MMA and As(V), respectively, for an injection volume of 100 µl, perhaps due to the small amount of sample employed for the extraction (5 mg) compared to other works.

There is only one application for As speciation that describes the use of ICP-OES detection, in combination with ion chromatography (IC) and HG, as described by Tsopelas et al. [128]. The acid extracts containing PM are passed thorough anion and cation exchangers placed in glass columns. As(III) is extracted with methyl-isobutyl-ketone (pH 2) with 1% APDC. The remaining solution (pH 4) passes first thorough the cation exchanger to retain DMA. The pH of the effluent is adjusted to 7 before entering the anion exchanger for separation of MMA and As(V). The following solutions are employed for elution: 4M NH_3 for DMA, acetic/acetate buffer for MMA, and 1M HCl for As(V). Although this separation procedure seems more cumbersome than the previous described chromatographic separations based on HPLC, the provided LODs are similar: 0.1, 0.4, 0.3 and 0.4 ng m^{-3} for As(III), DMA, MMA and As(V), respectively. The analysis by IC-HG-ICP-OES of TSP, PM10 and PM2.5 samples from an industrial area in Greece showed that As(V) was the main As species. Also, As(III) was detected in one sample, whereas MMA and DMA were no detected in any samples.

7.3. High performance liquid chromatography-inductively coupled plasma-mass spectrometry

Other analytical methodologies described in the literature avoid the HG step, by the direct coupling of HPLC to ICP-MS. In this case, Jakob et al. [74] employed HPLC-ICP-MS for speciation of methylated As species. ICP-MS was operated in the collision cell mode with H_2. Rh was used as internal standard (m/z 103), and the m/z 75, 77 and 82 were measured to ensure that no chloride interference at m/z 75 was recorded. The elution order by anion exchange chromatography is TMAO, DMA and MMA with an ammonium carbonate (pH 10) mobile phase. As TMAO elutes close to the void volume, its identification was confirmed in a cation exchange column with a mobile phase of pyridine (pH 2.7 adjusted with formic acid). The given LODs, considering the extraction procedure of the samples and the analytical method, were extremely low, of approximately 0.3 pg m^{-3}, which are the most sensitive in the consulted bibliography. When applied to PM10 samples from Argentina, the authors found TMAO in all of them, in a 4-60 pg m^{-3} range, with maximum concentrations of 16 and 6 pg m^{-3} of DMA and MMA, respectively. TMAO was always the major organic species (66-69%), followed by DMA (13-19%).

In view of the results of Jakob et al. [74], it can be found a possible reason for the apparent discrepancy with those other analytical methodologies that have not detected methylated As in PM samples. The limits of detections provided by other authors for methylated As species (e.g. DMA and MMA) lie between 0.3-0.4 ng m^{-3} with HG-ICP-OES detection [128], and 1.16-1.97 ng m^{-3} with AFS detection [123], more than an order of magnitude than those reported by [74]. Therefore, their LODs do not allow them to detect organic arsenic species at the pg m^{-3} level. However, there may be other reasons to explain these discrepancies, rather than the analytical technique employed for detection, as the calibration graph employed for HPLC-ICP-MS is 5-30 µg l^{-1} [74], which is not very different with the different techniques: 1-10 µg l^{-1} with both HG-ICP-OES [128] and AFS [123]. One plausible reason is due to the natural origin of the methylated compounds. As they originate from micro biological activity, their concentration in the air at a concrete sampling point is completely unpredictable, and may not be even present at the pg m^{-3}. The second reason (considering that mehthylated As are in fact present in the samples), is the extraction procedure. As explained in the previous section, reference [74]. employed the whole filter sample for their study, as they indicate that “filters were cut in quarters and placed in a Teflon bomb,”, and the extract, after freeze drying is redissolved in 1 ml of water. On the contrary, in the other mentioned studies, only a portion of the filter is extracted (e.g. 1.2 cm^2 of a total of ca. 400 cm^2 [125], three-quarter section [123], or a not specified portion [128]) usually with a larger volume of extractant, e.g. 10 ml of HCl, $NH_2OH{\cdot}HCl$ or $NH_4H_2PO_4$ solution. This possible explanation can be supported by the results of Huang et al. [89], who also employed HPLC-ICP-MS for As speciation of PM2.5 samples taken at Guanzhou (China). In this case, a strip 1”x8” strip of the filter was extracted with 10-25 ml of a H_3PO_4 solution and microwave radiation. After centrifugation, the supernatant was diluted 10-50 fold before analysis. In this case, the authors were able to detected As(III) and As(V), but not MMA or DMA.

Another aspect that have to be considered is the correct identification of TMAO and As(III), as they elute close to the dead volume using anion exchange chromatography. As indicated previously, only is one case [74], the authors have confirmed the identification of TMAO by cation exchange (retention time 12 min using a 50 mM pyridine solution (pH 2.7)). Therefore, the identification of low concentration of As(III) in rural areas should be confirmed in this way. However, it is unlikely that the published data about high As(III) in PM found at large cities (e.g. 4.7 ng m^{-3} in TSP samples from Beijing [127], 4.0 ng m^{-3} in Guanzhou [89] or 1.2-2.1 ng m^{-3} in Huelva near a copper smelter [124-126]) may be attributed to TMAO, which is produced at the pg m^{-3} by microbiological activity.

7.4. Analytical techniques for volatile methylated arsines

As mentioned before, there are no recent studies about volatile arsines in the air. After the initial study of Johnson and Braman in the 1970’s [71], only an attempt has been performed more recently by Jakob el al. [74]. Volatile arsines are collected in a cryoptrap and carried afterwards to a cryofocusing unit of a GC-ICP-MS. The liquid N_2 has to be first removed before GC separation, followed by ICP-MS analysis. This methodology has been used with samples handled in the lab, and therefore more work has to be performed with ambient air samples.

8. Quality Assurance/Quality Control (QA/QC)

The purpose of QA/QA procedures is to minimize random and systematic errors related to the different steps involved in the analytical process. Of the different parameters to evaluate them, the most common one about As determination in air is trueness. The QA/QC evaluation has been focused on the use of certified reference materials (CRMs), and has been divided here into two sections, regarding total As and As speciation.

8.1 QA/QC for total As determination

QA/QC of the analytical process (sample treatment and analytical determination) is estimated by most authors using certified calibration standards, analysis of blanks and also analysing CRMs, which are submitted to the same sample chemical treatment (e.g. digestion or extraction) and analysis as the samples. To obtain reliable results, the matrix of the CRMs should be as close as possible to the one of the studied samples, in this case, particulate matter. A great number of the works employed at least one of the following CRMs: NIST SRM 1648 (urban particulate matter, certified value for As 115.5±3.1 mg kg^{-1}) [55, 59, 63, 66, 68, 79, 82 , 87 ,98 107], NIST SRM 1649a (urban dust, certified value for As 67±2 mg kg^{-1}) [65] and NIST SRM 1633b (fly ash, certified value for As 136.2±2.6 mg kg^{-1}) [58, 77, 80, 82, 106].

Only in some cases the authors expressly indicated the recovery, compared to the certified value. For SRM 1648, the following recoveries have been reported: Onat and Sahin (99%) [55], Hueglin et al. (112%) [68], García-Aleix et al. (85-91%) [79]. Some authors indicate the obtaained value for SRM 1648: Beceiro-González et al. found 110 ± 4 mg kg^{-1} [98], Tsai et al. [87] 110.1 ± 5.5 mg kg^{-1}, and Goix et al. [107] 112 mg kg^{-1}. Others just indicate that a maximum difference with the certified value is allowed (e.g. 20%) [64]. For SRM 1649a, Paisas et al. [65] obtained a 64.0 mg kg^{-1}, whereas Singh et al. [80] indicated recoveries of 99.3 ±0.4% for SRM 1633b. It is interesting to mention the study of Wang et al. [81], who compared several digestion procedures with SRM 1648. The authors found low recoveries (74-82%) for SRM 1648 when HNO_3 and $HClO_4$ were employed, and that the recoveries improved to 96-101% when HF was also added. Also, the same authors [82] indicated that for ICP-MS analysis, both SRM 1648 and SRM 1633b gave more accurate values if $HClO_4$ was not employed for acid digestion. The recoveries with or without $HClO_4$ were 308% vs. 117% for SRM 1648, respectively, and 423% vs. 129% for SRM 1633b, respectively. This difference is attributed to the $Ar^{40}Cl^{35}$ interference with the same m/z as As.

Other reference materials also described in the literature have been used to a lesser extent. Morales-García et al. [88] employed QC-TMFM-C (Trace metals on filter media C, No.0901501). The authors indicated that the trueness of their study provided values in the range of 99.6 to108.2 % for all the metals, compared to the certified values. Gioda et al. [85] has employed NIST SRM 2583 Indoor Dust, with a 76% recovery of the As certified value. Sometimes, the matrix of the CRM is not so similar to PM. For example, Yang et al. [127] checked the quality assurance of the extraction procedure by spiking with As species a standard soil of Tibet (GBW 08302, National Institute of Metrology P.R. China), with a extraction recovery of ca. 90%. Also, Sun et al. [93] employed a standard soil (standard reference material GBW 07405, from the National Research Center for Geoanalysis, China) to verify the precision and accuracy of their methodology. The element recovery percentage from the standard reference material was between 90.1% and 106.4%. Although these recoveries are quantitative, they should be handle we care, as they do not resemble the complex matrix of particulate matter.

As mentioned in a previous section, the number of digestion and extraction techniques employed for sample treatment is diverse, as well as the detection techniques. However, in view of the data of their QA/QC procedures, most of the authors are able to obtain good accuracy when analysing CRMs with similar matrices as PM. Therefore, the necessity to develop a standard method of sample treatment for As determination in PM is not necessary, as long as the authors can provide enough information about the quality of their results. However, in some other studies, no indication of quality control of the sample treatment based on CRMs is indicated, as in [61, 67, 70, 71, 69, 75, 91, 99, 100], and additional information (e.g. blanks, spiking experiments) is necessary to evaluate the quality of their procedures.

For PIXE, NIAA and XRF, which do not need a chemical treatment, quality control should be referred to the analytical determination of As. This has been assessed through the use of QA/QCBCR-128 NIST-2783 filters [54], although the authors do not indicate either the certified values or the obtained values for comparison. Other studies that use PIXE [50] or INAA [60] do not indicate the use of CRMs. For XRF, no indication of the use of CRM is given [113].

A shortcoming of the most common reference materials described in the literature (SRM 1648, SRM 1649a and SRM 1633b) is that they correspond just to the particulate matter, dust or fly ash, but these solid materials are not collected on a sampling media. Therefore, they do not completely represent the real conditions of the laboratory digestion, which consider real PM samples collected upon filters. In this sense, a common procedure is to add a small quantity of the CRM to a blank filter and perform the corresponding sample treatment and analysis. As an alternative, more realistic approach are the use of NIST SRM 2783 “Air Particulate on Filter Media”, corresponding to PM2.5 deposited upon a polycarbonate filter membrane (11.8 ± 1.2 ng), and CRM SL-MR-2-PSF-01, based on incineration waste ashes deposited on quartz filters, as it has been described by Oster el al. [133]. The As certified value for this later material is 0.47±0.04 µg/filter. The use of these CRMs can help to validate the sample treatment procedures in a more suitable way.

8.1 QA/QC for As speciation

At present, there are not CRMs with certified As species in particulated matter. Therefore, some authors have evaluated the trueness of their analytical methodology by studying the recovery of blank filters and filters exposed to PM, to which inorganic As standards were added. Rabano et al. [120] found for unexposed filters recoveries of 95 and 100% for As(III) and As(V), respectively. For filters exposed to PM, the recoveries were lower, 79% and 97%, for As(III) and As(V), respectively. This indicates the effect of the matrix sample of the measurement of As. Similarly, Mukai and Ambe [117] also added DMA to filters containing PM, and found a recovery of 92% after HG-CT-AAS analysis. In a posterior study [118] considered adding MMA, DMA and TMA to the filters that after extraction were analysed by HG-GC-AAS. The recovery results with a basic extraction employing a NaOH/EDTA solution ranged 77-94%. When an acid solution was employed (HCl/EDTA), the recovery improved to 98-105%. In the study of Nakamura et al. [119], with a methodology similar to Mukai and Ambe, no information regarding recoveries was provided.

Other speciation based on liquid chromatography indicate the recovery after extraction of inorganic As species, comparing to the total As content obtained either by chemical digestion or a direct analysis (e.g. INAA). Šlejkovec et al. [123] obtained extraction efficiencies of 22.0-45.9 % with water and phosphate extraction when applied to fine and coarse particles that were analysed afterwards by HPLC-HG-AFS. Better recoveries were obtained by Oliveira et al. [124] trying other extractants with TSP samples: 81% with a $NH_2OH{\cdot}HCl$ solution and sonication, 86% with a H_3PO_4 solution and microwave assisted extraction, and 94% with a $NH_2OH{\cdot}HCl$ solution and microwave assisted extraction. This third extraction condition has been applied by the same authors for the extraction of PM10 samples (recovery 91-105%) [125] and PM2.5 samples (recovery 91-104%) [126, 134] using HPLC-HG-AFS. In these studies, the total As was estimated by acid digestion and ICP-MS, employing SRM 1633b for quality control of the total As determination. In a similar way to these results, Yang et al. [127] also employed H_3PO_4 extraction of TSP samples. The recoveries, corresponding to inorganic species (no methylated ones were found), were in the 81-99% range, in consonance with the previous results of Oliveira et al. [124]. Moscoso-Pérez et al. [129] used pressurised liquid extraction with PM10 samples analysed by HPLC-HG-AFS. As in the above studies, they compared the sum of the extracted As species (in most of them only As(V)) with the total As content (determined by ICP-MS]. Although they do not indicate the percentage of recovery, they indicated that the results of the extraction do not differ from the total content.

Tsopelas et al. [128] employed HCl extraction of TSP samples followed by IC and HG-ICP-OES. Their results indicated that the type of filter media affected the extraction recovery of spiked samples: 98% for polycarbonate filters and 82% for glass filters. In this case, the authors applied the extraction procedure to TSP in which only inorganic As (mostly As(V)) was found. The application of a candidate reference material IPL-1 containing As(III), DMA, MMA and As(V) showed a good trueness (deviation between -5.6%. and +6.6%). However, IPL-1 is a soil sample, so its matrix differs from PM samples. Jacob et al. [74] considered spiking SRM 1648 with DMA and TMAO, performing HPLC-ICP-MS analysis after extraction with H_2O_2. The results showed extraction efficiency slightly higher than 69%.

Overall, the results of these studies indicate that for inorganic As speciation, the QA/QC procedures are sufficiently supported by the provided data, but more research has to be done in relation to methylated As, with the difficulty of concentrations in the pg m^{-3} range.

9. Trends and challenges

Arsenic in ambient air is a topic that will continue being of scientific interest in the near future, considering that there is legislation that regulates its concentration, like in Europe and China (6 ng m^{-3} in PM10). Therefore, more studies are expected to be undertaken to check if the air quality fulfil the targets values.

From an analytical point of view, there are several trends and challenges that have to be addressed in future research, considering particle size of PM, sampling time, organic As species and bioaccessibility of As. First of all, the atmospheric samples considered in the existing literature and summarised in this review are focused on PM10 and PM2.5, corresponding to coarse and fine particles. As arsenic tend to concentrate in the particles of smaller diameters [135], their health implication has to be considered in respect to the fraction below PM2.5. In this sense, recent works concerning PM deal with ultrafine particles [136], those with aerodynamic diameter lower than 0.1 microns (PM0.1), with the capacity to reach the central nervous system and enhance some illnesses (e.g. atherosclerosis and cardiovascular ischemic events) [137, 138]. The determination of the chemical composition of ultrafine particles is therefore of interest, including the determination of trace metals and As. The small mass of ultrafine particles present in PM, in comparison to PM10 and PM2.5, will obligate to develop new analytical methodologies to deal with the fact of the little mass of sample.

Secondly, another aspect briefly considered in previous studies is to obtain a more detailed information for sampling times shorter than 24 h. It is interesting to characterize the influence on ambient air of a punctual emission source. Nowadays, this is possible only with “streaker” samplers followed by PIXE analysis, which allows sampling on an hourly basis [139, 140]. However, PIXE is a technique not easily available in many labs, whereas most of the analysis of total As is performed by ICP-MS or ET-AAS. Also, PIXE does not provide information regarding As speciation. For a sampling time of just one hour, sample treatment strategies should be developed both for total As and As speciation, regarding the most commonly techniques (ICP-MS, ET-AAS and AFS).

A third consideration is about the As species in speciation studies. It is clear than the existing methodology based in liquid chromatography with atomic spectroscopy detection is able to determine inorganic As species in PM at the ng m^{-3} level. However, it seems that is not able to determine DMA, MMA or TMAO at the concentration at they are usually found, in the pg m^{-3} range. Either sample treatment or analytical detection should be improved if these species are to be determined. Also, few studies are available about volatile methylated arsines. Sample collection of these gaseous species is still an analytical challenge.

Finally, some studies have indicated the necessity of performing bioaccessibility studies of As in PM samples. They should not be focused only on total As content, but also consider speciation analysis. More studies are required in relation to the different As species that can be found in atmospheric samples, considering study areas worldwide and comparable extraction procedures.

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