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Arsenic and antimony speciation in atmospheric particulate matter of Andalusia

Memoria para optar al grado de doctor
presentada por:

Louay Alsioufi

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Bajo la dirección de los doctores:

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TESIS DOCTORAL

ESPECIACIÓN DE ARSÉNICO Y ANTIMONIO EN MATERIAL PARTICULADO ATMOSFÉRICO DE ANDALUCÍA

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إلـى عـائـلـتـي

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Abbreviations

AAS: Atomic absorption spectroscopy
AFS: Atomic fluorescence spectroscopy
AEI: Average exposure indicator
APDC: Ammonium pyrrolidinedithiocarbamate
BC: Black carbon
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
IPCC: Intergovernmental Panel on Climate Change
INAA: Induced neutron activation analysis
LA: Laser ablation
LOD: Limit of detection
LOQ: Limit of quantification
MS: Mass spectrometry
MMA Monomethyl arsenic
MW: Microwave
OES: Optical emission spectroscopy
PAH: Polycyclic aromatic hydrocarbons
PBAPs: Primary biological aerosol particles
PIXE: Particle induced X-ray emission
PLE: Pressurised liquid extraction
PM: Particulate matter
TMA: Trimethyl arsenic
TMAO: Trimethylarsine oxide
TSP: Total suspended particles

UFP: Ultra fine particles
VOC: Volatile organic compounds
WHO: World Health Organization
XRF: X-ray fluorescence

1. Introduction

1. Introduction

1.1. General considerations of atmospheric particulate matter (PM)

1.1.1. Definition and classification of PM

Atmospheric PM also refiered as atmospheric aerosol, is defined as material suspended in the air in the form of minute solid particles or liquid droplets. The term aerosol refers to the solid or liquid particles in air or another gas (Finlayson-Pitts, 2000: Seinfeld and Pandis, 2006).

PM particles can be classified by their aerodynamic properties because they govern the transport and removal of particles from the air, their deposition within the respiratory system. Aerodynamic properties are associated with the chemical composition and sources of particles (WHO, 2003).

According to the diameter the particles, most of the PM studies consider classification of the particles as TSP, PM10 and PM2.5. Total suspended particles (TSP) include particles of sizes up to about 50 µm. PM10 (also called ”coarse particles”) include particles with aerodynamic diameter less than 10 um. PM2.5 consists of fine particles with aerodynamic diameters less than or equal to 2.5 µm. Other more recent studies consider also the ultra fine particles (UFP) which correspond to those particles with diameter <0.1 µm (WHO, 2003; Dominici et al, 2010; Kumar et al, 2014).

Apart from size, PM can also be classified in other ways, such as anthropogenic vs. natural source, or primary vs secondary particles. The natural sources of particulate matter can be volcanic eruptions, seismic activities, geothermic activity, unprovoked fires in the wilderness, atmospheric resuspension due to strong winds and transport of natural particles from arid regions (EU, 1999). This definition of natural sources has been amended in the air quality directive in the European Union (emission of pollutants not caused directly or indirectly by human activities) (2008/50/CE). By this definition, also the marine aerosol is included, which was not considered as such in previous directives (EU, 1999).

Also there is another classification of PM as primary and seconday particles which depends on the formation process. Primary particles are those emitted directly from a source and

therefore include particles that arise directly from combustion sources such as road vehicles and power stations, as well as those generated by mechanical processes, for example, quarrying and agricultural harvesting. Other major source of the primary particles is the land and the sea, through entrainment of soils by the wind and the generation of marine aerosol particles by the bursting of air bubbles entrained in breaking waves (WHO, 2003).

Secondary particles are not emitted directly from sources, either natural or anthropogenic. Rather, they are formed in the atmosphere as a result of chemical reactions (e.g. SO_4^{2-} formed from SO_2) that lead to the formation of substances of low volatility, which consequently condense into the solid or liquid phase, thereby becoming PM. Such particles generally result from atmospheric oxidation processes and the substances oxidized may be either natural or anthropogenic in origin.

The term secondary describes primarily the process whereby gas-phase chemical reactions involving specific precursor gases produce low volatile products which are capable of *homogeneous nucleation* to form tiny new particles that can then increase in size by coagulation and capture by pre-existing ambient particles. The term also describes the process whereby the low volatile gas-phase reaction products condense onto pre-existing ambient particles, the so called *heterogeneous nucleation* process. While homogeneous nucleation may potentially increase both the number of aerosol particles and the mass of aerosol particles per unit volume in the atmosphere, Homogenous nucleation operates in the ultrafine particle size range and heterogeneous nucleation across the ultrafine and fine particle range (Kumar et al, 2014).

Secondary particles are included mostly in the range of fine particles, they also form a large extent of anthropic origin. Both classifications (primary and secondary, or natural and anthropogenic) are complementary, so that we can find natural emissions and anthropogenic primary and secondary. The primary natural particles come mainly from resuspension from soil, Ocean, volcano, and biogenic sources.

1.1.2. Mineralogical composition of PM

Atmospheric particulate matter can be considered as a complex system in terms of mineralogical and chemical composition. Depending on the sampling areas (e.g. rural, urban, industrial), mineralogy and chemistry of the particles overall is varied.
It can be considered the following principal five groups:

– Mineral fraction

Mineral aerosols or desert dust particles are soil particles suspended in the atmosphere in regions with easily erodible dry soils, little vegetation and strong winds (Mahowald et al, 2014).

This group contains carbonic such as: calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) as well as silicate (quartz, feldspars and clays, kaolinite and illite, and traces of plaster ($CaSO_4 \cdot 2H_2O$) and iron oxide (Fe_2O_3). Iron compounds in soil dust absorb visible radiation contributing to atmospheric warming, while scattering of mineral dust particles leads to surface cooling (Alfaro et al, 1998; Fuzzi et al, 2012)

Soil dust particles are entrained into the atmosphere in a several step process. Wind moves particles of about 100 – 200 µm. After that, these particles can break apart or eject smaller soil particles upon impacting the soil. The new formed smaller particles (< 50 µm) are entrained into the boundary layer, and can be transported long distances as it is shown in Fig.1.1 (Mahowald et al, 2014). Mineral dust importance has increased due to its effects on human health. In Europe the Saharan dust is associated with the transport of biogenic particles, allergens and pathogens to the Mediterranean regions (Fuzzi et al, 2015). Episodes of Saharan dust transport over Europe are responsible for exceedances of PM10 levels in these regions. For example, more than 70% of exceedances of the PM10 daily limit at rural background sites in Spain are due to dust outbreaks (Querol et al, 2009).

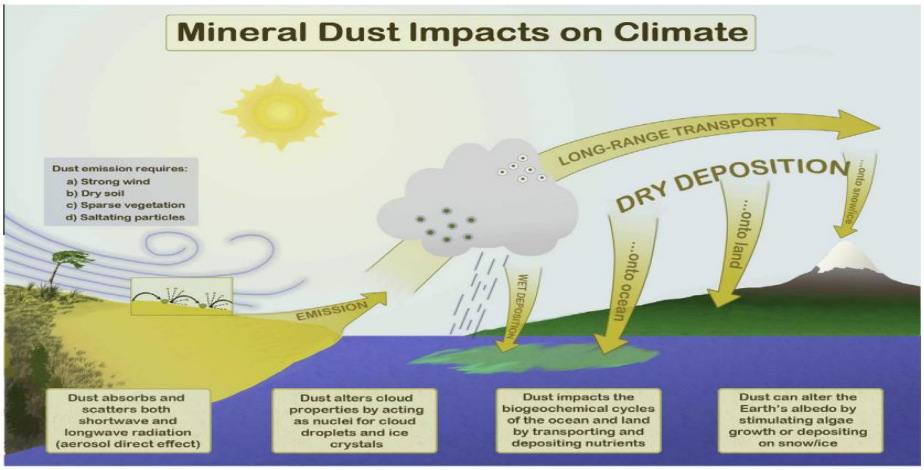

Fig.1.1. Schematic of interactions between dust and climate and biogeochemistry (Mahowald et al, 2014).

–Marine aerosol

Is one of the largest components of primary natural aerosols in the Earth's atmosphere. They can affect the radiation budget (the balance between incoming energy from the sun and the outgoing longwave radiation (thermal) and reflected shortwave energy from the Earth)as well as cloud physics in the atmosphere by scattering light and act and act as cloud condensation and ice nuclei. Also, they can interact with anthropogenic pollution and affect gas-phase chemistry (through depletion of acids such as HNO_3 and halogens).

It is chemical composition is similar to the seawater, consisting mainly of NaCl, KCl, $CaSO_4$, magnesium and potassium, being mainly thick coarse particles (> 20um), but also depends on the mechanism of formation (Kok et al, 2012: Fuzzi et al, 2015).

A scheme of marine aerosol formation and processing is reported in Fig. 1.2. Primary marine aerosols are generated by bubble bursting from breaking waves and capillary action at the ocean surface due to stress exerted by the surface winds, and hence their production depends on wind speed (Fuzzi et al, 2015; Quinn and Bates, 2011).

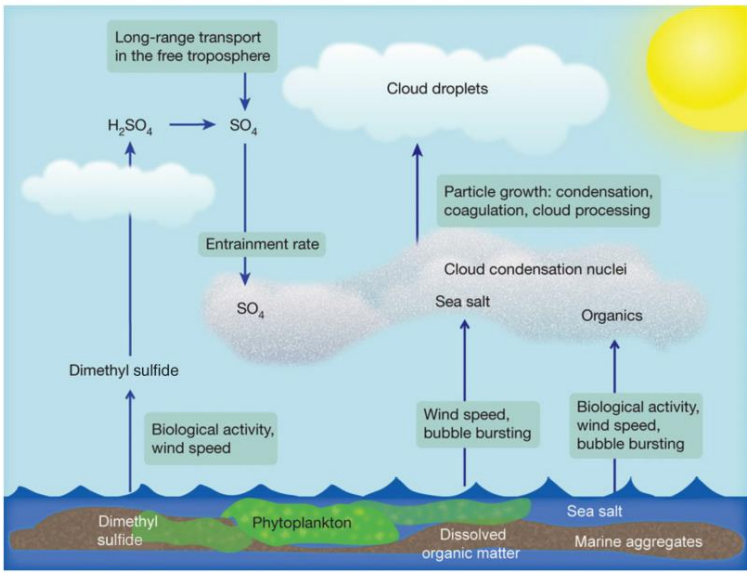

Fig.1.2. Scheme of marine aerosol formation (Quinn and Bates, 2011).

-Secondary inorganic compounds

SO_4^{2-}, NO_3^-, and NH_4^+ are the main components of this group, SO_4^{2-} are generated primarily through the oxidation of SO_2 (Hobbs, 2000).

$$SO_2 + OH \rightarrow HSO_3$$

$$HSO_3 + O_2 \rightarrow HSO_2 + SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The SO_2 and NO_x have many sources, such as combustion sulfur-containing fuel and fossil fuel combustion. The HNO_3 reacts with NH_3 to form particulate $NH_4\ NO_3$. This reaction is reversed, where the equilibrium constant directly depends on the humidity and inversely on the temperature. In spring the emissions of NH_3 reach the maximum in Europe due to fertilizer application. In United States and Europe, NH_3 emission control has been proposed as a cost-effective measure to control secondary inorganic aerosol (SIA), and thus PM levels, (Fuzzi et al, 2015).

-Organic compounds

They are classified into volatile and semi volatile compounds. They can be subdivided into organohalogen compounds which contain compounds such as PCB, DDT and polycyclic aromatic hydrocarbons (PAH) that come from incomplete combustion of organic matter and compounds derived from petroleum.

Wide expanses of plant mass (especially conifers) are considered the main sources of gaseous precursors of *secondary organic aerosols.* Plants emit significant amounts of volatile organic compounds (VOC), consisting mainly of carbon and hydrogen (including isoprene and terpene), oxygenates compounds and less of sulfur. (Fehsenfeld et al, 1992 in Puxbaum y Konig, 1997; Fuzzi et al, 2015).

-Primary biological aerosol particles (PBAPs)

They contain a large range of different biological components, including microorganisms (algae, bacteria and fungi) and dispersal material such as fungal spores, pollen, viruses and biological fragments that are directly emitted to the atmosphere from their sources. Their atmospheric concentrations are about 25% of total aerosol mass globally (Jaenicke, 2005; Despres et al, 2012: Fuzzi et al, 2015).

-Volcanic emissions

Volcanic emissions are important sources of PM in both the troposphere and stratosphere through direct emission of primary volcanic dust, or through emission of gaseous sulfur species capable of reacting to from secondary sulfate particles. Volcanos release the ashes that have a silicate composition, sulfate and chloride and gases of high temperature of volatilization (SO_2, HCl, HF and SiF_4). Fig.1.3 shows the processes involved in the formation of the sulfate layer (Penner et al, 2001).

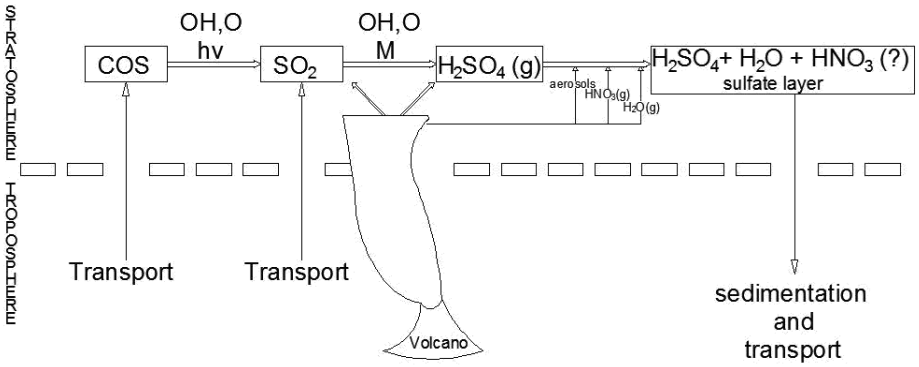

Fig.1.3. Schematic of the process responsible for the stratospheric sulfate layer (Hobbs et al, 2000), where M represents an inert molecule that absorbs excess molecular energies. COS is carbonyl sulphide.

1.1.3. Chemical Composition of PM

The major components of PM can be classified according to their soluble and insoluble character. The soluble compounds take up water from the atmosphere at high relative humidities, thereby turning from crystalline solids into liquid solution droplets. The main soluble compounds are: ***sulphate***, which arises mainly as a secondary component from atmospheric oxidation of SO_2; ***nitrate***, normally present as NH_4NO_3, which results from the neutralisation of HNO_3 vapour by NH_3, or as sodium nitrate ($NaNO_3$), due to displacement of hydrogen chloride from NaCl by HNO_3 vapour; ***ammonium*** **and** ***chloride***, coming from marine aerosol.

The major insoluble compounds are; ***elemental carbon***, which corresponds to black, graphitic carbon formed during the high temperature combustion of fossil and

contemporary biomass fuels; ***organic carbon***, which can be a primary or secondary inorganic compounds, where the primary compounds come from automotive or industrial sources, and the secondary from the oxidation of volatile organic compounds (VOCs); ***mineral components***, also considered as crustal material rich in elements such as Al, Si, Fe and Ca.

Other minor insoluble compounds are ***trace elements*** which corresponds to metals and metalloids (e.g. Sb, Pb, Cd, Hg, Ni, Cr, Zn and As) and trace organic compounds (e.g. PAHs and VOCs), It is made up of a very large number of individual organic compounds, each of which is present at a very low concentration (UK-AIR Department for environment, food and rural affairs, 2005).

1.1.4. Residence Time

The residence time of the particulate and gas phase of a particular compound in the atmosphere depends on its source and atmosphere cleans up mechanism. In the case of aerosols it depends also on its size. If the globally averaged concentration of a trace constituent in the atmosphere does not change significantly over a given time period, the rate at which the constituent is injected into (and/or produced within) the atmosphere must equal the rate at which it is removed from the atmosphere. Under such steady-state conditions, we can define the *residence time* (t) of a trace constituent in the atmosphere as:

$$t = M/F$$

Where *M* is the amount of the constituent in the atmosphere (in kg) and *F* is the rate of its removal (in kg s^{-1}) from the atmosphere.

Particles with diameter <0.01 µm have residence times ≤1 day. The major removal mechanisms for particles in this size range are diffusion to cloud particles and coagulation. Particles ≥20 µm diameter also have residence times ≤1 day, but they are removed by sedimentation, impaction onto surfaces, and precipitation scavenging.

In contrast, particles with diameters (0.2–2 µm) have strong sources but weak remove process Consequently, these particles have relatively long residence times, reaching several hundreds of days in the upper troposphere, but precipitation scavenging and impaction reduce these residence times to a few tens of days in the middle and lower troposphere.

Moreover the residence time also depends on the physico-chemical properties of the components considered. Table 1.1 lists the residence times of some of the major gases in the atmosphere, of which the DMS and nitrogen are those that have a shorter and higher residence time collected respectively (Hobbs, 2000).

Table 1.1. Residence time of some atmospheric gases (adapted from: Hobbs, 2000).

Gas	Chemical Formula	Residence time
Nitrogen	N_2	1.6 x 10^7 years
Oxygen	O_2	3000–4000 years
Argon	Ar	1.6 x 10^7 years
Carbon dioxide	CO_2	3-4 years
Methane	CH_4	9 years
Hydrogen	H_2	~2 years
Nitrous oxide	N_2O	150 years
Carbon monoxide	CO	~60 days
Ozone	O_3	Days–weeks
Hydrogen peroxide	H_2O_2	1 day
Nitrogen species	NO_y	Variable
Ammonia	NH_3	2–10 days
Sulfur dioxide	SO_2	Days
Dimethylsulfide (DMS)	CH_3SCH_3	0.7 days
Hydrogen sulfide	H_2S	1–5 days
Carbon disulfide	CS_2	~120 h
Hydroxyl radical	OH	~1 s

1.1.5. PM Size Distribution

Airborne particles have irregular shapes, and their aerodynamic behavior is expressed in terms of the diameter of an idealized spherical particle known as aerodynamic diameter. Particles are sampled and described on the basis of their aerodynamic diameter (is the size of a unit-density sphere with the same aerodynamic characteristics), which is usually simply referred to as particle size. Particles having the same aerodynamic diameter may have different dimensions and shapes.

PM particles can be classified by their aerodynamic properties because these properties affect the transport and removal procces from the air and their deposition within the

respiratory system and they are associated with the chemical composition and sources of particles (WHO, 2003).

Particles in the atmosphere are frequently treated in terms of the modes summarized in Fig 1.4 which also shows the major sources and removal processes for each one.

All aerosols are made up of a variety of sizes. Their size distribution refers to change in concentration with particle size. The concentration of an aerosol can be expressed as a function of different particle parameters: number, surface area, mass, volume, although the property more commonly considered, for their effects on health and the environment is the concentration/the mass. The units normally used are g m^{-3}, mg m^{-3}, µg $m^{-3}$and ng m^{-3}.

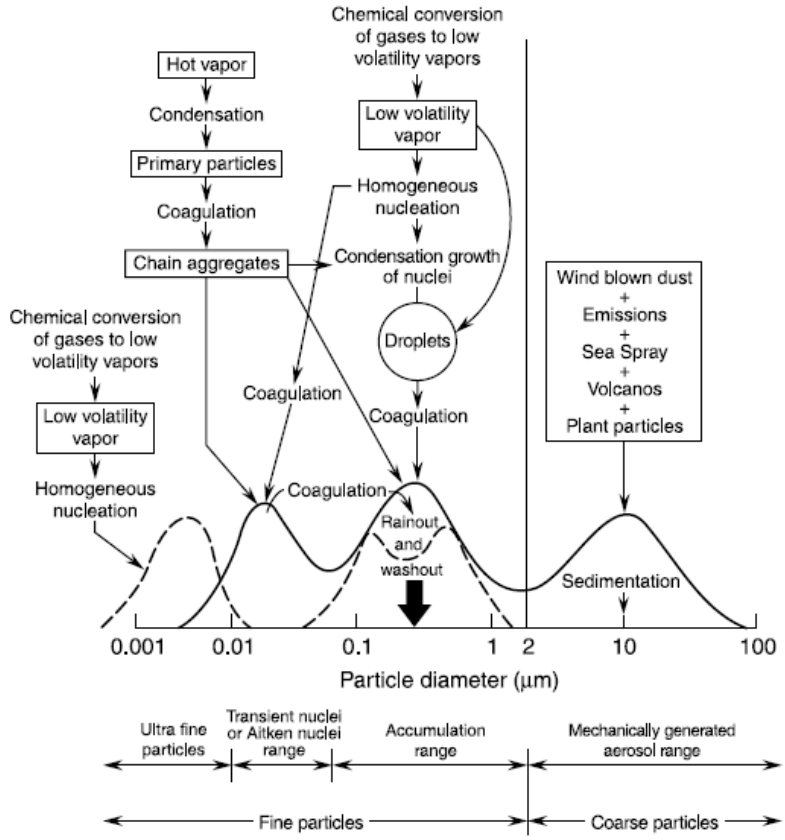

Fig.1.4. Schematic of an atmospheric aerosol size distribution (Finalyson Pitts, 2000).

– *Nucleation mode*

Particles with diameters ≤50 nm can be originated primarily by combustion particles emitted directly into the atmosphere from high temperature sources and also by homogeneous nucleation. These particles have a relatively short liftimes and end up in accumulation mode Fig.1.5.

– *Accumulation mode*

These particles extending between 50 nm and 1 µm in size, they can be formed by vapor condensation on already existing particles or by coagulation processes from the nucleation mode. They have a long atmospheric lifetime, typically 7–30 days, although their life time can be reduced due to some removal process (incorporation into rain).

– *Coarse particle mode*

Comprises particles greater than 1 µm, formed mechanically (anthropogenic source) more than nucleation and condensation processes.because of their large size, the coarse particles readily settle out or impact on surface, so their lifetime in the atmosphere is only a few hours. (UK-AIR Department for environment, food and rural affairs, 2005).

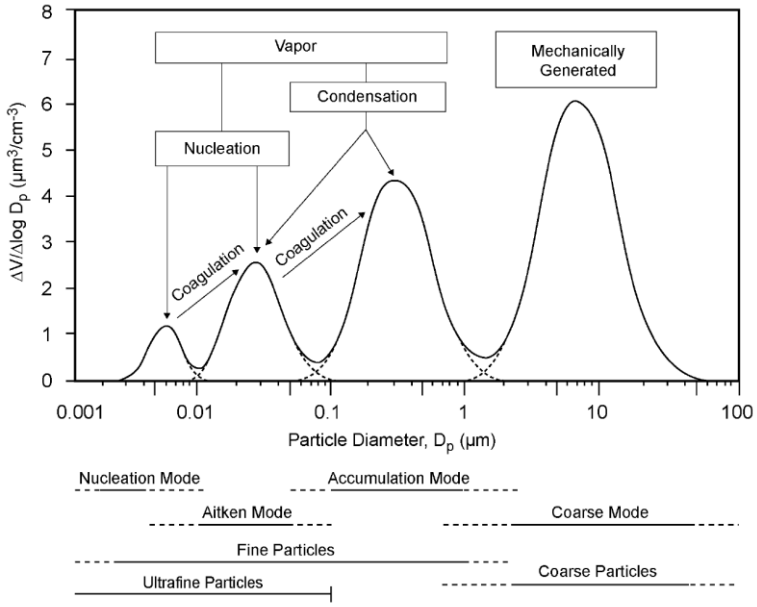

Fig.1.5. Mode distribution according to particle size (EPA, 2004).

1.2. Harmful effects of PM

Due to the world wide industrization, the largest fraction of the PM in the atmosphere comes from anthropogenic sources. Anthropogenic PM has many harmful effects of human health, climate, ecosystem and many other effects (Brimblecombe 2001; Pérez, 2007).

1.2.1. Effects on health

The World Health Organization (WHO) estimates that PM air pollution contributes to approximately 800 000 premature deaths each year, ranking in the 13th leading cause of mortality worldwide. (Anderson et al, 2012b).

Exposure to such particles can affect both the lungs and the heart. The term "inhalable coarse particles" refers to particle larger than 2.5 µm and smaller than 10 µm in diameter, they can be found near roadways and dusty industries (coal mining and production of iron, steel ceramic and rubber tyers), while the term"fine particles" comprises particles that have 2.5 µm in diameter and smaller (such as those found in smoke and haze (Philpott, 2015).

According to UNE (EN 12341, 1999) PM can be classified into an inhalable particle (<30 µm), extra thoracic fraction (>10 µm), thoracic fraction (<10 µm), tracheobronchial fraction (10-2.5 µm) and alveolar fraction (<2.5 µm) (Figure 1.6).

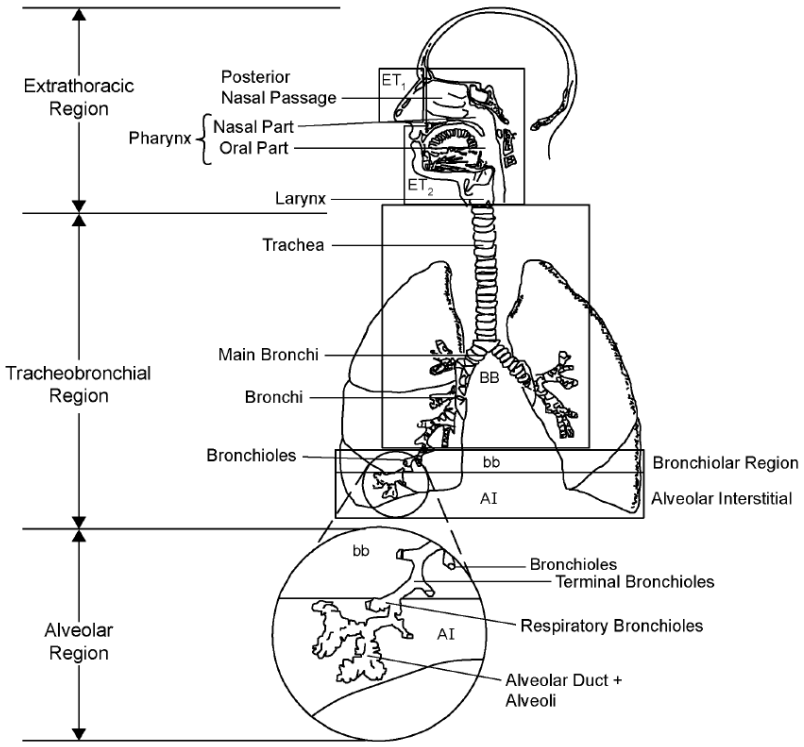

Fig.1.6. Scheme of the human respiratory apparatus (EPA, 2004).

Ambient PM is a recognized threat to public health on a global scale, not only in highly polluted environments. Epidemiological and human exposure studies show that both long- and short-term exposure to PM correlate with cardiovascular and respiratory morbidity and mortality (Brook et al, 2010; WHO, 2013a; Fuzzi et al, 2015).

Lung problems such as chronic bronchitis, reduced lung functions and even premature death have been associated with long term exposure to aerosol (EPA, 2003). Lower relative risks were reported for PM short-term exposure (Pope and Dockery, 2006). One of the largest efforts to investigate PM short-term effects was the National Morbidity, Mortality, and Air Pollution Study (NMMAPS).

The APHEA project (Air Pollution and Health: a European Approach) investigated daily mortality data from 32 European cities and observed that mortality was associated with PM exposure: the daily mortality counts associated with 10 μg m^{-3} of PM10 increased by 0.52 %, and it increased by 0.76% and 0.71% for cardiovascular and respiratory mortality,

respectively. The effects were more pronounced during the first and second day for total mortality and cardiovascular mortality, while respiratory mortality showed more prolonged lagged effects in pollution hot spots, such as Netherlands. PM alone was responsible for a loss in statistical life expectancy of up to 12–36 months Fig.1.7. (CAFE, 2005; Fuzzi et al, 2015).

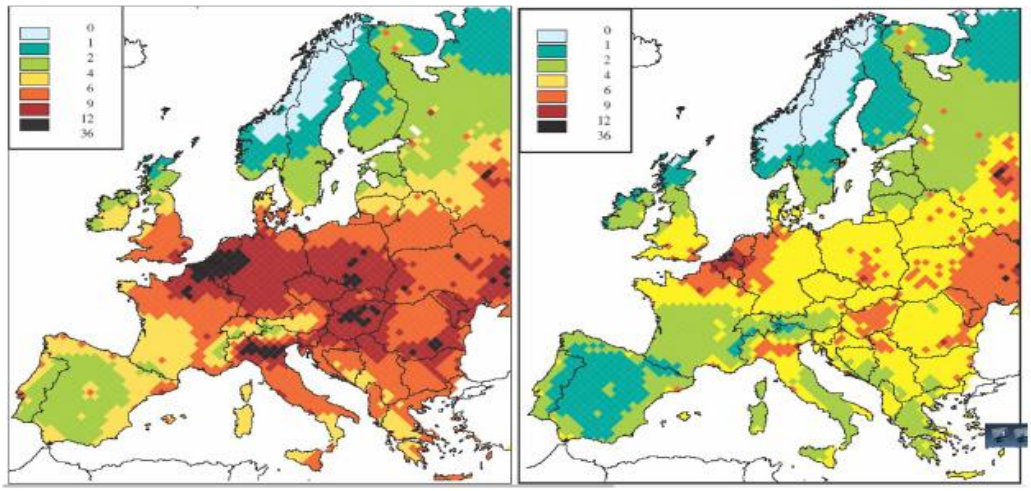

Fig.1.7. Loss in statistical life expectancy due to anthropogenic PM2.5 for the year 2000 on the left and the baseline current legislation in 2020 on the right (CAFE, 2005).

1.2.2. Effects on climate

Aerosols effect on radiative forcing of the climate system. The radiative forcing is defined as the change imposed by certain forcing agents such as the aerosol particles in the energy balance of the earth that eventually changes regional and global temperatures (IPCC, 2013, 2016).

Aerosol particles scatter and absorb solar radiation depending on their chemical composition or refractive index. A fraction of the solar radiation is scattered back to space leading to a cooling effect. Another fraction of the solar radiation is absorbed by the particles leading to warming effect. These effects are called direct aerosol forcing of climate. The direct effect depends strongly on the size distribution and the chemical composition of the aerosol. An example of these effects are carbonaceous particles (mainly

elemental carbon EC) and diesel vehicles, which contribute in a very important way to atmospheric warming (Perez, 2007; IPCC, 2013; Kumar et al, 2014).

Aerosol particles act as nuclei for cloud and fog formation. Cloud (and fog) droplets scatter and absorb also solar radiation depending on the size and amount of incorporated absorbing material, respectively. Aerosol particles induce modifications of the cloud albedo, the droplet concentration number, the lifetime of clouds and the frequency of the precipitation. These effects are called indirect aerosol forcing of climate (IPCC, 2013; Stocker et al, 2013; Mahowald et al, 2014).

Furthermore, uncertainties are great. intergovernmental panel on climate change (IPCC) estimates the average direct radiative forcing, through scattering of incoming radiation for sulphate, biomass and fossil fuel black carbon (BC) aerosols and the indirect forcing, through cloud condensation nuclei effects for all aerosols (Fig.1.8) (IPCC, 2007 and 2013).

The quantification of aerosol radiative forcing is more complex than the quantification of radiative forcing by greenhouse gases because aerosol mass and particle number concentrations are highly variable in space and time. This variability is largely due to the much shorter atmospheric lifetime of aerosols compared with the important greenhouse gases. Spatially and temporally resolved information on the atmospheric burden and radiative properties of aerosols is needed to estimate radiative forcing (IPCC, 2013).

1.2.3. Effects on ecosystems

Atmospheric particles can directly interact with ecosystems and have many physical effects on it. The wet deposition of atmospheric particles, when acid species are incorporated to rain drops produces the phenomena known as acid rain. PM can also deposite on the leaves and affect their capability to perform the photosynthesis. Also, the deposition of nitrate and ammonia can contribute to the eutrophication of lands, lakes and surface waters (Jickells, 2005; Petroff et al, 2008; Prajapati, 2012).

1.2.4. Other effects

PM has effects on visibility (it causes reduction of visibility through scaterring and absorption of visible lights by particles and gaseous pollutants such as NO_2) and also has effects on the buildings producing the degradation of construction materials exposed to the atmosphere in urban areas, like cement and metallic structures of buildings and monuments, because of their interaction with the surface (Costa et al, 2009; Elias et al, 2009).

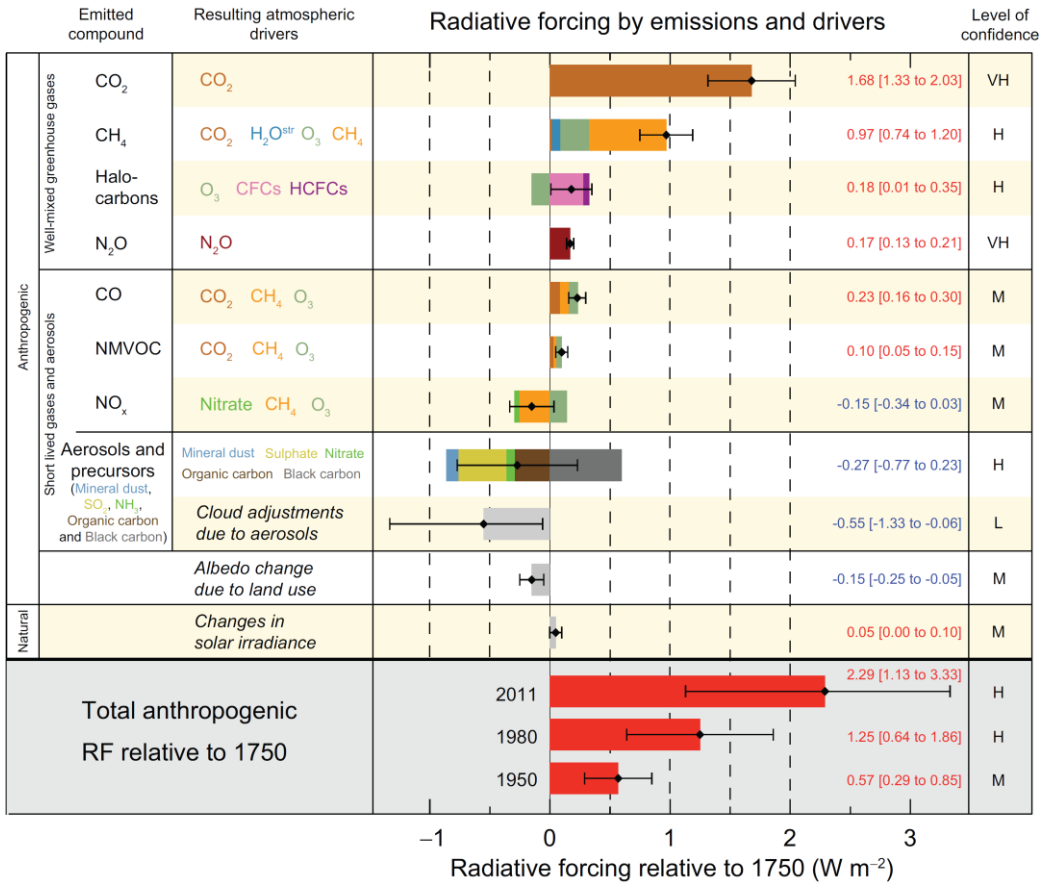

Fig.1.8. Radiative forcing estimates in 2011 relative to 1750 and aggregated uncertainties for the main drivers of climate change (IPCC, 2013).

1.3. PM legislation

Atmospheric PM is monitored in air quality networks due to the above explained adverse health effects, its visibility reduction properties and its effects on climate. According to the EU legislation (2008/50/EC), the European standards for PM_{10} levels were set to be 50 µg m^{-3} (24 hours average, not to be exceeded more than 35 times per year) and 40 µg m^{-3} as an annual average and 25 µg m^{-3} annual average for PM2.5.

The directive 2008/50/EC also contains a new definition, the average exposure indicator (AEI) which represents the average level determined of PM2.5 on the basis of measurements at urban background locations throughout the territory of a Member State and which reflects population exposure. It is used to calculate the national exposure reduction target and the exposure concentration obligation.

The reference AEI for the year 2010 is calculated as the mean concentration of the years 2008, 2009 and 2010. The AEI for the year 2020 shall be the three-year running mean concentration averaged over all those sampling points for the years 2018, 2019 and 2020. The AEI is used for the examination whether the national exposure reducion target is met Table 1.2.

Table 1.2. Exposure reduction target relative to the AEI in 2010 (adapted from directive 2008/50/EC).

Initial concentration ($\mu g\ m^{-3}$)	Reduction targe (%)	Year by which the exposure reduction target should be met
< 8.5 = 8.5	0 %	2020
> 8,5 — < 13	10 %	
= 13 — < 18	15 %	
= 18 — < 22	20 %	

The Spanish regulation Real Decreto 102/2011 published in (BOE, 2011), set objective values for some pollutants in PM10 in order to not exceed this value at 2013, as shown in table 1.3.

Table 1.3. Objective values in the BOE for some pollutants (adapted from Real Decreto 102/2011)

The pollutant	Objective values	Completion date
As	6 ng m^{-3}	1 January 2013
Cd	5 ng/m^3	1 January 2013
Ni	20 ng/m^3	1 January 2013
Benzopyrene $C_{20}H_{12}$	1 ng/m^3	1 January 2013

1.4. PM of anthropogenic origin in Andalusia

Andalusia (8 M inhabitants) is the southernmost region of Spain. It is located in the boundary between two continents (Europe and Africa) where the Mediterranean meets the Atlantic across the Strait of Gibraltar. The Iberian Massif and the Betic Range are separated by a large depression (the Guadalquivir basin) that crosses Andalusia from NE to SW. These regions have very different climatic (decir) and topographic patterns Fig .1.9.

Fig.1.9. Andalusia map (http://blogde5cpraltoguadalquivir.blogspot.com.es/p/conocimiento-del-medio.html).

Due to its large area, the Andalusian region is characterized by great geographic diversity. Its geography - especially of the western provinces - is dominated by the fertile valley of the Guadalquivir River and his numerous tributaries. The depression of the valley separates the Sierra Morena mountain range in the north from the Bética ranges in the southeast. Half of the Andalusian surface is mountainous, one third on a level of more than 600 meter altitude and even 46 peaks are higher than 1000 meters. The highest mountains of the Spanish peninsula are situated in the Sierra Nevada Mountains: the Mulhacén (3.481 meters) and the Veleta (3.398 meters).

Many authors have studied the PM in Andalusia in several researches, the studies have shown that PM10 levels in Spain contain a high proportion of resuspended anthropogenic and natural mineral particles (Querol et al, 2002, 2007, 2009; Gonzalez-Castanedo et al, 2015).

Similar to other Spanish monitoring stations, between 70 and 80 % of them are located in traffic and industrial hot spots, presenting average annual PM10 levels and number of exceedances of the daily limit value higher than other regions of Europe with more rural and urban background monitoring sites (de la Rosa et al, 2010).

In this work we have selected five monitoring stations at uban sites of Andalusia with traffic influence (Granada Norte in Granada, Lepanto and Alnasir in Cordoba) and industrial influence (Parque Joyero in Cordoba and Campus in Huelva).

1.4.1. Huelva

The city of Huelva is located in southwest Andalusia. This city is of about 160 000 habitants. It extends over a flat area where the Odiel and Tinto rivers converge. It has two main industrial states: Punta del Sebo industrial state, situated about 1 km to the south of the city, and Nuevo Puerto, situated 4.5 km southeast the city, Fig.1.10.

- Punta del Sebo industrial estate

It contains the following industries:

- *Fertiberia, Rhodia-Foret:* industries of acid phosphoric and derivatives. Production of mono-phosphate ammonium and diammonium, acid phosphoric and fertilizer complex.
- *Atlantic Copper*: This is the second cast of Cu most important of Europe, with an annual production of 320 000 tons. It is also a main producer of sulfuric acid.
- *Endesa:* It has recently been modernized with the addition of a natural gas combined cycle 400MW power that replaced the old central biofuel/fuel gas.

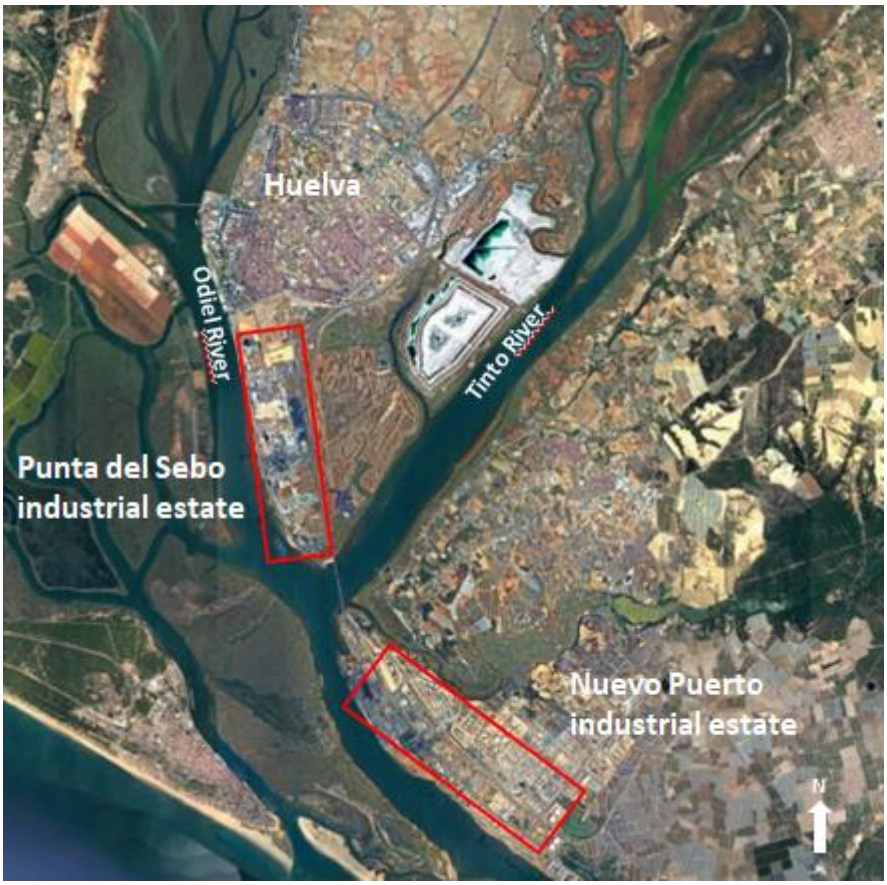

Fig.1.10. Main industrial estates in Huelva (Punta del Sebo and Nuevo Puerto).

- Nuevo Puerto industrial estate

In which the following industries are found:

- *CEPSA*: Production of fuels and raw materials for the petrochemical industry, asphalts, sulfur, etc.
- *CEPSA Química*: Petroleum processing industry (fuel oil, naphtha, diesel, phenol, acetone, methylated).
- *Huntsman Tioxide*: Manufacture of pigments, starting basically from the ilmenite attacked with sulfuric acid.
- *Algry Quimica*: Manufacturing choline derivatives.
- *Union FENOSA:* Power generation in combined cycle power plant consisting of three generating groups each one has 400WM power.

- *Air Liquide*: Gas production of industrial and medical applications (oxygen, nitrogen and argon).
- *Grupo Aragonesas*: Gas production of industrial and medical applications (oxygen, nitrogen and argon).
- *AURECAN*: Oil recycling.
- *Fertiberia Palos*: Production of ammonia and urea.

In addition to the industrial influence, the monitoring station of Huelva is also influenced by traffic. In 2014 this city has a vehicle fleet composed of 69 165 cars, 5 409 mopeds, 7 466 motorcyclists, 3 746 vans and 5 720 trucks, in total it has 92 840 motor vehicles, as sumarised in Table 1.4 (DGT, 2014).

Table 1.4. Vehicles types and their percentages in Huelva (adapted from DGT, 2014).

Vehicle type	Units	Total motor vehicles	Percentage %
Mopeds	5 409		6
Motorcycles	7 466		8
Cars	69 156	92 840	74
Vans	3 746		4
Trucks	5 720		6

Several researchers have studied the industrial emission effects in Huelva. High level of P, As, Cu, Zn, Pb, Se and Bi were found in this city, these levels being higher than at other Spanish urban sites. The mean As concentrations in PM10 samples in 1999 slightly exceed the mean annual target value proposed for PM10 by the European Commission for 2013 (6 ng/m^3) (Sanchez de la Campa et al, 2008 and 2007). According to the speciation studies that have been made in Huelva, As(V) is the main arsenic species found in Huelva followed by As(III) (Sanchez-Rodas et al, 2007).

Similar results have been confirmed in another work that studied the chemical characterization of PM in Andalusia. High As, Cu, Zn, Se and Bi concentrations are derived from Cu and brass smelters, located in Huelva and Cordoba, respectively. The As concentration in Huelva reached 6.5 ng m^{-3}, while the rest of the sampling stations of Andalusia have values less than 1.6 ng m^{-3} Fig.1.11 (de la Rosa et al, 2010).

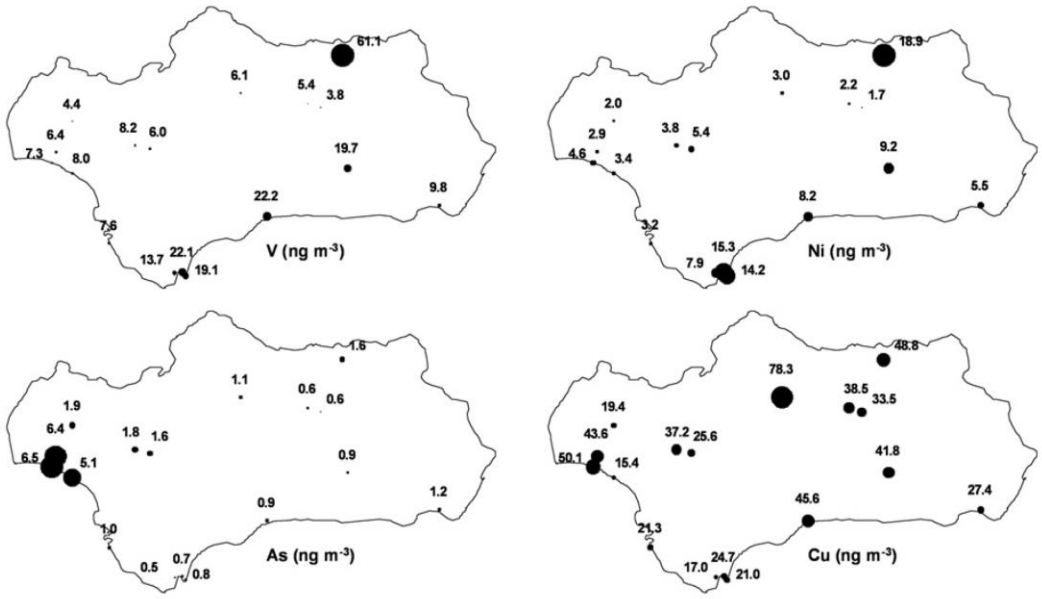

Fig.1.11. Some trace elements concentrations in Andalusia (adapted from de la Rosa et al, 2010).

For this work, one station has been selected in Huelva (El Carmen Campus) in order to study the As level in the city during 5 years (2010-2014) due to its proximity to a near copper smelter. PM10 and PM2.5 sampling were carried out by high volume samplers ($30m^3/h$) (model MCV PM1025-CAV) using quartz filters to collect PM samples. El Carmen Campus is an urban background station, located in the west of the city, at the Huelva University. It is part of the network of Vigilance and Control of Air Quality of the department of environment of the Andalusian autonomous goverment (Fig.1.12.a and b).

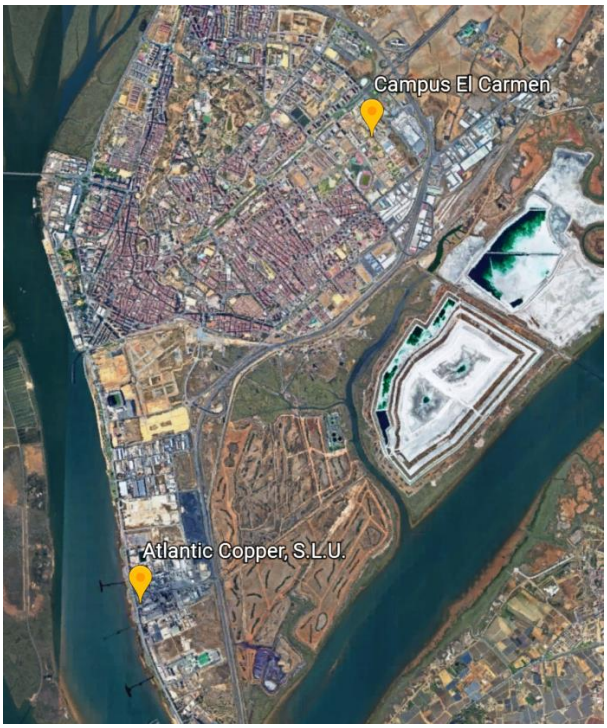

Fig.1.12.a. Location of El Carmen Campus monitoring station and the copper smelter near Huelva.

Fig.1.12.b. Monitoring station at the University of Huelva (El Carmen Campus).

1.4.2. Cordoba

Situated in southern Spain, it is a moderately sized modern city; its population in 2011 was about 330 000. Cordoba has the warmest summer high temperatures in Spain and Europe with average temperatures around 37 °C in July and similar heat in August. Winters are mild with isolated frosts. The city is on the banks of the Guadalquivir River, and it has easy access to the mining resources of the Sierra Morena.

The air quality of this city is affected by traffic and metallurgy emissions (brass industries). The most important factories in Cordoba are: Peninsular Del Latón, Latones Del Carrion factories (Manufacture and distribution of brass) and Grupo Cunext (copper industry). The brass factories in this city are the major source of Sb in the PM Fig.1.13.

Fig.1.13. Brass and copper factories in Parque Joyero Industrial Estate of Cordoba.

Road traffic has been considered one of the main sources of air pollution in Cordoba. The number of vehicles registered in 2014 is 211 803 motor vehicles (16 888 mopeds, 23 746 motorcycles, 144 674 cars, 12 797 vans and 10 894 trucks) Table 1.5 (DGT, 2014).

Table 1.5. Vehicles types and their percentages in Cordoba (adapted from DGT, 2014).

Vehicle type	Units	Total motor vehicle	Percentage %
Mopeds	16 888		8
Motorcycles	23 746		11
Cars	144 674	211 803	68
Vans	12 797		6
Trucks	10 894		5

In Cordoba three monitoring stations have been selected in this work (Lepanto, Alnasir and Parque joyero). Lepanto and Alnasir are urban areas with traffic influence while in Parque joyero the industrial influence is higher than the other stations due to the Brass and Copper factories. At the three sampling stations, each sample corresponded to a 24 h period. The sampling frecuency was in all the cases 1-2 times a week. The sampling period was 2011-2013 in Alnasir and Lepanto monitoring stations, and 2011-2012 for Parque Joyero. The location of the three monitoring stations is represented in Fig.1.14.a,b and c.

Fig.1.14.a. Location of the hree selected monitoring stations in Cordoba.

Fig.1.14.b. Alnasir monitoring station, an urban area with traffic influence.

Fig.1.14.c. Lepanto monitoring station an urban area with traffic influence.

PM10 sampling was carried out by high volume samplers (68 m^3 h^{-1}) (model Grasseby–Andersen) using quartz filters to collect PM samples. Another intensive sampling campaign was also performed at the brass industry of Cordoba between 11th- 31st October 2012, with

the aim of investigating the relationship between the metallurgic airborne emissions and the geochemical anomalies observed in PM at the industrial estate of this city. The campaign involved sampling the fugitive emissions inside the brass industriy. They correspond to not canalized gases that arise and escape via openings of the industrial installations. It was performed with a high volume sampler equipped with a Total Suspended Particle (TSP) inlet that was located close to the smelting furnaces, in order to characterize the overall PM emission and to avoid the filters clogging.

1.4.3. Granada

Granada is located at the foot of the Sierra Nevada mountains, at the confluence of four rivers, the Beiro, the Darro, the Genil and the Monachil. It sits at an average elevation of 738 metres above sea level, yet is only one hour by car from the Mediterranean coast, the Costa Tropical. The population of the city of Granada proper is about 472 000, ranking as the 13th largest urban area of Spain. This city has also an import urban traffic (170 000 vehicles in 2014), but no important metallurgic estates in its surroundings table 1.6 (DGT, 2014).

Table1.6. Vehicles types and their percentages in Granada.

Vehicle type	**Units**	**Total motor vehicle**	**Percentage %**
Mopeds	17 081	17 0792	10
Motorcycles	25 535		15
Cars	109 184		64
Vans	9 590		6
Trucks	7 299		4

In Granada, one sampling station has been selected, which is the Granada Norte station. It is situated in an urban area with traffic influence. The study period of the sampling period in this station was between 2011 and 2013.

PM10 sampling was carried out by high volume samplers (68 m^3 h^{-1}) model TISH. All PM10 samples corresponded to 24-h periods, taken on a weekly basis. Quartz fibre filters

(Munktell) were used to collect PM samples. The location of the monitoring station is shown in Fig.1.15.a.b.

Fig.1.15.a. Location of Granada Norte monitoring station in Granada.

Fig.1.15.b. Granada station, an urban area with traffic influence.

2. Objectives

2. Objectives of the thesis

The main objective of this study is to perform antimony and arsenic speciation studies in atmospheric particulate matter of Andalusia, in order to identify the emission sources of these elements. To achieve this goal, the following specific objectives have been considered:

1. Develop an extraction method for Sb speciation in atmospheric PM samples, based on liquid extraction of the samples aided by microwave radiation, and followed by analysis combining high performance liquid chromatography, hydride generation and atomic fluorescence spectroscopy (HPLC-HG-AFS).

2. Conduct Sb speciation studies in PM10 samples in the cities of Cordoba and Granada in the period (2011-2013), in order to distinguish between traffic and industrial sources.

3. To perform a revision of the state of the art of As in atmospheric PM, considering analytical steps such as sampling, sample treatment, and analysis of both total and speciation at different particle size.

4. Conduct As speciation studies in PM10 and PM2.5 samples in the city of Huelva, in the period 2010-2014, in order to evaluate the industrial emission and its contribution to the air quality of the historical series 2001-2015.

2. Objetivos de la tesis

El objetivo principal de este estudio es realizar estudios de especiación de antimonio y arsénico en material particulado atmosférico de Andalucía, con el fin de identificar las fuentes de emisión de estos elementos. Para alcanzar este objetivo, se han considerado los siguientes objetivos específicos:

1. Desarrollar un método de extracción para la especiación de Sb en muestras de PM, basado en la extracción líquida de las muestras ayudadas por radiación de microondas, y seguido por análisis de cromatografía líquida de alta resolución acoplada a generación de hidruros y espectroscopia de fluorescencia atómica (HPLC-HG- AFS).

2. Realizar estudios de especificación de Sb en muestras de PM10 en las ciudades de Córdoba y Granada en el periodo 2011-2013, con el fin de distinguir entre tráfico y fuentes industriales.

3. Realizar una revisión bibliográfica sobre el estado de la técnica de As en material particulado atmosférico, considerando pasos analíticos como el muestreo, el tratamiento de la muestra y el análisis tanto del total como de especiación de As en diferentes tamaños de partícula.

4. Realización de estudios de especiación de As en muestras de PM10 y PM2.5 en la ciudad de Huelva, en el período 2010-2014, para evaluar la emisión industrial y su contribución a la calidad del aire en la serie histórica 2001-2015.

3. Antimony

3. Antimony

3.1. Antimony and its properties

3.1.1. Antimony throughout history

Sb is an element with no known biological role. It has been used in medicine, veterinary and cosmetics. It is impressive that this metalloid was prescribed in the past as the universal remedy for syphilis, chest pains and especially for fever (Amarasiriwardena et al, 2014).

Humans have used Sb since the Early Bronze Age. Excavations at Tello in Ancient Chaldea found fragments of an antimony base that dates back to 4000 B.C. In ancient times stibnite (Sb_2S_3), which is the most common form of antimony sulfide, was the main ingredient of *kohl*, a black paste used by the Egyptians as an eye makeup (Pacheco-Torgal, 2012).

Sb, together with lead, was used in the Roman Period producing a long history of contamination of waters, sediments and soils. The Babylonians knew how to obtain compounds of antimony and used it as an ornament for vessels. In the middle Ages antimony it was used for the manufacture of laxative pills, and during the early sixth century antimony and potassium tartrate was known as an expectorant (Emsley, 1998).

The alchemist Basil Valentine (1565-1624), sometimes presented as the discoverer of antimony, was the first to describe the extraction of antimony compounds from its sulfide ore in his treatise “The Triumphal Chariot of Antimony,” published around 1600. The origin of the word "antimony" is uncertain; all suggestions have some difficulty either of form or interpretation. The popular etymology, from ἀντίμοναχός *anti-monachos* or french *antimoine*, still has adherents; this would mean "monk-killer", and is explained by many early alchemists being monks, and antimony being poisonous. The arabic word for the substance, as opposed to the cosmetic, can appear as إثمد *ithmid,* which became from the latin word *Stibium*. Another popular etymology is the hypothetical Greek word ἀντίμόνος *antimonos*, "against aloneness", explained as "not found as metal", or "not found unalloyed" (Butterman et al, 2004).

Sb was used during the First World War as it was found to be the best alloying material for lead to produce munitions capable of armor plate penetration. Also it was used for other ammunition types such as detonators, tracer bullets and armory (Anderson, 2012).

3.1.2. Physical and chemical properties of Sb

Antimony is in the nitrogen group (group 15) and has an electronegativity of 2.05 (Fig. 3.1). As expected from periodic trends, it is more electronegative than tin or bismuth, and less electronegative than tellurium or arsenic. Antimony is stable in air at room temperature, but reacts with oxygen if heated, to form antimony trioxide, Sb_2O_3.

It has four allotropes, three metastable forms (explosive, black and yellow) and a stable metallic which is a brittle, silver-white shiny metal. While the black and yellow are the unstable forms this metastable allotrope transforms into the more stable allotrope. The two main Sb isotopes are: ^{121}Sb with a natural abundance of 57.36% and ^{123}Sb with a natural abundance of 42.64% (Gouda, 2012).

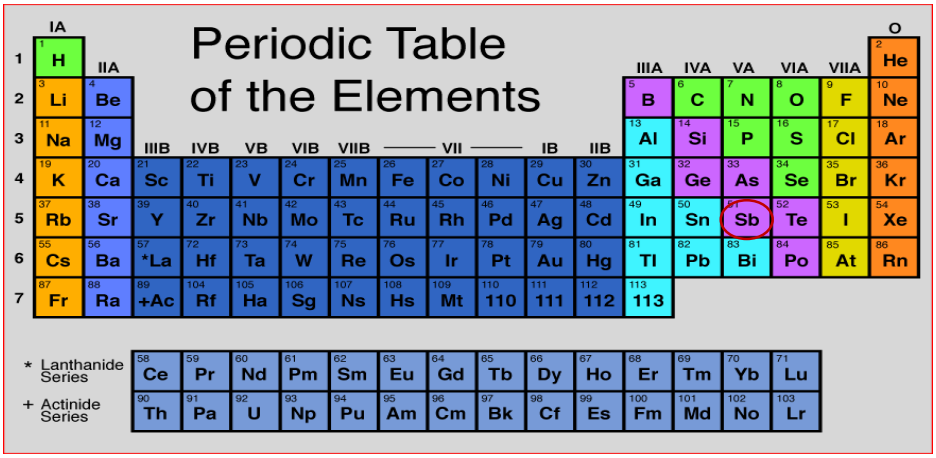

Fig. 3.1. Periodic table of elements (https://periodictable-mrstaylor.wikispaces.com/P8 +Nitrogen).

Sb can display different oxidation states (-II, 0, III, V) but in reality only lose three or five electrons, being Sb(III), Sb(V) the oxidation states which are mainly present in environmental materials. Hydrolysis of Sb results in $[Sb(OH)_3]^0$ and $[Sb(OH)_6]^{-1}$ respectively,

both species are predominant in the range of pH of most natural waters (Haynes, 2014; Coursey et al, 2015).

The melting point of antimony is 630 °C and its boiling point is 1 635 °C. It is a relatively soft material that can be scratched by glass. Its density is 6.68 g cm^{-3}. It's a moderately active element that does not combine with oxygen in the air at room temperature. It also does not react with cold water or with most cold acids. It does dissolve in some hot acids (H_2SO_4 and HNO_3) and in aqua regia.

3.2. Antimony compounds

3.2.1. Abundance and distribution

Sb is one of the natural components of the Earth's crust. Its abundance is about 0.3 mg g^{-1}, with no significant difference between the upper and the lower continental crust (Smichowski et al, 2008a).

World reserves of antimony are estimated to be about 1.8 million metric tonnes. China accounts for about 90% of the world's mined production and the vast majority of the reserve base. Also China with four other countries (Bolivia, Republic of South Africa, Tajikistan and Russia) currently account for the major total world antimony production, as summarized in Fig. 3.2 (Carlin, 2011; Anderson, 2012).

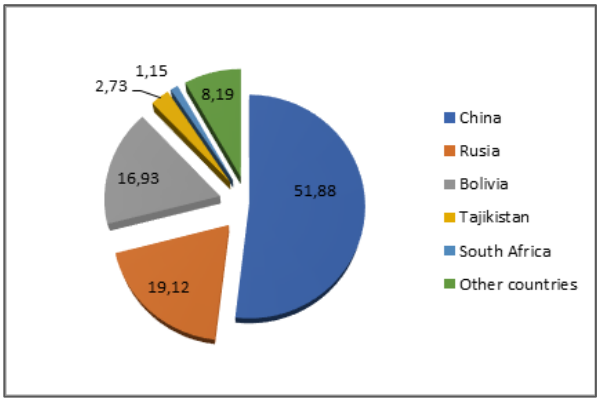

Fig. 3.2. Percentage of the distribution of the world reserves of Sb in 2012 (https://mcgroup.co.uk/news/20140328/china-held-52-global-antimony-reserves.html).

In water the Sb is found dissolved in rivers and lakes is usually less than 5 parts of antimony in 1 billion parts of water (ppb) and it is found attached to particles of dirt, the pentavalent state is the predominant in aerobic water while the trivalent is the predominant in the anaerobic conditions due to the anthropogenic activities In soil Sb soil concentrations range from less than 1 to 8.8 ppm, with a mean of 0.48 ppm (Sundar et al, 2010).

Considering the presence in air, the concentration of Sb ranges from a nano gram per cubic meter (ng m^{-3}) to about 170 ng m^{-3}. One of the most important sources of Sb in PM is the brake abrasion dust generated by the friction brake of automobiles, therefore, essential to determine the Sb emission factor that originates from automotive braking in order to quantitatively evaluate the contribution of automobiles to the atmospheric Sb concentration (Lijima et al, 2008).

3.2.2. Main Sb chemical compounds

-Oxides and hydroxides

This group contains compounds such as (Sb_2O_3) and (Sb_2O_5). Unlike oxides of phosphorus and arsenic, these various oxides are amphoteric, do not form well-defined oxoacids and react with acids to form antimony salts (Greenwood et al, 1997; Von Uexküll et al, 2005).

Antimonic acid exists only as the hydrate $HSb(OH)_6$, forming salts containing the antimonate anion $Sb(OH)_6^-$. Dehydrating metal salts containing this anion yields mixed oxides (Godfrey et al, 1998).

-Sulfides and halides

Many antimony ores are sulfides, mainly as stibnite (Sb_2S_3), whereas antimony pentasulfide is non stoichiometric and features antimony in the +3 oxidation state and S-S bonds. Moreover Sb reacts with halogens. The two types of halides are SbX_3, where X is F, Cl, Br, or I, and SbX_5, where X is F or Cl. SbF_5 and $SbCl_5$ are liquids formed by the reaction of SbF_3 and $SbCl_3$ with, respectively, fluorine and chlorine. While SbF_5 has no industrial application, $SbCl_5$ is used in organic synthesis (House, 2008).

-Antimonides, hydrides and organoantimony compounds

Sb forms antimonides with metals, such as indium antimonide (InSb) and silver antimonide (Ag_3Sb). The alkali metal and zinc antimonides, such as Na_3Sb and Zn_3Sb_2, are more reactive. Treating these antimonides with acid produces the unstable gas stibine (SbH_3). Stibine can also be produced by treating Sb^{3+} salts with hydride reagents such as sodium borohydride (Kahlenberg, 2008).

The main organoantimony compounds correspond to methylated species. Various authors refer to the presence of monomethyl (CH_3SbH_2) and dimethyl ($(CH_3)_2SbH$) in water, rivers and in aquatic animals where the monomethyl compounds forms are more abundant than dimethyl. Trimethylantimony ($(CH_3)_3Sb$) is also produced as a result of biological activitiy of algae and plants (Sayago et al, 2002).

3.3. Uses and applications of Sb

Sb and its compounds have been widely used in industrial production and daily life since the rapid development of industry in the 19th century. Sb compounds have several applications as flame retardant, batteries, brake pads and many other uses as described below (Fig. 3.3) (McCallum, 2005).

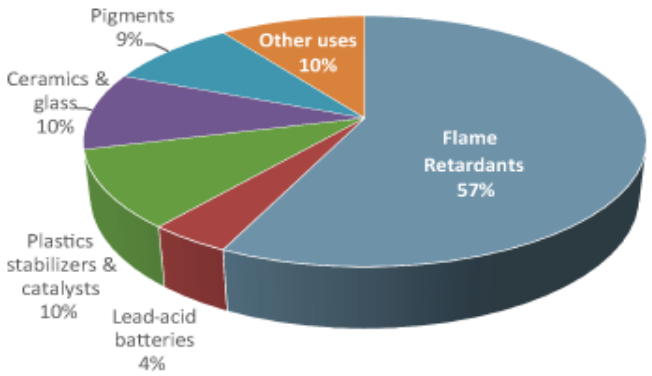

Fig. 3.3. Estimated U.S. consumption of primary antimony in 1999 (adapted from Butterman et al, 2004).

3.3.1. Flame retardant

Sb_2O_3 is the most important antimony compound produced. It can be used with halogen compounds flame retardants in many industries such as plastics, textiles, paints and rubber. As a synergist, the main advantage realised by the addition of Sb_2O_3 is to reduce the amount of halogenated flame retardants applied to the polymer (Anderson et al, 2012).

The mechanism of its function can de divided in three steps:

- 1-Stop action of thermal de-composite chain reaction under gas phase.
- 2-Sealing action against oxygen under gas phase (Air sealing effect).
- 3-Formation of carbonaceous char under the solid phase.

3.3.2. Brake pads

Sb is used in the form of Sb_2S_3 that serves as a lubricant to reduce vibrations and to improve friction stability. Percentages up to 7% of Sb as Sb_2S_3 are used in brake pads (or linings) as lubricant to reduce vibrations and to improve friction stability.

A characteristic “organic brake pad” is a multicomponent polymer matrix composite typically formulated of more than 10 constituents. The matrix is often a phenolic resin and different raw materials, typically metals, metal compounds, various minerals, ceramics, polymers and carbonaceous components that have been used in different brands. The content of metals, especially Fe, may influence the toxicity effect by inducing oxidative stress (Malachova et al, 2016).

It is believed that when Sb is released from brake pads into the atmosphere as an aerosol, it is oxidized to Sb_2O_3 by reaction with airborne oxidants. This process constitutes the main source of Sb in the coarse fraction of PM (Uexkull et al, 2005; Fujiwara et al, 2011).

3.3.3. Batteries

Sb is used as a hardener in electrodes for lead acid batteries during more than a century. However, this use is in decline as the antimony content of the typical automotive battery alloys has decreased from 7% to 1.6% in the last decade. Therefore, the use of antimony in the batteries will be reduced and will be replaced by calcium alloys, aluminum and tin over time (Carlin, 2011).

3.3.4. Other uses

Moreover, antimony as sodium antimonate ($NaSbO_3$) is also used in the production of glass as a bleaching agent for optical glass mainly used for cameras, photocopiers, binoculars, glasses, glass tubes and fluorescent light. Sb_2O_3 and GeO_2 are used as catalysts in the polymerization of polyethylene terephthalate (PET), which used in the manufacture of bottles and many other products. Also, many common plastics are susceptible to degradation by color and ultraviolet light (UV) and therefore must be protected with the addition of stabilizers. Antimony has been used for this purpose during a long time especially in the rigid forms of plastic (Thiele, 2004).

The principal medical application of the Sb is in the treatment of leishmaniasis based on trivalent antimony potassium tartrate $K_2Sb_2(C_4H_2O_6)_2$. Because of its high toxicity and unstable in tropical climate, it was replaced by pentavalent antimony. Nowadays the most commonly used organic compounds of antimony (Sb) are sodium antimony gluconate ($C_{12}H_{38}Na_3O_{26}Sb_2$) and meglumine antimoniate ($C_7H_{18}NO_8Sb$) (Haldar et al, 2011).

3.4. Antimony toxicity and human exposure

Sb presence in air, soils, sediments, surface/ground-water and biological systems have received considerable attention worldwide nowdays due to its adverse consequences on human health (Herath et al, 2017).

3.4.1. Sb toxicity

Sb toxicity occurs either due to occupational exposure or during therapy. Occupational exposure may cause respiratory irritation, pneumoconiosis, antimony spots on the skin and gastrointestinal symptoms, as listed below.

- *Acute effects*

Skin and eye effects are the main effects cuased by inhalation of Sb during short time of exposure. Eye effects include ocular conjunctivitis, while the skin effects consist of a rash made of of pustules around sweat and sebaceous glands which is called Sb spots. Oral exposure to antimony in humans has resulted in gastrointestinal effects (EPA, 2000; Sundar et al, 2010).

- *Chronic effects*

In antimony industry workers, pneumoconiosis (lung desease caused by dust inhalation) and clinical signs such as coughing and laryngitis have been reported. Chronic exposure to antimony trioxide and/or pentoxide dust (8.87 mg Sb /m^3 or greater) was observed to cause theses symptoms, although thses workers also exposed to a variety of other compounds like arsenic oxide, iron oxide, hydrogen sulfide, and sodium hydroxide.

Other respiratory effects reported in workers include chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions, and respiratory irritation (characterized by chronic coughing, wheezing and upper airway inflammation).

Other effects on humans due to the chronic exposure to Sb are increased blood pressure, heart muscle damage and gastrointestinal disorders (Sundar et al, 2010; U.S. Department of Health and Human Services, 2017).

- *Genotoxicity*

-Due to lack of in vivo studies, genotoxicity in humans cannot be determined at this time. Two studies of pentavalent organic antimony found positive results for micronuclei formation (Hantson et al, 1996; Lima et al, 2010) or DNA damage (Lima et al, 2010; U.S. Department of Health and Human Services, 2017).

- *Carcinogenicity*

The toxicology of antimony and its compounds is known from three sources: its medicinal use over centuries, studies of process workers in more recent times, and, currently, studies of its presence in modern city environments and in domestic environments.

Sb_2O_3 is classified as possibly carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer (Cooper et al, 2009; Sundar et al, 2010; Herath et al, 2017).

-*Other Effects*

Sb affects the reproductive system, causing many disturbances in the menstrual cycle, as reported in women exposed to various Sb compounds in a metallurgical plant. However, the study that reported these findings was not clear about concurrent exposure to other chemicals, nor did it provide the characteristics of the controls used.

Gastrointestinal effects after repeated prolonged exposure to airborne $SbCl_3$, Sb_2S_3 or Sb_2O_3 were seen to cause abdominal pain, diarrhea, vomiting and ulcers (Sundar et al, 2010).

3.4.2. Human exposure to antimony

The use of antimony alloys in various components of automobiles and transportation vehicles has led to a significant increase of Sb emissions in the environment. Also the workers in the industries producing antimony, antimony trioxide, metal mining, smelting and refining, coal-fired power plants and refuse incineration have an occupational exposure to Sb and other metals such as arsenic and lead.

Humans can be exposed to Sb via three main routs: inhalation, oral and food. Nowdays the use of antimony in industries has increased the importance of the inhalations rout (Sundar et al, 2010; Belzile et al, 2011).

-Inhalational Exposure

Health effects have been observed following inhalational exposure to several antimony compounds e.g., Sb_2O_3, SbH_3, Sb_2S_3, Sb_2O_5, $SbCl_3$, S_5Sb_2, etc. Aerosols containing small particles composed of antimony compounds with low water solubility (e.g., particles of antimony oxides) are retained in the lungs for a longer period of time than those containing larger particles with high water solubility (e.g., particles of antimony tartrate). As other trace elements, Sb travels through the atmosphere as part of its global biogeochemical cycling process (Belzile et al, 2011).

-Oral exposure

Typical concentrations of dissolved Sb in unpolluted surface waters are usually well below 1 $\mu g \cdot l^{-1}$, mostly in the range of tens to hundreds of $ng \cdot l^{-1}$. In a 1996 report, the World Health Organization suggested the average intake of Sb from drinking water should be less than 8 $\mu g \cdot d^{-1}$. However the guidelines of Health Canada (2008) estimate the daily intake from drinking water to be 2.8 μg, calculated from a mean value of 1.87 $\mu g\ Sb \cdot l^{-1}$ and an average daily consumption of 1.5 l. Both values of daily intake can be considered as overestimated if accepting that many tested drinking waters show concentrations below 1.0 $\mu g \cdot l^{-1}$. Sb_2O_3 is the most important catalyst used in the manufacturing of polyethylene terephthalate (PET). Most commercial PET material typically contains 190–300 $mg \cdot Kg^{-1}$ Sb and bottled waters become more contaminated during storage due to Sb leaching. These values could reach to 2 $\mu g \cdot l^{-1}$ of Sb due to heating by illumination and extended storage of bottled mineral waters (Carneado et al, 2015; Belzile et al, 2011).

-Food

Different groups of food contain Sb like that crop plants and mushrooms, milk and dairy products, fish and seafood, juices and wines, products and processed food, spices and seasoning products, and dietary supplements. The Sb content in foodstuff is generally relatively low and the toxicity can come from PET containers used for ready-to-eat food, due to the use of the element in this plastic manufacturing process and its possible migration from the container to the food (Belzile et al, 2011).

3.5. Antimony in the air

Sb has aroused a wide concern among the public as a global pollutant. Studies of atmospheric emission inventories of antimony started in the early 1980s. Sb emmisions to the air come from both natural and anthropogenic sources. Anthropogenic inputs are about 100 to 200 fold higher than the natural sources. For this reason, Sb is considered part of the atmospheric pollutants and its determination in the total PM as well as in the corresponding inhalable fractions represents an important parameter in evaluating the possible implications onto the public health (Smichowski et al, 2008a).

Global Sb emissions in 2010-were estimated at about 1904 tonnes, with fuel combustion as the major source category. Asia and Europe account for about 57% and 24%, respectively, of the global total emissions, and China, the United States, and Japan rank as the top three emitting countries Fig. 3.4.

The residence time of Sb in the atmosphere is 1−2 weeks, anthropogenic activities have imposed a substantial influence on the worldwide geochemical cycle of this element. Ambient Sb concentrations in air have been described worldwide. For example in urban Canada, the US and in Europe were at ranges of 13-125 ng m^{-3}, 0.5-171 ng m^{-3} and 2-470 ng m^{-3}, respectively, dramatically higher than concentrations found in remote and rural areas (0.0008-7 ng m^{-3}) (Chen et al, 2008; Tian et al, 2014).

Atmospheric Sb emissions from various anthropogenic activities can be assessed from five large source categories: fuel combustion, nonferrous metals production, pig iron and steel production, waste incineration and brake wear (Tian et al, 2014).

In the nature, Sb is commonly enriched in coals and fossil fuels. Fuel combustion is considered to be the most important anthropogenic activity emission source. Sb concentrations in coals throughout the world are at a range of 0.05-10 µg g^{-1}, and the

worldwide average concentration is estimated about 1 µg g^{-1}. Due to the high temperatures produced in the fuel combustion or industrial production, Sb is generally released to the atmosphere attached to particulate matter, and it exhibits increasing enrichment with decreasing particle size. Most of the Sb compounds are released to the atmosphere combined with fine particulate matter instead of coarse particulate matter (Pacyna, 2001; Tian et al, 2013) Sb commonly attaches to particulate matter in the form of Sb(III) and Sb(V). The determination of Sb in atmospheric aerosols and related matrices can be problematic due to its often very low concentration. A great care should be devoted in sample preparation of blanks in order to minimize contamination (Shotyk et al, 2004; Marconi et al, 2011).

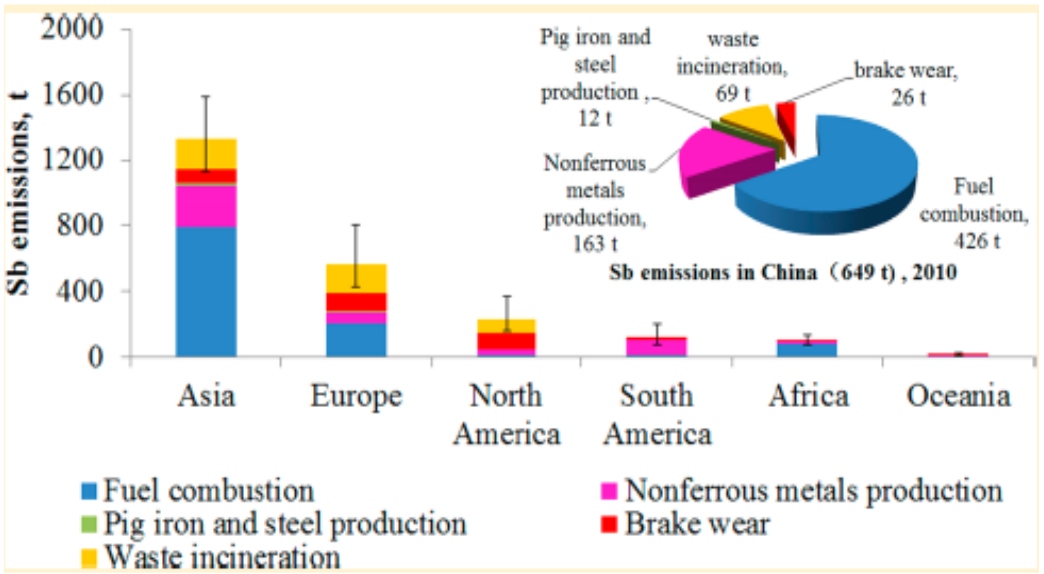

Fig. 3.4. Global Sb emission at 2010 (Tian et al, 2014).

3.6.Total Sb determination in PM

3.6.1. Sample treatment

Two general approaches have been applied to airborne particulate matter, dusts and ashes: leaching (partial dissolution) and total dissolution. In the first case, a selective dissolution of elements is performed. For PM deposited on filters, the filter is not dissolved and it is

the method of choice in studies of fractionation of metals and metalloids (Smichowski et al, 2004). In total dissolution procedures, the complete sample and the filter (total or a portion) are dissolved (Furuta et al, 2005). The complete digestion of PM sample presents advantages such as being more representative in comparison to a direct solid sampling technique that only uses a small portion of the filter (e.g., X-ray fluorescence). Furthermore, the digestion procedures that use microwave radiation (MW) avoid losses of more volatile elements such as Sb. There is also less possibility expected of interferences in diluted samples.

Numerous analytical techniques and experimental approaches have been proposed in the last two decades to identify and measure Sb aimed at obtaining reliable results and correct evaluations in the field of environmental chemistry.

Aerosol samples are normally collected on different kind of filters. Since PM contains a variety of components including oxides, carbonates, silicates and organic compounds, this makes it difficult to digest. That is the reason why strong acid oxidizing mixtures in combination with high pressure and temperature conditions have been used for sample digestion such as HNO_3, $HClO_4$ and H_2SO_4. Non oxidizing acids are also used. HCl is mixed with HNO_3 to form aqua regia which has more oxidizing power than the acids alone. HF is also used to break up the silica matrix and to dissolve mineral constituents.

The microwave radiation treatment has been used for the total Sb determination in combination with HNO_3, H_2O_2 and HF. The HF was evaporated by heating the sample solution on a hot plate, and pure water (Furuta et al, 2005).

One of the procedures that have been used to determine the total Sb that comes from the brake pads in PM is to digest the air filtres in open PTFE vessels with a mixture of HNO_3, H_2O_2 and HF. The filters were dissolved in HNO_3 and heated. Then, the other reagents were added carefully and the solution heated for another 2 h. In a last step, the solution was slowly evaporated nearly to dryness and the residue dissolved in HNO_3 (Dietl et al, 1997).

Another procedure employes MW-assisted digestion using a mixture of HNO_3, H_2O_2 and HF, the HF was evaporated by heating the sample solution at 200 ^oC on a hot plate, and 0.1 mol l^{-1} of nitric acid was added to obtain a 50 ml sample (Lijima et al, 2007; Lijima et al, 2008; Lijima et al, 2009).

A comparasion has been made between two digestion procedures, wet ashing digestion with open vessel and microwave extraction to put in solution 17 elements present in coal fly ash reference materials. In spite of the problems related to the use of open systems

above described, the authors reported that open vessel acid digestion (H_2SO_4, HNO_3, HF and $HClO_4$) was far superior to the efficient MW procedure (Lachas et al, 1999).

In this sense, the digestion of quartz fibre filters have been widely used in combination with a mixture of acids. HF and HNO_3 were added to a portion of the filter placed in PTFE vessel and heated overnight at 90 ^oC in an oven. Afterwards the sample was heated to dryness in a hotplate at 180 ^oC. $HClO_4$ was then added and heated again to dryness, and redissolved in 5% HNO_3 (Querol 2000; Sanchez de la Campa et al, 2011). Other authors have employed a mixture of HNO_3, HF, $HClO_4$ in MW during 60 min for the digestion of this type of filters (Varrica et al, 2013).

In the case of glass fibre filters, they were digested with aqua regia in a laboratory microwave oven. A portion of the filter was weighed accurately into the PTFE vessels of the MW digestion system, 12 ml of aqua regia was added the vessels were closed inserted into the microwave oven. After that the vessels were allowed to cool down for about 30 min and opened carefully. The content of each vessel was diluted to 15 ml with water before the analysis. Also an Sb extraction has been done of another portion of the filter by adding 12 ml. The mixture was left in the ultrasonic bath at room temperature for 1 h. After that the extract was diluted to 15 ml with water and the extract decanted from the filter residues before the analysis (Castilho et al, 2012).

Sb has been also determined in other materials related to PM such as fly ash and road dust. In the case of fly ash a mixture of HNO_3, HCl and HF has been added for acid MW assited digestion, and boric acid (H_3 BO_3). The total Sb content has been compared with a three step extraction scheme using water, , hydroxylamine chloride solution and a mixture of acids (HNO_3, HCl and HF). Sb was mainly found in the residual fraction. (Smichowski et al, 2008b).

Another study on fly ash material have compared between three methods of digestions for this type of samples; 1) Ultra sound digestion with aqua regia during 9 min 2) ultra sound digestion with HNO_3 during 9 min and then HNO_3 and HF were added during 18 min and 3) MW digestion with HNO_3 + HF during 15 min. The most suitable methods in this work was the second one (LLander et al, 2011). In the case of dust road the same acid mixture has been used for sample digestion , in this case using a hot plate for heating (Fujiwara et al, 2011).

3.6.2. Analytical techniques

Several analytical techniques have been proposed to identify and measure Sb aimed at obtaining reliable results and correct evaluations in the field of environmental chemistry.

Atomic spectrometric methods based on flame atomic absorption spectrometry (FAAS) (Castilho et al, 2012), atomic fluorescence spectrometry (AFS) (Alsioufi et al, 2016) and plasma-based techniques, namely inductively coupled plasma-optical emission spectrometry (ICP-OES) (LLander, 2011) and inductively coupled plasma-mass spectrometry (ICP-MS) have been extensively used to determine Sb in different kind of samples (Fujiwara et al, 2011).

Less common techniques used along or combined with preconcentration or hydride generation steps, for total Sb determination in different kind of matrices included microwave induced plasma-atomic emission spectrometry (MIP-AES) (Dietz et al, 1999), neutron activation analysis (NAA) (Dorea et al, 1990), x-ray fluorescence and spectrometry (XRF) (Haffer et al, 1997), laser induced fluorescence (Pacquette et al, 2001), anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and differential pulse polarography (DPP) (Wagner et al, 1996; Shpigun et al, 2003).

Another choice for the determination of the Sb is hydride generation (HG) combined with a diversity of atomic and plasma-based techniques, as they improve the sensitivity of the measurement and minimize the problems associated to matrix interferences. In spite of the known advantages, HG is affected by different kind of interferences in the liquid and gaseous phase. To alleviate or solve this drawback, the physical and chemical generation conditions have to be carefully optimized or the use of complexing or masking agents has to be considered. Antimony as stibine SbH_3, is separated from the matrix and preconcentrated with a significant improvement of the detection limit with the aid of trapping systems (e.g., cold traps) in conjunction with hydride generation (Chen et al, 2003; Zhang et al, 2005). A common procedure when using hybride generation is to reduce Sb(V) to Sb(III) before analysis using KI/ascorbic acid, HCl and boric acid mixture (LLander et al, 2011).

The validation of the sample treatment in posterior determination of Sb in PM is based on the use of standard reference materials (SRMs). There are few available SRMs. Some authors have used NIST SRM 1648 which is made of urban particulate matter, with a reference value (non-certified) for Sb of 45 $\mu g\ g^{-1}$ (Zheng et al. 2000). Other SRMs described in the literature are based on coal fly ash such as NIST SRM 1633b with a reference value (non-certified) of 6 mg Kg^{-1} (Querol et al, 2002), whereas NIST SRM 1633c has certified value of 8.56±0.19 mg Kg^{-1} Moreover BCR 176R (City Waste Incineration Ash) with certified value of 418±18 $\mu g\ g^{-1}$ has been also described in the literature (Castilho et al, 2012).

3.7. Analytical techniques for Sb speciation in PM

The term “speciation” has often been used to indicate the analytical activity of identifying chemical species and measuring their distribution. Sometimes, it is used to indicate that a method gives more information on the form in which the element is present than other more commonly applied techniques.

The term speciation is also used to indicate the distribution of species in a particular sample or matrix. For example, one might say, “The toxicity of arsenic depends strongly on its speciation”. Speciation in this sense is thus synonymous with “species distribution”.

The International Union for Pure and Applied Chemistry (IUPAC) has published guidelines or recommendations for the definition of speciation and speciation analysis (Templeton et al, 2000):

- The speciation of an element is the distribution of an element amongst defined chemical species in a system. The elemental speciation can be defined as the analysis leading to the determination of the distribution of a particular element in a sample chemical species. Moreover, they are normally associated with oxidation states, the existence of organometallic compounds or complex formation (Marcus et al, 2000).

- Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample. The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.

Likewise, the quality and quantity of the various species that are present in a matrix will be responsible for the toxicological impact of an element rather than its total concentration (Stab et al, 1992; Toyoka, 1999).

In speciation analysis, chromatographic methods are widely used for the separation (Ellis et al, 1997), while spectroscopic techniques are used for detection (Taylor, 2000; Imran et al, 2006), although the application of other methods is also possible (Vieira et al, 2009).

The Sb speciation has some analytical problems due to the lack of certified reference materials, low and ultra-low analyte contents in the samples and problems related to

unsuitable peak resolution and detection. Peak tailing, especially in the case of Sb(III) peak, appears while using liquid chromatography-(Michalski et al, 2012).

In most cases speciation is performed combining a chromatographic technique with a suitable spectroscopic detection. Gas chromatography (GC) and high-performance liquid chromatography (HPLC) are especially attractive techniques for speciation analysis. Particularly HPLC displays great flexibility and can be used to separate nonvolatile and thermally labile compounds. GC coupled to mass spectrometry (GC-MS) provides useful molecular information about volatile Sb species.

The most used techniques for Sb speciation in PM is HPLC can be coupled with ICP-MS (Lijima et al, 2009), ICP-OES (Fujiwara et al, 2011) and AFS (Alsioufi et al, 2016). For non-chromatographic speciation synchrotron radiation X-ray absorption spectroscopy (SR-XAS).in combination with near-edge part (XANES) of the absorption spectra has been also porposed (Varrica et al, 2013).

3.7.1. HPLC-ICP-MS

ICP is an analytical technique used for elemental determinations. The technique was commercially introduced in 1983 and has gained general acceptance in most laboratories. This analytical technique has been combined to HPLC. Currently the HPLC-ICP-MS is the most widespread coupled analytical technique for Sb speciation, since it has great sensitivity, as well as an excellent capacity for multi elemental and isotope analysis.

Speciation of Sb by using HPLC-ICP-MS is very common for several types of samples such as urine, blood, plasma, food (Miekeley et al, 2002) and air (Zheng et al, 2000a,b). Analyzing Sb in the air is so important because anthropogenic emission has resulted in high concentrations of Sb in the environment (Smichowski et al, 2008b).

There are a few articles that study the speciation of Sb in PM, most of them based on the use of HPLC-ICP-MS. Zheng et al. (2000a) were the first ones to use this analytical technique for the analysis of inorganic Sb species in PM. The baseline separationof inorganic Sb(III) and Sb(V) was achieved by using a mobile phase of 2 mmol l^{-1} phthalic acid 5 mmol l^{-1} EDTA at pH 4.5 on a silica-based anion-exchange column. It was found that retention time of Sb(III) and Sb(V) increased when the EDTA concentration decreased. In this study the Sb species were extracted from PM samples by adding Milli-Q water and stirring continously with magnetic stirring bar for 2 days at room temperature. The pH of the mobile phase was studied and the authors found that the retention time and peak intensity of Sb(V) were not

affected by pH change. Sb(III) was niether affected in the range of pH 2-7. At pH values higher than 7, it was observed a shift in the retention time and 10% of oxidation to Sb(V).

Zheng et al. (2001) also studied the Sb speciation in PM but with another extraction media, replacing the water by a citric acid solution 26 mmol l^{-1}, which has several advantages such as: improving the chromatographic separation, stabilizing Sb compounds, preventing Sb(III) from oxidizing to Sb(V) during the ultrasonic assisted and microwave assisted extraction and alleviating the adsorption of Sb compounds on the sample surface. A complexation effect of Sb compounds with citric acid was observed using electrospray mass spectrometry (ES-MS). It was found that both Sb(III) and Sb(V) could form complexes readily with citric acid in an aqueous solution at room temperature. These complexes were found to be very stable in various matrices (water and aqueous extracts of PM). The chromatographic separation was achievd by PRP-X100 anion-exchange column with 10 mmol l^{-1} $EDTA^{-1}$ mmol l^{-1} phthalic acid (pH 4.5) as a mobile phase.

Trimethylantimony specie (TMSb) and several hydride active unknown Sb species were for the first time detected in PM by Zheng et al. (2000b). The speciation of Sb in PM was performed using both anion-exchange and size-exclusion HPLC-ICP-MS detection, in order to to check the reproducibility of the developed analytical method. A Japanese quality control sample for PM with a certified Sb concentration of 92 mg g^{-1} issued by Japan Environment Agency, was used in this study. Water, EDTA and phosphate ($NH_4H_2PO_4$) were used for the extraction of Sb species.

To separate TMSb and inorganic Sb species, another two chromatographic systems were developed: a) an anion-exchange HPLC consisted of a PRP-X100 column with 10 mmol l^{-1} and TMAH (pH 12) as a mobile phase (Fig. 3.5a). With this system, although Sb(III) was not eluted due to its strong retention on the column, TMSb and Sb(V) can be separated. Another chromatographic separation was also tried using size-exclusion HPLC column with 50 mmol l^{-1} of Tris (pH 7.4) as a mobile phase. With this system, Sb(III), Sb(V), and TMSb species can be separated (Fig. 3.5b). Based on this study, Sb(V) was the predominant species for PM samples and TMSb also was detected with other unknown species, whereas the Sb(III) was not detected.

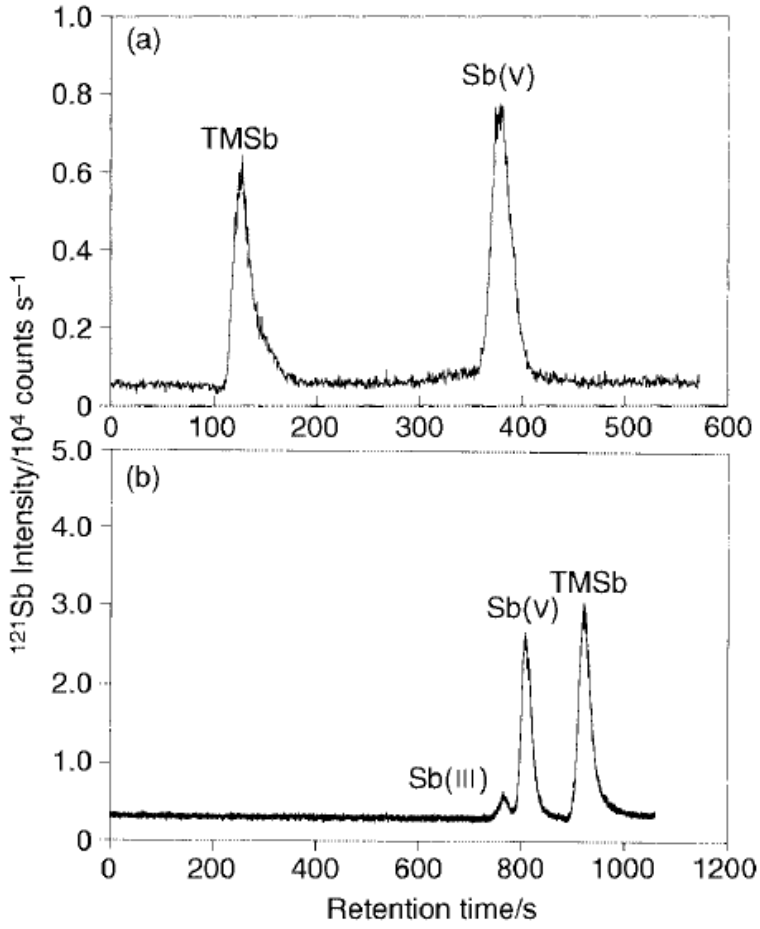

Fig. 3.5. HPLC-ICP-MS chromatogram of Sb standards solutions (Zheng et al, 2000).

Miravet et al. (2006) studied the speciation of Sb in coal fly ash and also in volcanic ash (Miravet et al, 2007). In both cases, a sodium citrate solution (1 mol l^{-1}, pH 5) was used as extractant using end-over-end agitation during 16 h. The presence of Sb(III) and Sb(V) in volcanic ash leachates was reported for the first time. Sb(III) was the main species in the leachates, although minor amounts of Sb(V) were also detected in all the extracts. The Sb determination was done by HPLC-ICP-MS, and the species have been separated by an anion-exchange column (PRP-X100) using a gradient elution with di-ammonium tartrate 250 mmol l^{-1} pH 5.5 and KOH 20 mmol l^{-1} at pH 12.0.

Another procedure of Sb extraction from PM with shorter extraction time has been described by Lijima et al. (2009). In this case, citric acid 30 mmol l^{-1} was used as exctractant in an ultrasonic bath during 30 min. This extractant was used to avoid the oxidation of Sb(III)

to Sb(V). Both Sb species were separated on a PRP-X100 anion exchange column using a mixture of 10 mmol l^{-1} EDTA and 1 mmol l^{-1} phthalic acid (pH 4.5) as a mobile phase under isocratic conditions. Sb(III) is predominant in the coarse fractions whereas Sb(V) is distributed in both the fine and coarse fractions. The size distributions of the total Sb concentration exhibit a bimodal profile in which peaks corresponded to fine (0.50–0.70 mm) and coarse (3.6–5.2 mm) fractions. The speciation analysis demonstrated for the first time that Sb(III), which is the more toxic form, is dominated by coarse fractions whereas Sb(V) is distributed in both the fine and coarse fractions.

Sb speciation in PM that come from brake pads were also studied by IC-ICP-MS (Canepari et al, 2010; Marconi et al, 2011). The PM samples were extracted with EDTA and potassium hydrogen phthalate (KHP) in an ultrasonic bath during 20 min.The low recovery percentages obtained (75%) for fine particles suggests the presence of nano-particles aggregates in the analysed solutions, which are retained by the chromatographic column. These authors showed that this IC-ICP-MS method is fast and easily applicable to intensive monitoring campaigns, and allows the analysis of the two main inorganic forms of extractable Sb in atmospheric PM samples. Analyses of different type of brake pads and road dust showed that brake pads abrasion is the main source of atmospheric Sb(III) in urban coarse particles and the Sb(III)/Sb(V) ratio is mainly driven by the temperature reached by the pad during the braking process. Also, the spontaneous conversion of Sb(III) into Sb(V) in the atmosphere was not observed. The Sb(III) concentrations in PM are comparable or even higher than Sb(V), in contrast with other environmental matrices. The results obtained from PM size-segregated samples (from 10 to 0.03 μm using 13 stage low pressure impactor) indicate that a relevant fraction of the total extracted Sb in particles having aerodynamic diameter < 1 μm (fine fraction of PM) is in the form of solid nano-particles suspended in the solution. The nanoparticles contribution may be easily estimated as the difference between ICP-MS and IC-ICP-MS analysis.

3.7.2. HPLC-HG-AFS

Atomic fluorescence is a spectroscopic process based on absorption of radiation of specific wavelengths by an atomic vapour with subsequent detection of radiationally deactivated states via emission in a direction (typically) orthogonal to the excitation source. Both the absorption and the subsequent atomic emission processes occur at wavelengths which are characteristic of the atomic species present. AFS is a very sensitive and selective method for the determination of a number of environmentally and biomedically important elements such as mercury, arsenic, selenium, bismuth, antimony, tellurium, lead and cadmium.

AFS coupled to HG has received increasing attention because its suitability for Sb determination at trace levels due to its high sensitivity, wide dynamic range (4–6 orders of magnitude), simplicity and very low instrumental cost (Chen et al, 2003; Zhang et al, 2005). The limits of detection achieved for Sb are comparable to those reported for ICP-MS. The main advantage of fluorescence detection compared to absorption measurements is the greater sensitivity achievable because the fluorescence signal has a very low background.

AFS represents a suitable alternative to the other atomic and mass spectrometric techniques. AFS has been described to be superior to AAS and similar to ICP-MS regarding sensitivity and linear calibration range, with further advantages (simplicity, lower acquisition and running costs, robustness and ease of operation) (Sanchez-Rodas et al, 2010).

Three Sb species can be measured by HPLC-HG-AFS, the two oxyanions, antimonite Sb(III) and antimonate Sb(V) and TMSb. These species generate volatile hydrides in acid media with $NaBH_4$ solutions.

In order to measure the Sb levels in the PM filters, different extraction media have been used to extract of Sb quantitatively from the filter. Different reagents have been compared in order to study the Sb in glass filters collected in heavy traffic streets from Buenos Aires (Argentina) (Bellido et al, 2009). Diammonium tartrate, hidroxilammonium clorhidrate, citric acid + ascorbic acid, phosphoric acid and citrate solutions were the acids that have been used with the assistance of the ultrasound probe to extract the Sb from the fly ash filters. The higher extraction recoveries were obtained with a 100 mmol l^{-1} hidroxilammonium clorhidrate aqueous solution assisted by the ultrasound probe operated at 50W during 3 min. The extracts were analyzed by HPLC-HG-AFS.

The instrumentation of Bellido et al. (2009) consists of a liquid chromatograph (JASCO PU 1580 HPLC pump) fitted with a PRP-X100 anion-exchange column (100 mm x 4.1 mm, 10 µm particle size). The optimized mobile phase was a 200 mmol l^{-1} diammonium tartrate (pH 5 adjusted with HCl, with a flow rate of 1.5 ml min^{-1}). Post-column derivatization for Hydride Generation was accomplished adding 1.5% $NaBH_4$ (in 1% NaOH) and 1.5 M HCl solutions by means of a peristaltic pump (Minipuls3, Gilson, France). The volatile hydrides were transported to a gas–liquid separator, using argon as carrier gas. H_2 at a flow rate of 60 ml min^{-1} was added at the gas–liquid separator, in order to stabilize the flame of the AFS detector at a flow rate of 1.0 ml min^{-1}.

The extraction method was applied to filters with Sb concentration higher than 8 ng m^{-3}. The speciation results of duplicate analysis showed that the two Sb inorganic species were

present in the four considered samples, both at similar concentrations, although Sb(V) levels are usually higher. This indicate that PM was affected by heavy traffic, and the high Sb found has been attributed to the direct emissions from the vehicles in the form of exhaust, brake wear and tyre wear, and indirectly through its presence in paved road dust.

Another study about analytical methods for the determination of total Sb, Sb(V) and Sb(III) in road dust and PM in quartz filter by HPLC-HG-AFS was developed (Quiroz et al, 2013). The authors have compared the oxalic acids with other acids (mandelic, tartaric and malonic, citric acid and EDTA). Oxalic acid 100 mmol l^{-1} in 1% w/v ascorbic acid (antioxidant) at 70 °C in closed vessel microwave extraction was chosen as extraction procedure, without adding the antioxidant, the Sb(III) can be oxidized to Sb(V).

Analytical methods were applied to airborne particulate matter (< 10 μm), and road dust (< 37 μm) samples. 70% of total antimony extracted from road samples was Sb(III) indicating an anthropogenic origin of this element. The separation was achieved by a short Hamilton PRP-X100 column (100 mm × 4.1 mm) with small particle size (5 μm).

The citric acid has been used also to study the Sb speciation in coal fly ashes with aqueous solutions (Miravet et al, 2006). Speciation analysis of the coal fly ash extracts by HPLC-ICP-MS and HPLC-HG-AFS was carried out in order to identify the presence of individual Sb species. Sb V) was the main Sb species in the leachates, although minor amounts of Sb(III) were also detected in some extracts. Several extraction procedures were tested based on the use of end-over-end agitation combined with aqueous solutions at six different pH (1, 2, 3, 7, 11 and 12) and citrate 1 mol l^{-1} at pH 5. Citrate at pH 5 gave the best extraction efficiency for samples.

In the present work of this PhD thesis, we have considered to use HPLC-HG-AFS for the speciation study of Sb in PM samples from cities of Andalusia, as this technique has been demonstrated to be suitable for this type of samples. The next Fig.3.6 shows the instrumentation employed in the lab while Fig. 3.7 corresponds to a Sb chromatogram of 5 μg l^{-1} standard obtained by HPLC-HG-AFS.

Fig. 3.6. Instrumental coupling of HPLC-HG-AFS which is used in the present thesis.

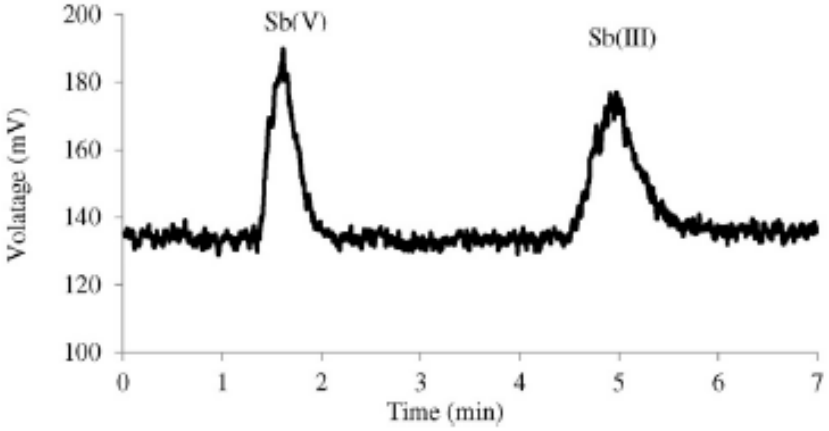

Fig. 3.7. Sb chromatogram standared obtained by HPLC-HG-AFS (Alsioufi et al, 2016).

4. Arsenic

4. Arsenic

4.1. Arsenic and its properties

4.1.1. Arsenic throughout history

Arsenic (As) is widely distributed in all compartments of the environment, due to natural or anthropogenic sources. It is a substance that has been well known to both the 'healer' and the 'poisoner' throughout history. It was used throughout the history as a potent poison to kill off kings and emperors and facilitate rich inheritances (Hughes et al, 2011; Frith, 2013).

In the 19th century As was used to treat trypanosomiasis, while in the 20th century a drug called Salvarsan, which was hailed as "the arsenic that saved", was used to treat syphilis. This new therapy was discovered by Paul Ehrlich's and Sahachiro Hata's. Nowadays arsenic trioxide is used to treat acute promyelocytic leukaemia (Vahidnia et al, 2007; Bosch et al, 2008; Antman, 2001; Frith, 2013).

The word arsenic is derived from the Persian *zarnikh* and Syriac *zarniqa*, later incorporated into ancient Greek as *arsenikon,* which meant "masculine" or "potent" and referred primarily to orpiment, or yellow arsenic. The word became *arsenicum* in Latin and *arsenic* in old French, from which the current English term is derived (Frith, 2013).

4.1.2. Physical and chemical properties

As is classified chemically as a metalloid, it is widely distributed in the Earth's crust, usually combined with other metals, sulphur or oxygen. It occurs naturally as an element, ranks as the 20th most occurring trace element in the Earth's crust (NRC, 1977). As appears in Group 15 (V) of the periodic table, below nitrogen and phosphorus. Chemically it is classified as a metalloid, having both properties of a metal and a nonmetal; however, it is frequently referred to as a metal. Its association with some nonweathering-resistant mineral deposits (e.g., sulphide minerals) has contributed to its release in large amounts into the environment.

Arsenic exists mainly in three oxidation states (i.e., -3, +3, +5). In oxidizing environmental conditions, As^{5+} species are more stable and predominant, whereas in reducing environmental conditions, As^{3+} species are predominant. Under anaerobic conditions, arsenite can be reduced to arsine by microorganisms in soil (Feng et al, 2001).

As cobine with oxygen slowly at room temperature but when it heated in air with oxygene form arsenic trioxide (As_2O_3), which is a blue flame, this compound has garlic-like odor. It does not dissolve in water or most cold acids. It does react with some hot acids to form arsenous acid (H_3AsO_3) or arsenic acid (H_3AsO_4) (Gokcen, 1989; Norman, 1998).

4.2. Arsenic compounds

4.2.1. Abundance and distribution

The terrestrial abundance of As is around 1.5-3 mg kg^{-1}. Before man's activities had an effect on the balance of nature As was distributed ubiquitously throughout the Earth's crust, soil, sediments, water, air and living organisms, but now the man activities affect the level of arsenic in the earth. For example As may accumulate in soil through use of arsenical pesticides, and in dust from the burning of fossil fuels (Mandal et al, 2002).

World reserve and reserve base of As are thought to be 20 and 30 times, respectively, world annual production. The annual production of As_2O_3 was 36 400 and 36 000 during 2014 and 2015, respectively (Fig. 4.1) (USGS, 2016).

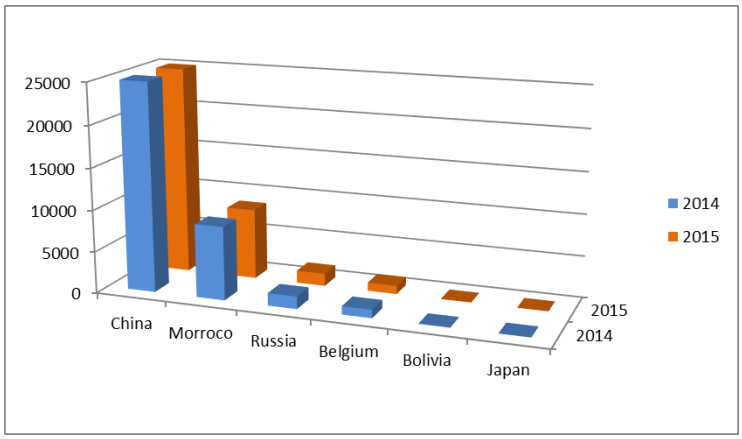

Fig. 4.1. World production of As_2O_3 during 2014 and 2015 (adapted from USGS, 2016).

4.2.2. Main Arsenic chemical compounds

Compounds of arsenic resemble in some respects those of phosphorus which occupies the same group (column) of the periodic table. As is less commonly observed in the pentavalent state, however the most common oxidation states for arsenic are: −3 in the arsenides, such as alloy-like intermetallic compounds, +3 in the arsenites, and +5 in the arsenates and most organoarsenic compounds.

-Inorganic compounds

As forms odorless and colorless oxides (As_2O_3 and As_2O_5), which are hygroscopic and readily soluble in water to form acidic solutions. As(V) acid is a weak acid. Its salts are called arsenates which are the basis of arsenic contamination of groundwater, a problem that affects the population worldwide.

Sulfur compounds of arsenic are known such as orpiment (As_2S_3) and realgar (As_4S_4which were formerly used as painting pigments. All trihalides of As(III) are well known except the astatide which is unknown. Arsenic pentafluoride (AsF_5) is the only important pentahalide, reflecting the lower stability of the +5 oxidation state. One of the simplest As compound is the trihydride, the highly toxic and flammable arsine (AsH_3). This compound is generally regarded as stable, since at room temperature it decomposes only slowly. At temperatures of 250–300 °C decomposition to arsenic and hydrogen is rapid (Greenwood et al, 1997).

-Organic compounds

A large variety of organoarsenic compounds are known, which are the result of biological activities. This procces can be summarized in the Fig.4.2. As combines easily with carbon to form a wide variety of organic compounds with one or more As-C bonds.

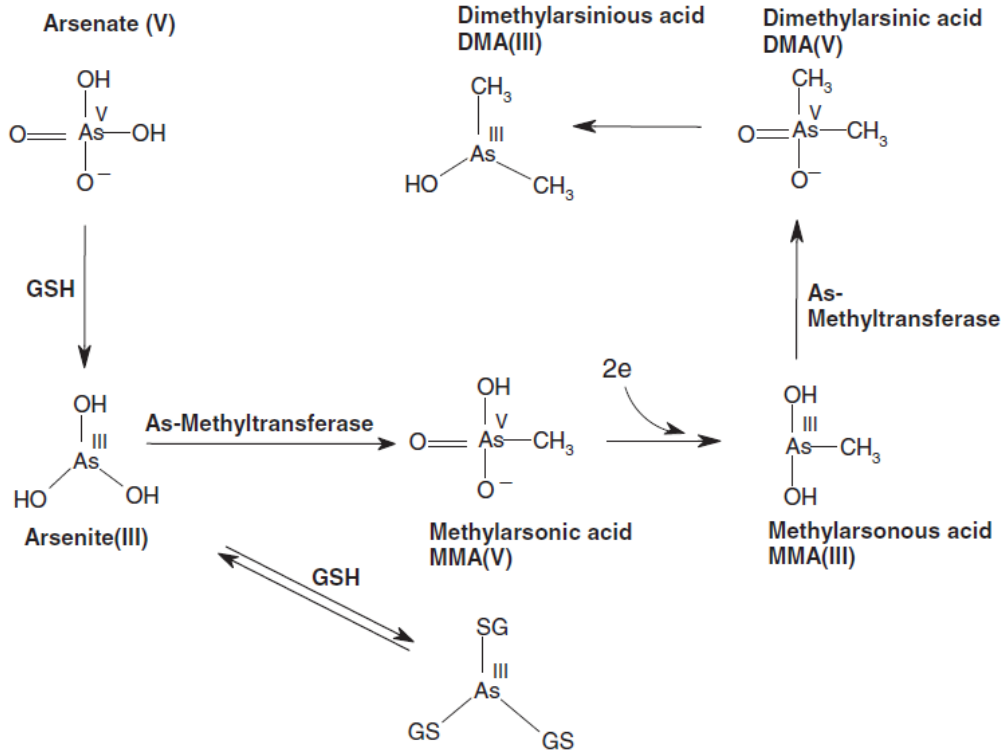

Fig. 4.2. Metabolic cycle of inorganic As (Jomova et al, 2011).

Some examples of arsenic compounds are: monomethylarsonic acid MMA, dimethylarsinic acid DMA and more complex molecules, such as arsenobetaine. Many As organic compounds were developed as chemical warfare agents during World War I, including vesicants such as lewisite and vomiting agents such as adamsite (Girard, 2010; Radke et al, 2014).

4.3. Uses and applications

There is a proven health threat to humans and the environment during As extraction, recovery and processing, and the emissions caused by these activities. As can be used in several product sectors for example in wood preservation, various photoelectric devices (wireless phones and high-speed computers, laser printers), glassware, and it is use as an alloying element to improve corrosion resistance and tensile strength in copper alloys (Zevenhoven et al, 2007). In a lead acid battery, a minute percentage (0.01–0.50 wt%,

average 0.255 wt%) of As is present in the lead to increase the strength of grids. The use of As in the lead-acid battery sector is shown in Fig. 4.3.

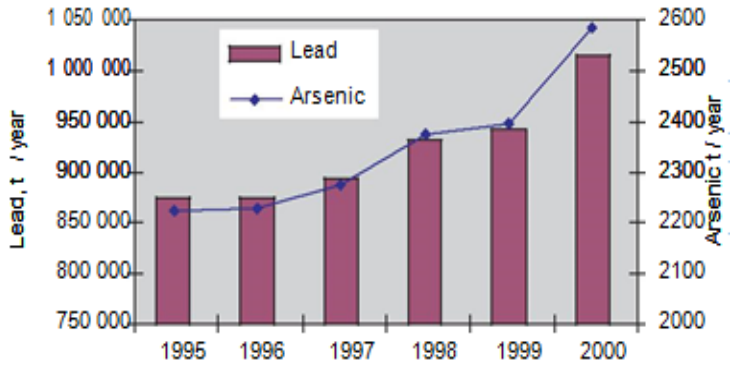

Fig. 4.3. Amount of As in lead acid batteries in the EU-15 nations, 1995-2000 (Zevenhoven et al, 2007).

As_2O_3 is used in the glass industry of the European Union (500 tonnes annually) as a fining agent (mixing of molten glass and the removal of air bubbles during the melting process) and decolouring agent. Nowadays the nordic countries have replaced this compound by antimony oxide. In the United Stated 700 tonnes of arsenic oxide is used annually in the glass industry (Zevenhoven et al, 2007).

Arsenic inorganic compounds such as $Ca_3(AsO_4)_2$, $PbHAsO_4$ and Na_3AsO_4 were used in the agriculture as insecticides or pesticides, although these uses have gradually disappeared due to the toxic effects of these compounds. As has also been used with wood preservation salts in the form of chromated copper arsenate (CCA) to guarantee longer lifetime of wood products and to protect them from deteriorate that come from a wide range of organisms including insects, fungi, bacteria and animals. Another important inorganic compound which is the gallium arsenide (GaAs) is used in the microelectronics industry due to its semiconductor properties (Zevenhoven et al, 2007; Jomova et al, 2010). Arsenic acid (H_3AsO_4) was used extensively as a cotton desiccant for many years in US (Mandal et al, 2002).

4.4. Arsenic toxicity and human exposure

As exposure occurs from inhalation, absorption through the skin and, primarily, by ingestion of, for example, contaminated drinking water. In 2001, the WHO recommended a limit value for As in drinking water of about 10 μg l^{-1} .Inorganic As can be found in air, while a variety of other inorganic arsenates (AsO_4^{3-}) or arsenites (AsO_2^-) occur in water and soil (Magalhaes, 2002; Chou et al, 2007; Jomova et al, 2011).

As in food occurs as relatively organic compounds, the largest source of As in food is seafood followed by rice, mushrooms and poultry. Arsenobetaine $C_5H_{11}AsO_2$ is the organic compound that can be found in seafood, which is less toxic than other inorganic compounds. The toxicity of As occurs through industrial exposure, from contaminated wine or moonshine, or by malicious administration (Smedley et al, 2002; ASTDR, 2007; Jones, 2007; Petroczi et al, 2009; Nepusz et al, 2009; Jomova et al, 2011).

As(III) is the major As species that enter the human body, while just a small amount of As(V) can cross the cell membrane via an energy-dependent transport system, after which it is immediately reduced to As(III). Both inorganic and organic forms leave the body by urine. Inorganic As leaves within several days, although some will remain for several months or even longer (ASTDR, 2007; Jomova et al, 2011). Fig. 4.4 summarize some of the As human exposure sources.

Children also may be exposed to small amounts of As from hand-to-mouth activities from playing on play structures or decks constructed out of CCA-treated wood, although its potential exposure is less than the would received food air or water (ASTDR, 2007).

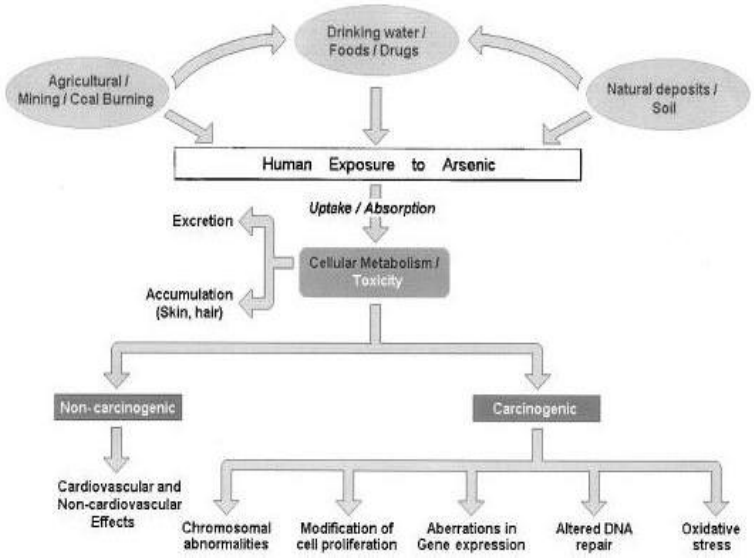

Fig .4.4. Sources of human exposure to As and various modes of As toxicity (Roy et al, 2002).

As has various effects on human health and can causes many health problems, and is now recognized to be one of the world's greatest environmental hazards (Singh et al, 2015). Some of the health problems that can be produced by As intake are described below.

4.4.1. Genotoxicity

Many studies have shown that As induces chromosomal aberrations and sister chromatid exchange. Similar studies using human, mouse and hamster cells explored a potential enhancement of DNA damage, DNA repair enhancement or the inhibition of DNA synthesis (Helleday et al, 2000; Jomova 2011).

4.4.2. Dermal Diseases

As exposure during so much time leads to lesions on the skin, including hyperkeratosis and hyperpigmentation, and may develop cancer in later stages, sometime taking several decades (Lage et al, 2006; McCarty et al, 2007; Jomova et al, 2011).

4.4.3. Cancer

As(III) is more toxic than the As(V) dut to its pronounced ability to release iron from the ironstorage protein ferritin (Salnikow et al, 2008). Free iron may catalyse the decomposition of hydrogen peroxide via the Fenton reaction, thereby forming the reactive hydroxyl radical which can cause DNA damage. As can produce skin many cancers such as: skin cancer, lung cancer and stomach cancer, althouth the methylated As is less toxic than the inorganic species methylation may lead to formation of reactive and carcinogenic trivalent methylated arsenicals. Thus the process of methylation of inorganic arsenic may provide a toxic pathway and both trivalent methylated arsenic (monomethylarsonous and dimethylarsinous acids) may possess harmful biological activity (Jomova et al, 2011; Yoshilkawa et al, 2008).

Worldwide exposure to urban air pollution, causes 8% of deaths due to lung cancer and 5% of deaths from cardiovascular diseases, for a total of two million premature deaths each year (Ciarroca et al, 2012).

4.4.4. Neurological disorders

Human exposure to inorganic As after both inhalation and oral exposure can cuase injury to the nervous sytem (Headache, seizure and coma). Prolonged exposures are typically characterized by a symmetrical peripheral neuropathy which in its early stages cuases by numbness in the hands and feet then further develops into a painful pins-and-needles sensation (Chakraborti et al, 2003; Jomova et al, 2011).

4.4.5. Other effects

As can affects the cardiovascular system producing hypertension, which can be explained by an enhanced myosin light-chain phosphorylation and an increase in calcium-sensitization in blood vessels, also long exposure to As can lead to myocardial depolarization and cardiac arrhythmias (Navas et al, 2005; States et al, 2009).

Clinical signs of gastrointestinal irritation, including nausea, vomiting, diarrhoea and abdominal pain, are observed in all cases of short-term high-dose and longer-term lower-dose exposures to inorganic arsenic. Many studied revealed that As also produce liver damage (Cirrhosis and elevated levels of hepatic enzymes) (Jomova et al, 2011).

4.5. Emission sources and legislation on As in the air

As is widely distributed in the Earth's crust, it is released to the environment from natural sources such as wind-blown soil and volcanoes, but their anthropogenic sources far exceed those from natural sources. Air represents an important route of dispersion, as it allows As to be transported globally (Holmes et al, 2004; ASTDR, 2007). Csavina et al. (2012) indicates that anthropogenic As emissions to the atmosphere represent a pathway for As dispersion underappreciated and potentially understudied (Fig. 4.5).

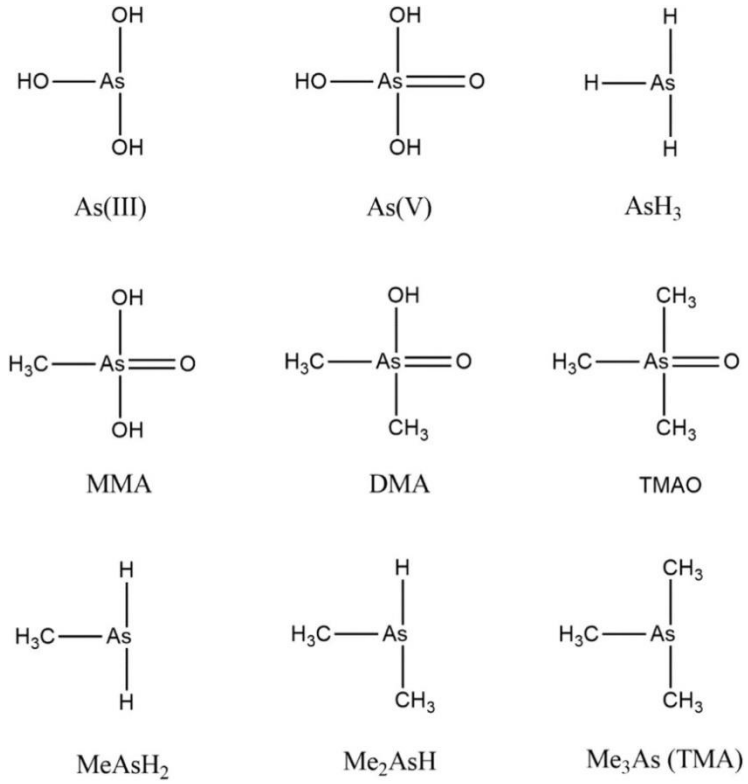

Fig. 4.5. As species in atmospheric samples (Sanchez-Rodas et al, 2015.)

One of the human activities that can emit As to the air is the Cu production from the 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 As that can be released during roasting. Pyrites can contain up to a 10% in weight of As that can be released during

roasting. The second activity that can lead to As emission is the coal burning, also the production of other metals (Pb, Zn and steel) results in the emission of As (Bowell et al, 2014).

The combustion of fuels (coal and petrol) is another important anthropogenic source. It has been estimated that the world average of As content in coals is 9.0±0.8 mg As kg^{-1} for bituminous coals (Yudovic et al, 2005), although some coals in China can contain higher concentration of As reach to several hundreds or thousands of mg As kg^{-1} (Ng et al, 2003; Zhao et al, 2008). However, petroleum is a minor emission source of As, which is about 0.26 mg As kg^{-1} (Han et al, 2003). The sum of Cu smelting and coal burning stand for a 60% of the anthropogenic As emission to the atmosphere worldwide (Matschullat, 2000). A detailed inventory of anthropogenic As emissions in the European Union (EU) can be found in Zevenhoven et al. (2007).

As concentration in the air in the 1980's was estimated between 0.8 and 1.74 x 10^6 kg, with a distribution of 85% in the north hemisphere and 15% in the south hemisphere. Nowadays, the mean worldwide concentration was estimated in 2.8 ng m^{-3}. This reflects the increasing in industrial activity in the world in relation to global As production since the industrial age to recent times (Chilvers et al, 1987; Han et al, 2003).

China is the most important emitter of As into the atmosphere. A recent review of Duan et al. (2013) has reported a mean value of 51 ng As m^{-3} corresponding to the ambient air of 44 main Chinese cities. These concentrations are higher than that found in urban areas of the EU (from 0.5 to 3 ng m^{-3}), with the exception observed in the vicinity of Cu or Pb smelters (Zevenhoven et al, 2007; Tian et al, 2009).

The first regulation that established an objetive target value of As in the ambient air was the EU in 2004, this directive (Directive 2004/107/EC) indicated 6 ng As m^{-3} in PM10 to be accomplished by beginning of 2013 (WHO, 2000).

China has adopted a National Ambient Quality Standard (NAAQS) (GB 3095-2012) with a similar value of 6 ng As m^{-3}. Other countries established values of 5.5 ng As m^{-3} (New Zealand) or 10 ng As m^{-3} (Alberta, Canada) (Alberta Government, 2011). However, the actual legislation target value is just for As total and not for the different toxic sepecies of this metalloid. Most of the countries do not establish a target value of As in the ambient air, although permissible exposure limits are usually established (e.g. 10 mg m^{-3} of inorganic arsenic and 0.05 ppm of arsine for occupational workers in the United States) (NIOSH, 2007).

4.6. Sample treatment for total As determination

Several types of filters have been used in the acid digestion in order to determine the total As, although Teflon filters are the used ones. In all digestion treatments a portion of the filter is cut and a mixture of acids is added to the vessel that has the filter portion assisted by thermal. The reaction vessel should be closed, to avoid possible losses due to the formation of As halides. The HNO_3 has been used in the digestion of the glass filters, by heating in sand bath (Serbula et al, 2010).

In the case of quartz filters, HF is used commonly with HNO_3, HCl or HNO_3:$HClO_4$ mixtures. However, using HF is discouraged due to its hazardous handling. Richter et al. (2007) used 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, while other authors used a mixture of HNO_3:$HClO_4$: HF on a heating plate for complete digestion, the digestion proccess last for 2-3 days (Alastuey et al, 2002; Fernandez-Camacho et al, 2010a). The actual legislation in EU recommmend using a mixture of HNO_3:H_2O_2 instead of using HF acid, and this mixture was also used for cellulose filters (Singh et al, 2010).

For PTFE filters, $HClO_4$ was employed. The digestion was achieved by a heating block at room temperature in an ultrasonic bath during 30 min (Thomaidis et al, 2003). Other articles don't specify that acids were used or the time necessary for the digestion process, they just indicate that acid digestion was made by hot plate (Acevedo et al, 2006). A mixture of HNO_3:H_2O_2 was also used in PTFE filter digestion and was put in closed reactors and placed in a microwave oven (Pandey et al, 1998).

In all of the above mentioned studies, the research group has selected the best digestion method following their own experience. There was no established method to select the best mixture for the acid digestion. All their results indicate that there was no loss recorded in the As due to the volatilization, or 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 dissolved in dilute acid before analysis.

Another study employed an optimized digestion method consists of two steps HNO_3 $HClO_4$ and then $HClO_4$ HF, by using either microwave or a high pressure bomb digestion (Wang et al, 1997). In a posterior article (Wang et al, 1999) the author tried different mixtures of HNO_3, $HClO_4$, H_2O_2 and HF. 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.

4.6.1. Sample single step extraction

Single step extraction can be used as an alternative method to samples, in order to reduce the time of sample treatment to few hours or minutes. For glass fibre filters EPA 3051A method was used. This method is based on acid leaching of the sample with a HNO_3:HCl mixture assisted by microwave radiation (Halek et al, 2010). Another method was also used for same type of filters (EPA 600/4-77-027a method). In this method a mixture of HNO_3:HCl and an ultrasonic bath at 50 ^oC during 50 min (Pasias et al, 2013) was used. Other authors extracted the As from PM samples only by using HNO_3 and sand bath heating (Serbula et al, 2010). Extracting As from PM samples at room temperatures with HF:HNO_3 mixture have been tested also (Gidhagen et al, 2002; Hedberg et al, 2005) but the extraction time was so long (4 days) in comparasion with other methods that heat the samples HNO_3 on a heating plate for 2 h (Gioda et al, 2006).

In the case of quartz filters, a faster extraction procedure has been employed by adding a mixture of HNO_3:HCl in a heating block at 90 ^oC for 90 min (Yadav et al, 2014). For cellulose filters, extraction of As is accomplished with HNO_3 assisted by microwave (Tsai et al, 2003). As these extraction procedures do not dissolve the filter that retains the PM, recoveries tests have to be performed to guarantee the extraction process.

Some studies focuses on the bio-accessible fractions of As, in order to assess human health risks associated to As in PM. The extraction was performed by adding water in all of this type of study, although the procedures change among the authors. In Singapore an aqueous extraction of PM samples were performed at room assisted by microwave, a lower extraction results were achieved (0.6-1.5 ng m^{-3} were extracted from a total of 12.4-35.5 ng m^{-3} of As) (Karthikeyan et al, 2006). The ultrasound was employed by some authors at 70 ^oC for PM samples in New York (Qureshi et al, 2006), indicating that 84% of the As is water soluble. Other authors used the ultrasound without heating to samples from Nanjing (China) (Wang et al, 2002). In this study no total continent is determined so the percentage of extraction cannot be calculated.

In another study other selective extraction methods have been proposed. A simple bio accessibility extraction test (SBET) based on glycine at pH 1.5 have been made indicating that mean As extractions of 47.5% and 48.2% for TSP and PM2.5, respectively (Hu et al, 2012).

The recent developments in the assessment of bio accessible trace metal fractions, including As, indicate leaching procedures and analysis in relation to the fractioning according to particle size, rather than speciation of As (Mukhtar et al, 2013).

4.6.2. Sample sequential extraction for total As

This procedure is normally used to distinguish the distribution of elements among the different mineral fractions of soils, but it has been extended to other types of samples, such as PM. There are a few articles that use with this topic. This procedure allows estimating the mobility of the metals, considering to fraction they are bound.

Some authors 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 (Richter et al, 2007).

Other articles used another procedure for As determination in PM samples, which is the BCR (Bureau of Certificate and Reference). It considers 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). The results of the works that used this procedure were similar, 70-80% of the As was found in the first and second fractions, these results indicate the mobile and bioavailable character of As (Feng et al, 2009; Sun et al, 2014; Li et al, 2015).

4.7. Analytical techniques for total As determination in PM

Many analytical techniques have been used to determine As in PM samples, although the most used techqniques are based on different types of atomic spectroscopy and mass spectrometry.

4.7.1. Colorimetry

Tabor et al. (1969) employed this method based on the As reduction to arsine with $SnCl_2$ and Zn, which reacts with a pyridine solution containing silver diethyldithiocarbamate and the resulting red complex were measured by photometry at 536 nm. This method was not effective because the minimum concentration of As that can be measured by this technique was 0.1 mg m^{-3}, while the As concentration in samples were in the range of ng m^{-3}.

4.7.2. Hydride generation-atomic absorption spectroscopy

The number of studies that use this method is reduced, nowadays there are other analytical methods that have better sensitivity, lower volume of samples and are capable of multi elemental samples.

In HG-AAS, the sample is acidified by adding acid such as HCl, after that $NaBH_4$ or KBH_4 solution is added. The formed arsine AsH_3 is transported by an inert gas carrier such as N_2 or Ar to the atomizer, which is a quartz tube that has a T shape. The atomization is achieved by heating the quartz tube electrically or by an air/acetylene flame. By using this method all the inorganic As species must have the same oxidation states in order to have a good results. A mixture of KI and ascorbic is usually added before determine As in the sample (Singh et al, 2010; Singh et al, 2011). The limit of detection LOD for HG-AAS indicated by these authors are between 0.17 and 1 mg 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.

Braman et al. (1977) indicated that hydride generation (HG) with ($NaBH_4$) for AsH_3 evolution was faster and less prone to interferences than the classical approaches using zinc or magnesium. This method gave better detection limits than colorimetry by a factor of two. In this work, the author 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.

HG-AAS has been applied to PM samples (urban sites) in Spain, with concentrations found up to 2.49 ng m^{-3} in La Coruna (Beceiro-Gonzales et al, 1997), in Greece found a maximum of 14.7 ng m^{-3} in Athens (Vassilakos et al, 2007), and in India a maximum of 5.58 ng m^{-3} reported in Delhi (Singh et al, 2010:2011) and 13.5 ng m^{-3} in Bombay (Tripathi et al, 1997).

4.7.3. 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 for As in PM10 (EN 14902:2005).

When employing ET-AAS for As determination, molecular interferences from the PM matrix should be taken into account. Some procedures have been porposed in order to determine As species without interferences such as, Zeeman background correction which consists of adding $Pd(NO3)^2$ (Onat et al, 2014) or a mixture of $Pd(NO3)^2$ and $Mg(NO3)^2$ (Welz et al, 1988; Thomaidis et al, 2003) as matrix modifier. A more recent procedure has been employed by a zirconium-iridium permanent as a modifier for simultaneous determination of As, Pb, Cd and Ni (Pasias et al, 2013). Other researches follow an established method for As determination by ET-AAS, corresponding to US EPA 7060A (Pandey et al, 1998: Spini et al, 1994).

This technique has been employed in many studies: in Delhi India the concentrations of As ranging 9-512 ng m^{-3} (Chakraborti et al, 1992) and in Puerto Rico two works studied As in PM and found low concentrations of As below 0.5 ng m^{-3} in PM2.5 and PM10 samples (Acevedo-Figueroa et al, 2006: Gioda et al, 2006).

A study in Taiwan analyzed urban aerosol PM10 and PM2.5 using ET-AAS, As concentrations between 0.18 and 12.4 ng m^{-3} were found (Tsai et al, 2003). While higher concentrations of As in PM were reported in in Serbia at Bot, these concentrations are high possibly due to the Cu smelter near the city, concentrations reached a maximum of 95.4-149 ng m^{-3} (Kovacevic et al, 2010: Serbula et al, 2010). In Turkey the As concentrations reached to 171.8 ng m^{-3} in industrial areas of Istanbul (Onat et al, 2014). In Athens Greece the concentrations were found 29.3 ng m^{-3} (Thomaidis et al, 2003).

There are some discrepancies between the LOD described in the literature, as they ranged from as low as 0.05 ng As m^{-3} (Onat et al, 2014) to 2 ng As m^{-3} (Serbula et al, 2010) 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.

4.7.4. Inductively coupled plasma-mass spectrometry (ICP-MS)

ICP-MS is one of the most used techniques for As determination in PM. It has the capability of multielemental analysis, and a low detection limits (e.g. LOD 0.05 ng m^{-3}) (Hueglin et al, 2005). It is also a recommended analytical technique, as indicated in the European Standard for As in PM10 (EN 14902:2005), and therefore its use is more extended than other techniques.

In Chile PM10 samples have been analyzed by ICP-MS in several areas some of them are located near a Copper smelter. The concentrations of As were between 30.7 and 190 ng m^{-3} (Gidhagen et al, 2002; Hedberg et al, 2005; Richter et al, 2007).

Many researches have been employed in several areas in Spain (Querol et al, 2009), such as industrial zones (Vicente et al, 2012; Garcia Aliex et al, 2014; Minguillon et al, 2009). In Huelva As concentration in air was reported between 5.4-9 ng m^{-3} with a maximum of 96 ng m^{-3}. High conentrations have been found in Huelva due to the copper smelter which is stuated near the city (Querol et al, 2002; Fernández-Camacho et al, 2010b).

In Bolivia high concentrations of As have been determined by ICP-MS in PM samples from Oruro, a mining area of Bolivia. The concentrations were between 24 and 45 ng m^{-3} in PM2.5 and PM10, respectively (Goix et al, 2011). Other studies conducted in Taiwan indicated mean As concentrations between 2.81 and 4.11 ng m^{-3} (Fang et al, 2012). In urban and rural areas of Switzerland the As concentrations reported below 1 ng m^{-3} (Hueglin et al, 2005). 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} (Querol et al, 2006).

Although ICP-MS is one of the best and most used method for determine As in PM, also some possible interference may occur from polyatomic ion. For example using $HClO_4$ with reference material such as 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 (Wang et al, 1999).

However, other authors indicate that the interference can be removed from the calibration solutions, but not from analysing the reference material by an arithmetic operation that includes the m/z 77 of $[Ar^{40}Cl^{37}]$. The authors point out that by adjusting the flow of the nebulizer to a low value, As concentrations in agreement with the certified values were found, possibly due to the diminution of other possible interferences, such as $[Co^{59}O^{16}]^+$ (Brown et al, 2004).

Wang et al. (1997) has been proposed using the Laser Ablation (LA) for sample introduction in the plasma with ICP-MS for PM samples collected on PTFE filters, with promising results, although no more references were published afterwards with LA.

In the present work the ICP-MS tehcniques was used in order to determine the total As in the air samples (PM10 and PM2.5). The Fig. 4.6 shows the ICP-MS (7900 Agilent Technology) employed in the lab.

Fig. 4.6. ICP-MS intrument used in the present thesis at CIQSO (University of Huelva).

4.7.5. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

There are a few articles that have been used this techniques in order to determine As in PM samples due to the poor sensitivity that have. Only samples with high As concentrations can be measured by this techniques, for examples the ones analysed in 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 (Querol et al, 2000). This technique also was used in Puebla City (Mexico) with a maximum of 4877 ng m^{-3}, due to the proximity of the active volcano Popocatepel (Morales-García et al, 2014).

Halek et al. (2010) used ICP-OES for As determination in PM samples in Tehran (Iran). This technique has been employed in combination with HG, 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 mg l^{-1}).

In Bahia (India), ICP-OES technique has been employed in combination with HG, improving the LOD to 1 mg l^{-1}, while the As concentrations found in this work reached up to 7.85 ng m^{-3} (Pandey et al, 1998).

4.7.6. Direct techniques

There are a few researches that use these techniques (PIXE, INAA and XRF) to determine As in PM samples. Although they have a good sensitivity, their use is limited due to their high cost, need of specialized laboratories and facilities, such as an isochronous cyclotron for PIXE, or a nuclear reactor for INAA, and the time of irradiation, which is of several days. This technique has 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 h sampling period and this can help in help to identify peaks of pollutants in ambient air (D'Alessandro et al, 2003; Fernandez-Camacho et al, 2012).

In 1980's PIXE was the first technique that has been employed for determination of As in PM samples of Beijing (China). As concentrations found between <0.28 and 10.3 ng m^{-3} (Winchester et al, 1984). The same technique was used in Chile near a copper smelter, where high concentrations of As were reported (23-241 ng m^{-3}) in fine particles (<2.5 µm) (Romo-Kroger et al, 1994).

In Portugal the INAA technique was used to determine As in PM10 and PM2.5 in Lisboa and other locations in mainland Portugal with mean As concentrations of 3.6 and 2.8 ng m^{-3}, respectively (Freitas et al, 2004: Freitas et al, 2005). Another use of this technique was reported in Budapest (Hungary), authors determined As concentration in urban samples, concentrations were between <0.30 to 5.3 ng m^{-3} (Slejkovec et al, 2000).

XRF techniques for PM samples have been few used, although can be used for multielemental determination in PM10. In Wuhan (China) this technique was employed and concentrations of As up to 64 ng m^{-3} were detected (Waldman et al, 1991), while lower concentrations were reported in Flanders (Belgium) 3.8 ng m^{-3} (Vercauteren et al, 2011). Studies carried out in Europe have demonstrated that XRF technique can provides similar reliable results as those obtained by ICP-MS or ET-AAS (Gerboles et al, 2011).

4.8. Sample treatment for As speciation in PM

4.8.1. Sampling and extraction for As speciation

In 1970's the firsty research on speciation of As in PM was developed in Tampa Bay (Florida). PM samples were collected from urban and suburban areas, two stages collector were used to distinguish PM > 0.3 mm which were retained onto glass fibre filters, and the combined gaseous and PM < 0.3 mm fraction retained onto silver plated pyrex beds placed

in a pyrex tube. As species were extracted by using an alkaline warm solution submitted to direct current discharge-OE, this procedure allow to distinguish between the methylated arsines and inorganic As species (inorganic species were the dominant ones in the samples) but did not allow to distinguish between the oxidation states of inorganic As (Johnson, 1975).

In Japan another works were performed to study the percentage of the methylated species of As collected from PM samples using glass or quartz fibre filters and extracted with a similar procedure as described (Johnson et al, 1975) by sonication with either a NaOH or HCl solutions HG was used with a $NaBH_4$ for posterior analysis. Two extraction methods were employed in these works (NaOH and HCl with or without EDTA). The best extraction was accomplished by adding EDTA with the results were similar by Johnson et al. (1975), methylated As species were found at low cencentrations in the pg m^{-3} level (Mukai et al, 1987a; Mukai et al, 1987b).

The first study about the speciation of inorganic species of As in coarse (TSP) and fine (PM2.5) fractions was in California. The authors used PTFE to to collect PM with high volume air captors~~,~~. PM filters were heated by diluted ethanol solution to reduce the hydrophobic nature of the collecting material. Extraction was accomplished by adding HCl solution in a Teflon vial, heating during 1 h at 85-90^{o}C, and then HG was performed in the extracts prior to the analysis by AAS. The extraction recovery for As(III) obtained to PM filters was about 79%, although the percentage was about 100% when the extraction method was applied to spiked unexposed filters with As(III) and As(V). The difference in both recoverires percentages is due to the nature of the PM matrix, which could be overcome by quantification using the standard addition calibration method. In this work the authors did not mention the methylated As that could be found in the PM samples (Rabano et al, 1989).

Other studies about the methylated As species in air samples were performed in California by Solomon et al. (1993) and in Isfahan, Iran by Telebi (1999). In California, PM was collected upon quartz filters and extracted with diluted HCl in a similar way as Rabano et al. (1989), while in Isfahan quartz filters were employed and digested with H_2SO_4 and HNO_3 for posterior analysis by HG-AAS. Methylated As species were not reported in both studies. The recovery percentage 60% for As(III) and 120% for As(V) in California. Although the authors indicated the effect of the matrix of PM on the extraction of the As species, a partial oxidation of the arsenite during sample extraction was observed. Other authors estimated that the possible matrix represented less than a 20% of difference in their samples (Rabano et al, 1989).

In 2000 and the following years, several authors used liquid chromatography (HPLC) combined to hydride generation and atomic fluorescence spectroscopy (AFS), for As speciation in air samples. By this hypnated techniques the organic and inorganic species of As can be detected, and a good extraction process have to be used without altering the distribution of the species applying a considering media compatible with the posterior analysis.

Coarse (PM2-10) and fine (PM2) particles were sampled in filters at urban sites of Budapest (Hungary) by Slejkovec et al. (2000). Two extraction solutions were used for this study (water and 0.1 mol l^{-1} phosphate solutions) and sonication was done during 3 h. Low extraction percentage was achieved by 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).

TSP samples were collected in Huelva (Spain) near to ~~a~~ a copper smelter, 3 extractions solutions were tested in this work water, 0.1 mol l^{-1} NH_2OH-HCl and 0.01 mol l^{-1} H_3PO_4 extracting solutions, with the aid of microwave (4 min) or sonication (15 min). The best extraction method for this study was 0.1 mol l^{-1} NH_2OH-HCl solution plus microwave oven extraction, with a percentage recovery of 94%. (Oliveira et al, 2005). By using H_3PO_4 assisted by microwave radiation the recovery percentage was 86%, while in Bejing China another study used the same extraction solution (H_3PO_4 with sonication) and reported a better extraction percentage of about 92% for the As(III) and As(V) (Yang et al, 2012).

Other authors in Huelva (Spain) used the same extraction procedure made by Oliveira et al. (2005), in order to determine the inorganic As species in PM2.5 and PM10 samples. The analysis was achived by using HPLC-HG-AFS (Sanchez-Rodas et al, 2007; Sanchez de la Campa et al, 2008).

At Aspropygos (Greece) coarse (PM10) and fine (PM2.5) PM were analyzed in an industrial site with a refinery and close to a highway, using glass or polycarbonate filters (Tsopelas et al, 2008). The extraction was done by using 9.5 mol l^{-1} HCl which gave a better extraction efficiency than 6 mol l^{-1} H_3PO_4, the extraction performed at room temperature by stirring, the propoed method has a relatively long time of extraction (2h), compared to others that used microwave or ultrasound bath in which the extraction time is of few minutes.

An alternative method to microwave extraction was proposed by Moscoso et al. (2008). In this work the author used the the pressure liquid extraction (PLE), EDTA was the extraction solution at 100 ^oC and a pressure of 1000 psi, during 5 min, with satisfactory results for inorganic As species. There are no more studies that use the PLE extraction for As in PM

samples. A second alternative is the technique of slurry sampling, as proposed by Macedo et al. (2010), mixing the sample containing PM with 4 mol l^{-1} HCl and sonication during 30 min. Again, no more studies have considered this possibility.

A new extraction method was reported by Jakob et al. (2010) for methylated As species from PM samples collected from urban sites in Argentina. The extraction was achived by 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. Methylated As samples (MMA, DMA and TMAO) were found at low concentrations (pg m^{-3}). The authors used the whole filters for the extraction, so there si no direct evaluation of the efficiency of the extraction procedure is given. Inorganic species of As were not quantified in the samples.

4.8.2. Selective extraction for As speciation

In this type of extraction, 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. (2014), who used a physiological based extraction test (PBET) with PM2.5 samples, consisting of a gastric solution simulating the chemical conditions of the gastrointestinal tract. The results indicated the presence of As(III) and As(V), as well as MMA and DMA. The inorganic species were the major ones in the samples with concentration of 15.53 ng m^{-3} for As(V) and 4 ng m^{-3} for As(III). The bioaccessible fraction represented a 32.76% of the total content of the sample. Hu et al. (2012) reported a higher perctange (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.

Nowadays there are a few articles about bioaccessibility of As in air samples. More research is advisable, considering more study areas and comparable extraction procedures. In relation to sequential extraction schemes for As speciation in PM, there is little information available.

A three step for As extraction was reported by Farinha et al. (2014) by using Milli-Q water, $CaCl_2$ and H_3PO_4 solutions and posterior analysis of the extracts by HPLC-HG-AFS. A low extraction percentage was achieved by using water for inorganic As species (6-11%) and higher for $CaCl_2$ and H_3PO_4 (13.8-68.5%). In this work no methylated species were reported.

Slejkovec et al. (2000) employed a two step 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%).

4.9. Analytical techniques for As speciation in PM

4.9.1. Hydride generation and/or cold trap-spectroscopy

Johnson et al. (1975) 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. By this method the authors quantified organic As in both PM and the gaseous phase, but they coud not distinguish between the methylated arsines and the corresponding organic acids. Therefore, the comparability to other studies is limited. This technique has not been applied in posterior studies.

The First-time measurements of the potentially toxic inorganic species of arsenic (arsenite arid arsenate) have been obtained in fine and coarse atmospheric particles in the Los Angeles area by Rabano et al. (1989). The separation was based on 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%. In other article that used the same method of separation, the accuracy was between 12-13% and the LOD was 0.23 ng m^{-3} espressed as concentration (Solomon et al, 1993).

Slurry sampling (SS) with hydride generation atomic absorption spectrometry (HG-AAS) was used to analyze 3 particulate matter samples collected in the Bananeira Village, Brazil by (Macedo et al, 2010). Total As in the extract is measured reducing its As(V) content to As(III) with a KI/ascorbic acid mixture, whereas As(III) was by masking As(V) with citric acid/sodium citrate buffer. The As(V) concentration is determined by the difference of the As Total 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. The results of this work indicated the most of 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.

Alkylarsenic species in PM samples in an agricultural area in Japan were investigated by Mukai et al. (1987a). The authors used 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. In this work the authors separated and detected MMA and DMA, whereas TMA overlapped with dimethyl, so they had to be quantified as the sum of both species. LOD in mass reported in this work was 0.5 ng for the organic As compounds.

The same authors published another article for As speciation in PM, in which they 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. AAS was used for the detection, and the chromatographic separation was performed by a programme of temperature from 25 ^oC to 180 ^oC. In this work EDTA solution during HG was added in order to avoid interferences with Fe, NO_3^- and NO_2^- (Mukai et al, 1987b).

In a similar way, Nakamura et al. (1990) collected the AsH_3 that evolve after HG into a U shaped tube with liquid N_2. In this case the trap was filled with chromatographic packing, which allowed the separation of MMA, DMA and TMA after heating with a nichrome wire and their detection by AAS. Sulphanilamide $C_6H_8N_2O_2S$ was added as masking agent to prevent the NO_3^- interference.

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

Of the different atomic detectors combined to liquid chromatography, AFS is the one most employed for As speciation analysis in PM samples, as it provides similar sensitivity as ICP-MS. Both detector have been compared for the speciation of As(III), DMA, MMA and As(V) by Gomez-Ariza et al. (2000). Fig. 4.7 shows the chromatogram correspondinf to a standard solution of the four arsenic species obtained with both detectors. In this work the authors indicated that AFS represents a useful detection for As speciation, with performance results and various advantages such as the benefits of lower running costs, shorter warm up times prior to analysis and easy handling.

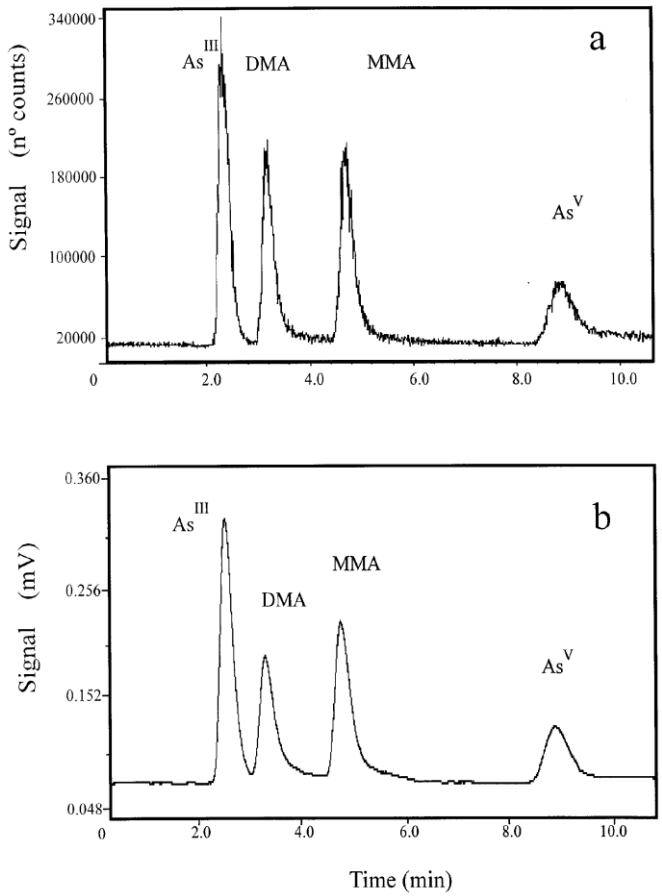

Fig. 4.7. As standard traces: (a) HPLC-HG-ICP-MS and (b) HPLC-HG-AFS corresponding to 5 mg l^{-1} of each species (Gomez-Ariza et al, 2000).

Slejkovec et al. (2000) used HPLC-HG-AFS method for As speciation in PM samples collected in Budapest, an anion exchange guard column for the separation of As(III), DMA, MMA and As(V) in PM extracts of samples using a potassium phosphate solution (pH 6) as mobile phase. HCl and $NaBH_4$ solutions were used for HG step, the AsH_3 were transported to a glass gas liquid separator and an Air flow transported them to the H_2 diffusion flame of an AFS detector. The LODs were 0.12, 0.04, 0.63 and 0.08 mg l^{-1}, respectively, for the four above mentioned As species. (Gomez-Ariza et al, 2000).

Farinha et al. (2004) employed HPLC-HG-AFS method with anion and cation exchange column to analyze sample of PM2.5 and PM10 of Portugal. No results were obtained were

obtained corresponding to cationic As species. By using anion exchange column inorganic As species were reported, but no methylated species were found in the samples.

In Huelva (Spain) many studies have used HPLC-HG-AFS methods in order to determine As in different air samples using, an anion exchange column with a phosphate buffer. This methodology has been employed for As(III) and As(V) speciation in samples of TSP (Oliveira et al, 2005), PM10 (Sanchez-Rodas et al, 2007) and PM2.5 (Sanchez de la Campa et al, 2008). The speciation analyses showed that As(V) was the main arsenic species found (80-90% of the total As content), followed by arsenite As(III). The high levels of arsenic species found in PM10 in Huelva have a predominant industrial origin, such as the one from a nearby copper smelter and no organic As species were found. LOD for As(III) was 0.1 ng m^{-3} and for As(V) was 0.4 ng m^{-3}, for a volume of injection of 200 μl.

Yang et al. (2012) used HPLC-HG-AFS with similar chromatographic conditions as in Refs. (Sanchez-Rodas et al, 2007; Sanchez de la Campa et al, 2008) for As speciation in TSP samples from Beijing (China). As(V) accounted for 81–99% of the extractable species in the TSP samples which showed that As(V) was the major fraction of the extractable As, with LODs 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. This is due perhaps to the small amount of sample employed for the extraction (5 mg) compared to other works. Organic species (MMA and DMA) were not found.

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. (2008). The acid extracts containing PM were passed thorough anion and cation exchangers placed in glass columns. The acid extracts containing PM were passed thorough anion and cation exchangers placed in glass columns. As(III) was extracted with methyl-isobutyl-ketone at pH=2 using an aqueous solution 1% of APDC. The aqueous phase containing As(V), MMA and DMA was adjusted at pH4 and passed through the cation-exchanger for the retention of DMA. The following solutions are employed for elution: 4 mol l^{-1} NH_3 for DMA, acetic/acetate buffer for MMA, and 1 mol l^{-1} HCl for As(V). As(V) was the predominant arsenic species in all samples with LOD of 0.1, 0.4, 0.3 and 0.4 ng m^{-3} for As(III), DMA, MMA and As (V), respectively. These LOD are similar to previous described chromatographic separations based on HPLC. Again, no methylated species were detected in this work.

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

Jakob et al. (2010) studied the speciation of methylated As species in air by using HPLC-ICP-MS method from samples collected from two different locations in Argentina. An anion exchange column with ammonium carbonate as mobile phase (pH 10) was used for the speciation of organic 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. A 50 mM pyridine solution adjusted to pH 2.7 with formic acid with a flow rate of 1 ml min^{-1} was used as mobile phase. For the identification of trimethylarsine oxide (TMAO), cation exchange was necessary because of its retention time was too close to the void volume and would not be different than other arsenicals cationic under these conditions Fig.4.8.

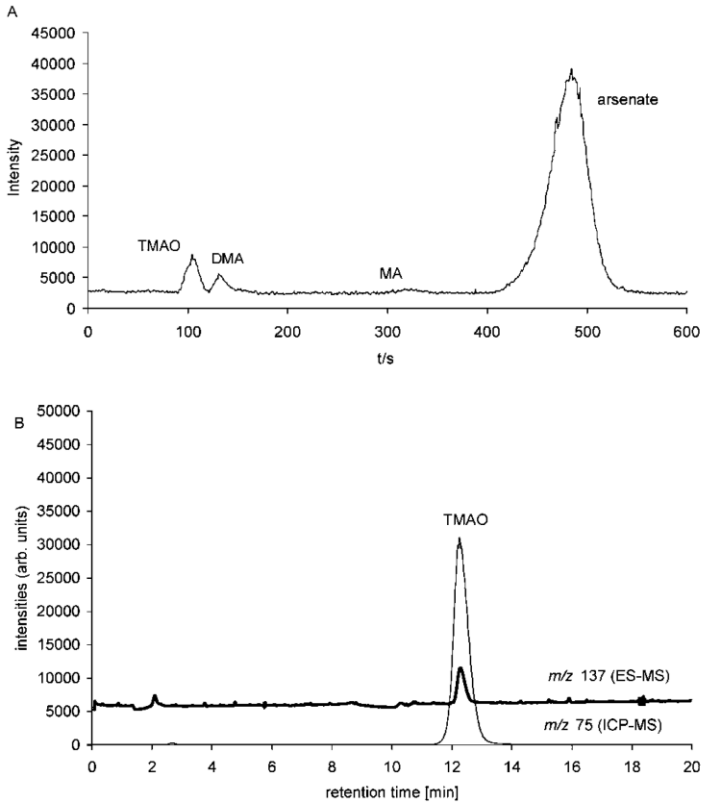

Fig. 4.8. PM10 extract measured by anion exchange ICP-MS is shown in (A) as m/z 75 (arsenic), while in (B) the identification of TMAO by cation exchange coupled to both ICP-MS (m/z 75) and by ES-MS (m/z 137) is shown (Jakob et al, 2010).

The LODs for this work considering the extraction procedure and the analytical methods were extremely low, of approximately 0.3 pg m^{-3}, which are the most sensitive in the consulted bibliography. When applied to PM10 samples, 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%).

By comparing this study with other mentioned studies that did not detected methylated As species in the air, it can be found a possible reason for the apparent discrepancy with those other analytical methodologies. The limits of detections provided by other authors for methylated As species (e.g. DMA and MMA) lie between 0.3 and 0.4 ng m^{-3} with HG-ICP-OES detection (Tsopelas et al, 2008) and 1.16-1.97 ng m^{-3} with AFS detection (Slejkovec et al., 2008), more than an order of magnitude than those reported by Jakob et al. (2010).

Also there are other reasons that can explain rather than the analytical technique employed for detection, for example the calibration graph considered for HPLC-ICP-MS is 5-30 mg l^{-1} (Jakob et al, 2010). However, there is no large difference between this value and other techinques values 1-10 mg l^{-1} with both HG-ICP-OES (Tsopelas et al, 2008) and AFS (Slejkovec et al, 2000).

Another reason is the different natural origin of the methylated As species. 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}. Also extraction procedure could be a possible reason, in PM samples from Argentine (Jakob et al, 2010) the whole filter was used for the extraction procedure, while only a portion is extracted (e.g. 1.2 cm^2 of a total of ca. 400 cm^2) (Sanchez-Rodas et al, 2007), three quarter section (Slejkovec et al, 2000), or a not specified portion (Tsopelas et al, 2008) usually with a larger volume of extractant, e.g. 10 ml of HCl, NH_2OH-HCl or $NH_4H_2PO_4$ solution.

Huang et al. (2014) studied the speciation of inorganic and methylated species of As in PM2.5 taken at Guanzhou (China) by HPLC-ICP-MS. 1'' x 8'' strip of the filter was extracted with 10-25 ml of a H_3PO_4 solution and submitted to microwave radiation during 20 min. Only inorganic species were detected in this work, no methylated species were found in PM2.5 samples. Anion exchange column was used in this study.

Another aspect that has 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 in one case (Jakob et al, 2010) the authors have confirmed the

identification of TMAO by cation exchange (retention time 12 min using a 50 mmol l^{-1} 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 (Yang et al, 2012), 4.0 ng m^{-3} in Guanzhou (Huan et al, 2014) or 1.2-2.1 ng m^{-3} in Huelva near a copper smelter (Oliveira et al, 2000; Sanchez-Rodas et al, 2007; Sanchez de la Campa et al, 2008) may be attributed to TMAO, which is produced at the pg m^{-3} by microbiological activity.

5. Results and discussion

5. Results and discussion

Los artículos que forman parte del apartado "Results and discussion" han sido retirados de la tesis debido a restricciones relativas a derechos de autor. En sustitución del artículo ofrecemos la siguiente información: referencia bibliográfica, enlace a la revista, y resumen.

-Alsioufi, L., Sánchez de la Campa Verdona, A.M., Sánchez Rodas, D.: "Microwave extraction as an alternative to ultrasound probe for antimony speciation in airborne particulate matter". Microchemical Journal. Vol. 124, págs. 256-260, (2016). DOI: 10.1016/j.microc.2015.09.004

Enlace al texto complete del artículo (solo para miembros de la UHU): https://doi.org/10.1016/j.microc.2015.09.004

RESUMEN:
An extraction method for Sb(V) and Sb(III) speciation in airborne particulate matter (PM) collected upon quartz filters has been developed, based on microwave extraction at 90 W with an 0.05 mol L− 1 hydroxylammonium chlorhydrate solution. The analysis of the extracts was performed by coupling high performance liquid chromatography (HPLC) with atomic fluorescence spectrometry (AFS). The parameters optimized were the volume of the extractant (5 or 10 mL, depending on the Sb concentration of the samples) and the time of extraction (6 min). The proposed microwave extraction method was compared to an existing one based on the use of ultrasound probe. Both extraction methodologies were applied to Sb spiked blanks (extracting solutions and quartz filters), and PM10 samples containing Sb collected at the city of Córdoba, an urban location of southern Spain. Similar and satisfactory results were obtained for spiked blanks with both methods. However, for PM10 samples quantitative results considering extraction efficiency (> 95%) were obtained only by the proposed method based on microwave extraction, higher than with ultrasound probe extraction (< 70%). Both Sb(V) and Sb(III) were found in the analyzed PM10 samples, Sb(V) being the main Sb species.

- Sánchez Rodas, D., Alsioufi, L., Sánchez de la Campa Verdona, A.M., González Castanedo, Y.: "Antimony speciation as geochemical tracer for anthropogenic emissions of atmospheric particulate matter". Journal of Hazardous Materials. Vol. 324, Part B, págs. 213-220, (2017). DOI: 10.1016/j.jhazmat.2016.10.051

Enlace al texto complete del artículo (solo para miembros de la UHU): https://doi.org/10.1016/j.jhazmat.2016.10.051

RESUMEN:

The chemical composition of airborne PM has been studied at the cities of Cordoba and Granada (South of Spain) between 2007 and 2013, considering four monitoring stations for PM10 sampling. Three monitoring stations were considered in Cordoba corresponding to urban background (Lepanto station), traffic (Alnasir station) and industrial estate (Parque Joyero station). The number of PM10 samples was 346 for Lepanto (obtained between 2007 and 2013), 20 for Alnasir (in 2013) and 221 for Parque Joyero (between 2012 and 2013). In Granada, 352 samples were obtained at Granada-Norte urban monitoring station (2007-2013), an area affected by heavy traffic. PM10 sampling was carried out by high volume samplers (68 m3 h−1) (model Grasseby-Andersen in Cordoba and model TISH in Granada). All PM10 samples corresponded to 24-hour periods, taken on a weekly basis. Quartz fibre filters (Munktell) were used to collect PM samples.

A half of each filter was digested with a mixture of HNO3, HF and HClO4 for the determination of a total of 47 major and minor elements by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Jobin Yvon ULTIMA2) and inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500).

Another filter portion (one quarter) was extracted with MilliQ-grade deionised water at 60 °C, and the major ions (SO42−, NO3−, Cl−and NH4+) content in the leachates were determined by ion chromatography (Dionex ICS-2500). The total carbon (Ctotal) content was determined using a LECO SC-144DR Instrument, using a 2.5 cm2 portion of the filter. Blank concentrations were subtracted for determining final concentrations in the samples. The analytical error was controlled and estimated by repeated analysis of certified reference material (NIST SRM 1633a fly ash). The error range for the elements was 5-10%.

In order to determine the contribution from the different sources to PM10 in each monitoring station of this study, a Principal Components Analysis (PCA) was performed with the obtained data according to source apportionment techniques and multilinear regression. This statistical study was performed for three of the four monitoring stations of the present study, with the exception of Alnasir, due to its small number of samples (only 20) for this station.

Another portion of each PM10 sample (1.2 cm2) was extracted for Sb speciation. The analytical procedure consisted of a liquid extraction with a NH2OH·HCl solution aided with microwave radiation, as it has been recently described for Sb speciation in PM samples. The Sb speciation analysis (Sb(III) and Sb(V)) of the liquid extract was achieved combining high performance liquid chromatography, hydride generation and atomic fluorescence spectroscopy (HPLC-HG-AFS), as it has been previously reported for PM samples. Of all the samples obtained at the study area, Sb speciation analysis was performed in those with significant Sb concentrations, higher than 3 ng m−3.

The results of PCA indicated that geochemical anomalies observed in the ambient air of Cordoba (mainly Cu, Zn, Pb and Cd) are closely related to the geochemical profile obtained from fugitive metallurgy emissions of the brass industries. These findings have been confirmed performing an Sb speciation analysis of PM10 samples, which allowed to distinguish between Sb(III) and Sb(V). The percentage of Sb(V) in PM10 found in the traffic station of Granada was 64-69%. At Cordoba, the percentage of Sb(V) was found to be higher (73-77%) at both urban backgroundand traffic stations,

indicating a possible second source of Sb in the PM of this city. The PM10 samples from the industrial station of Cordoba showed a 85-86% of Sb(V). A similar percentage (84-88%) of Sb(V) was found for the fugitive emissions of the brass industries, confirming this industrial source of Sb. These results show that Sb speciation can be a useful geochemical tracer to identify anthropogenic sources (traffic and industrial) emissions of PM.

-Sánchez Rodas, D., Sánchez de la Campa Verdana, A.M., Alsioufi, L.: "Analytical approaches for arsenic determination in air: A critical review". Analytica Chimica Acta. Vol. 898, págs. 1-18, (2015). DOI: 10.1016/j.aca.2015.09.043

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RESUMEN:

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 (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.

- Sánchez de la Campa Verdana, A.M., Sánchez Rodas, D., Alsioufi, L., Alastuey, A., Querol, X., Rosa Díaz, J.: "Air quality trends in an industrialised area of SW Spain. A success story." Journal of Cleaner Production. Vol. 186, págs. 465-474, (2018). DOI: 10.1016/j.jclepro.2018.03.122

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RESUMEN:
Copper smelters represent a major anthropogenic source of SO2 and sulphide-related elements into particulate matter, affecting the air quality of the surrounding areas. The implementation of measures to reduce the emission of gaseous contaminants and particles in industrial processes is a major issue, which aims to establish technological progress for cleaner production. In this sense, a long-range study covering the period 2001–2015 has been performed in the SW Spain, where one of the largest Cu-smelters in Europe is located. Trends of PM10 and PM2.5 levels and geochemical patterns were studied considering the following periods: prior (2001–2008), during (2009–2013) and after (2014–2015) the implementation of emission abatement technology (wet electrofilters, bag filters and lime injection) by this large industrial facility. The results evidenced relatively high concentrations of sulphide-related elements (annual mean of 6.1, 1.7, 0.7, 2.2, 2.0, 21.0 and 1.0 ng m−3 for As, Se, Cd, Sn, Sb, Pb and Bi, respectively) during 2001–2008. A reduction of 50% was observed for the last period (2.8, 0.5, 0.2, 1.6, 1.1, 6.7 an d 0.3 ng m−3 for the same elements, respectively) in PM10. A similar trend was observed for PM2.5 samples. However, the number of episodes of SO2 has not changed along the studied period (average 8 days/month), although the SO2 concentration during the pollution episodes has markedly diminished from maximum peak concentrations of 350 μg m−3 to 170 μg m−3. A high arsenic concentration is the main geochemical anomaly found in PM, reaching annual mean concentrations up to 10.4 ng m−3 in 2005 above the annual EU target value (6 ng m−3) in PM10, decreasing down to 2.7 and 2.9 ng m−3 in 2014 and 2015, respectively. However, sporadically high episodic levels are still recorded (e.g. 26.8 ng m−3 in 2014 and 14.9 ng m−3 in 2015).

5.1. Article 1

Microwave extraction as an alternative to ultrasound probe for antimony speciation in airborne particulate matter

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Resume of article 1: An extraction method for Sb(V) and Sb(III) speciation in airborne particulate matter (PM) collected upon quartz filters has been developed, based on microwave extraction at 90 W with an 0.05 mol l^{-1} hydroxylammonium chlorhydrate solution. Six PM10 (airborne particles with diameter 10 µm) samples were collected in southern Spain during 2011-2013. They belong to Air Quality Monitoring Network of the Andalusian Autonomous Government. Samples were collected by means of a Grasseby–Andersen high volume air sampler (68 m^3 h^{-1}) equipped with quartz glass microfiber filters (QF20S, Schleicher and Schuell) that retain the PM10 fraction.

Two samples corresponded to rural and urban sites in which Sb was not detected, and were selected for Sb spiking experiments. Also, four samples collected at the city of Cordoba with either high or low Sb concentration were analyzed for Sb speciation. Three of them corresponded to an urban background monitoring station influenced by traffic (Lepanto station), whereas the fourth one corresponded to an urban site with industrial influence (Parque Joyero station). They belong to a sampling campaign of 59 and 162 samples of PM10 performed at each monitoring station, respectively. Circular portions of 1.2 cm^2 of quartz filter samples containing the airborne PM10 were cut using a stainless steel hollow cylinder and placed in 50 ml polyethylene centrifuge tubes. $NH_2OH{\cdot}HCl$ 0.05 mol l^{-1} was used as extracting solution, trying volumes of 5 or 10 ml. The extraction was aided either by microwave radiation operated at 90 W between 2-6 min, or the use of an ultrasound probe with a 2 mm titanium tip, operated at 25-50 W between 30 s and 2 min. For total Sb determination of the samples, a portion of the filters containing PM were placed in a Teflon vessel and acid digested (HNO_3, HCl and HF) on a hot plate. The Sb determination was performed afterwards by ICP-MS.

Sample blanks were spiked using an Sb solution prepared in methanol, in order to optimize the extraction methodology. Two spiking procedures were considered. A first procedure was conducted by adding 100 µL of 1 mg l^{-1} solution containing both Sb(III) and Sb(V) in methanol to a circular portion of 1.2 cm^2 of quartz filter blanks or quartz filter samples containing airborne PM10. The samples were extracted afterwards with 5 ml of the extracting solution, either with microwave radiation or ultrasound probe. For the second procedure, the concentration of the Sb(III) and Sb(V) of the methanol spiking solution was increased from 1 ppm to 2 ppm. In this second case, the volume of the extracting solution was increased from 5 to 10 ml. The final concentration in the extracts was 20 µg l^{-1} for each Sb species.

The ultrasound probe was tried considering two operation powers of 25 W and 50 W with extraction volume of 5 ml and 10 ml. For an extraction with an operating power of 25 W, independently of the volume of extractants the extraction was not quantatively for the four spiked material, always lower than 70%, both at 30 s and 1 min. Also, it was observed

that using 5 ml of the extractant, the filters were partially decomposed during the sonication process after 60 s. If the volume employed was 10 ml, no damage was observed. Therefore, the operation power of the ultrasound probe was increased to 50 W to improve the extraction recovery, and the extracting volume was kept at 10 ml for further experiments. The spiked samples corresponding to an operation power of 50 W, 10 ml of extractant and different extraction times. It can be seen that for times of 60 s and 90 s, the extraction of Sb(V) was low (60%) while the Sb(III) extraction improved to 80%. An increase of the extraction time to 120 s provided quantitative results close to 100% for the blanks and over 90% for the samples. These latter conditions (50 W, 10 ml and 120 s) were selected for further PM sample analysis based on ultrasound probe extraction.

When employing microwave extraction, different extraction times were tested (2-6 min) in a microwave oven operated at 90 W. The results corresponding to 2 min extraction showed that the extraction recoveries were not quantitative; lower than 60% for both Sb(III) and Sb(V). When the extraction time was increased to 4 min, Sb(V) was effectively extracted in all the spiked samples, whereas Sb(III) extraction was still lower than 80%. Also, it was observed that extraction times greater than 3 min produced a partial damage of the filters, and loss of the extracting solution occurred due to boiling.

The extraction time in the microwave oven was increased to 6 min, applied either as (2+2+2) min or (3+3) min. The best results were obtained for the (2+2+2) min extraction procedure, with extraction recovery of 100% for the considered blanks and samples. For the second procedure using (3+3) min an partial oxidation of Sb(III) to Sb(V) was observed for the samples. Therefore, the extraction procedure with 5 ml of extractant and (2+2+2) min extraction was selected for the analysis of samples with low Sb content (< 10 ng m^{-3}). When the extraction time was increased to 6 min, either as (2+2+2)min or (3+3) min, the results were similar and satisfactory, with 100% recoveries for both blanks and samples.

The analysis of the extracts was performed by coupling high performance liquid chromatography (HPLC), hydride generation (HG) with atomic fluorescence spectrometry (AFS). The parameters optimized were the volume of the extractant (5 or 10 ml, depending on the Sb concentration of the samples) and the time of extraction (6 min). The proposed microwave extraction method was compared to an existing one based on the use of ultrasound probe. Similar and satisfactory results were obtained for spiked blanks with both methods. However, for PM10 samples quantitative results considering extraction efficiency (95%) were obtained only by the proposed method based on microwave extraction, higher than with ultrasound probe extraction (70%). Both Sb(V) and Sb(III) were found in the analyzed PM10 samples, Sb(V) being the main Sb species (65-85%).

5.2. Article 2

Antimony speciation as geochemical tracer for anthropogenic emissions of atmospheric particulate matter

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Quartile: Q1

Resume of article 2: The chemical composition of airborne PM has been studied at the cities of Cordoba and Granada (South of Spain) between 2007 and 2013, considering four monitoring stations for PM10 sampling. Three monitoring stations were considered in Cordoba corresponding to urban background (Lepanto station), traffic (Alnasir station) and industrial estate (Parque Joyero station). The number of PM10 samples was 346 for Lepanto (obtained between 2007 and 2013), 20 for Alnasir (in 2013) and 221 for Parque Joyero (between 2012 and 2013). In Granada, 352 samples were obtained at Granada-Norte urban monitoring station (2007-2013), an area affected by heavy traffic. PM10 sampling was carried out by high volume samplers (68 $m^3 h^{-1}$) (model Grasseby-Andersen in Cordoba and model TISH in Granada). All PM10 samples corresponded to 24-hour periods, taken on a weekly basis. Quartz fibre filters (Munktell) were used to collect PM samples.

A half of each filter was digested with a mixture of HNO_3, HF and $HClO_4$ for the determination of a total of 47 major and minor elements by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Jobin Yvon ULTIMA2) and inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500).

Another filter portion (one quarter) was extracted with MilliQ-grade deionised water at 60 °C, and the major ions (SO_4^{2-}, NO^{3-}, $Cl^-$and NH_4^+) content in the leachates were determined by ion chromatography (Dionex ICS-2500). The total carbon (Ctotal) content was determined using a LECO SC-144DR Instrument, using a 2.5 cm^2 portion of the filter. Blank concentrations were subtracted for determining final concentrations in the samples. The analytical error was controlled and estimated by repeated analysis of certified reference material (NIST SRM 1633a fly ash). The error range for the elements was 5-10%.

In order to determine the contribution from the different sources to PM10 in each monitoring station of this study, a Principal Components Analysis (PCA) was performed with the obtained data according to source apportionment techniques and multilinear regression. This statistical study was performed for three of the four monitoring stations of the present study, with the exception of Alnasir, due to its small number of samples (only 20) for this station.

Another portion of each PM10 sample (1.2 cm^2) was extracted for Sb speciation. The analytical procedure consisted of a liquid extraction with a $NH_2OH{\cdot}HCl$ solution aided with microwave radiation, as it has been recently described for Sb speciation in PM samples. The Sb speciation analysis (Sb(III) and Sb(V)) of the liquid extract was achieved combining high performance liquid chromatography, hydride generation and atomic fluorescence spectroscopy (HPLC-HG-AFS), as it has been previously reported for PM samples. Of all the

samples obtained at the study area, Sb speciation analysis was performed in those with significant Sb concentrations, higher than 3 ng m^{-3}.

The results of PCA indicated that geochemical anomalies observed in the ambient air of Cordoba (mainly Cu, Zn, Pb and Cd) are closely related to the geochemical profile obtained from fugitive metallurgy emissions of the brass industries. These findings have been confirmed performing an Sb speciation analysis of PM10 samples, which allowed to distinguish between Sb(III) and Sb(V). The percentage of Sb(V) in PM10 found in the traffic station of Granada was 64-69%. At Cordoba, the percentage of Sb(V) was found to be higher (73-77%) at both urban backgroundand traffic stations, indicating a possible second source of Sb in the PM of this city. The PM10 samples from the industrial station of Cordoba showed a 85-86% of Sb(V). A similar percentage (84-88%) of Sb(V) was found for the fugitive emissions of the brass industries, confirming this industrial source of Sb. These results show that Sb speciation can be a useful geochemical tracer to identify anthropogenic sources (traffic and industrial) emissions of PM.

5.3. Article 3

Analytical approaches for arsenic determination in air: A critical review

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Resume of article 3: 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 focuses on 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 ETAAS), as well those techniques capable of direct analysis of the solid sample (PIXE, INAA and XRF).

The PM sampling procedures employ air captors (flow rates ranging from 1 to 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 to several days.

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, whereas the U.S. EPA indicated the use of glass or quartz fibre filters for PM collection.

The material of the filter has to be free of impurities, and filters blanks have to be performed along with sample measurements standard pre-treatment procedure to remove impurities is to heat the filters before their use during several hours at few hundred degrees.

After PM sampling, the filters are summited in most case to a chemical treatment, depending on the analytical technique employed for As determination, usually atomic spectroscopy and/or mass spectrometry (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).

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 digestion of glass filters has been performed with HNO_3, heating in a sand bath or a heating block. For PTFE filters $HClO_4$ was used at room temperature in an ultrasonic bath, HNO_3:H_2O_2 mixture was also employed for PTFE filters 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. However, the use of HF is discouraged, due to its hazardous handling and also the use of $HClO_4$ due to the possible $Ar^{40}Cl^{35}$ interference with the same m/z 75 as As. 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.

As an alternative to sample digestion, arsenic can be extracted from the filters with acids, in order to reduce the time of sample treatment to few hours or minutes. EPA 3051A method consists of acid leaching of the sample with a HNO_3:HCl mixture assisted by microwave radiation. EPA 600/4-77-027a method employs a HNO_3:HCl mixture and an ultrasonic bath at 50 °C during 50 min. For PTFE filters, an extraction procedure has been proposed at room temperature with a mixture of HF:HNO_3, although the extraction time is long (4 days).

Another way to extract As from PM filters is samples sequntial extraction which aims to distinguish the distribution of elements among the different mineral fractions of soils. Two main procedures were used for this extraction, the first one is the Chester procedure which contains four extracting solutions for the following fractions: water soluble fraction (water), environmental mobile fraction (CH_3COONH_4 solution), bound to carbonate and oxides fraction (NH_2OH HCl solution) an organic and refractory associated fraction (HNO_3:HF:H_2O_2 solution). The second procedure is the BCR methodology (Bureau of Certificate and Reference), which considers also four fractions: acid soluble (CH_3COOH solution), reducible fraction (NH_2OH HCl solution), oxidable fraction (H_2O_2 solution followed by CH_3COONH_4), and residual (aqua regia digestion).

All the analytical methods that were employed along the last four decades for As determination in atmospheric samples are summarized, most of them based on different types of atomic spectroscopy and also mass spectrometry such as colorimetry, hydride generation atomic absorption spectroscopy, electrothermal-atomic absorption spectroscopy (ET-AAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectroscopy (ICP-OES) and direct techniques (PIXE, INAA and XRF).

In the case of As speciation, several extractants have been used in order to extract As(III), As(V) and organic species of As, such as NH_2OH HCl and H_3PO_4 solutions with the aid of

microwave radiation or sonication. Some authors used HCl with stirring at room temperatures but this method takes a relative long time of the extraction (2 h), compared to others based on microwave or sonication in which the extraction time is of few minutes.

There are a few As speciation studies that used a selective extraction, as it does not aim to extract all the As species in a single extraction step. As an example some authors employed 3 steps procedure with 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 and higher for $CaCl_2$+H_3PO_4.

Many analytical thecniques are used to determine As species. In this review a summary of these techniques and some studies that used them are explained. These techniques are: hydride generation and/or cold trap-atomic spectroscopy, high performance liquid chromatography-hydride generationatomic/mass spectrometry, high performance liquid chromatography-inductively coupled plasma-mass spectrometry. For inorganic species a crytotrap has been used, in which the volatile arsines are collected and carried afterwards to a cryofocusing unit of a GC-ICP-MS.

For As determination several CRM are employed. Most studies employing at least one of the following CRMs: NIST SRM 1648 (urban particulate matter, certified value for As 115.5±3.1 mg kg^{-1}), NIST SRM 1649a (urban dust, certified value for As 67±2 mg kg^{-1}) and NIST SRM 1633b (fly ash, certified value for As 136.2 ± 2.6 mg kg^{-1}). The purpose of QA/QA procedures is to minimize random and systematic errors related to the different steps involved in the analytical process. 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.

5.4. Article 4

Air quality trends in an industrialised area of SW Spain. A success story.

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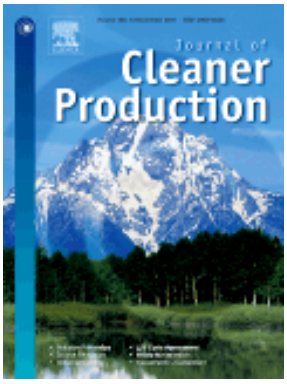

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Resume of article 4: The air quality of the city of Huelva (SW Spain), nearby one of the largest Cu-smelters in Europe, has been evaluated during the period 2001-2015. The geochemical composition of PM10 and PM2.5 samples was studied, as well as the SO_2 concentration in ambient air, considering three periods: prior (2001-2008), during (2009-2013) and after (2014-2015) the implementation of emission abatement technology (wet electrofilters, bag filters and lime injection). A total of 866 samples of PM10 and 805 samples of PM2.5 were obtained during the study period. Samples were acid digested, and major and minor elements were determined by ICP-MS and ICP-OES, respectively.

The SO_2 levels registered in Huelva are mainly related to the activity of Cu-smelter. Although the SO_2 concentration were below the legal limit (3 times per year of SO_2 > 125 μg m^{-3}/day; 24 times per year of SO_2 >350 μg m^{-3} SO_2/hour), there are daily impacts with concentrations above 20 μg m^{-3}. The number of daily impacts of SO_2 in Huelva has not changed along the studied period (average 8 days/month), although the concentration of the SO_2 during the impacts has markedly diminished from maximum peak concentrations of 350 μg m^{-3} to 170 μg m^{-3}.

The results obtained indicate high concentrations of sulphide-related elements (annual mean of 6.1, 1.7, 0.7, 2.2, 2.0, 21.0 and 1.0 ng m^{-3} for As, Se, Cd, Sn, Sb, Pb and Bi, respectively) in the PM10 samples collected in Huelva during 2001-2008. In the period 2014-2015 after the improvement of the emission control, a reduction of 50% or better was observed (2.8, 0.5, 0.2, 1.6, 1.0, 6.7 and 0.3 ng m^{-3} for the same elements, respectively) in PM10. In addition to mean values, the maximum concentrations of these elements in PM10 were also markedly lower for the 2014-2015 than for the 2001-2008 period.

Asimilar trend was observed for mean and maximum concentration of sulphide-related elements in PM2.5 samples. The results confirm that they concentrate preferentially in the fine fraction (ca. 50-75%) in comparison to the coarse fraction.

A seasonal variation observed for the concentration of the sulphide-related elements in PM. The maximum concentrations of As, Cd, Se, Bi are always found for summer and spring in PM10 for the studied period. This variation is not related to changes in the operation of the Cu-smelter, which is the same throughout the year, but to the meteorological conditions. As the sulphide-related elements are associated to the SO_2 registered in Huelva, they follow a similar seasonal trend, with maximum concentrations found in summer associated to sea breeze and North African dust outbreaks.

Arsenic is the main geochemical anomaly found in PM of Huelva, reaching annual mean concentrations up to 10.4 ng m^{-3} in 2005 above the target value (6 ng m^{-3}), decreasing to 2.7 and 2.9 ng m^{-3} in 2014 and 2015, respectively. However, further monitoring studies in

Huelva are required, as high As events are still registered above the target value (e.g. 26.8 ng m^{-3} in 2014 and 14.9 ng m^{-3} in 2015).

Arsenic speciation analysis showed that inorganic As(V) represents the main arsenic species in the PM samples (>90%) in relation to As(III). The trend in the studied period indicates a reduction in the proportion of As(V) in PM10 from 97% in 2010 to 90% in 2014. This reduction in the percentage of As(V) is due to a decrease of the concentration of As(V), not to an increment of As(III). Nevertheless, episodes with a high As(III) proportion (50%) are still registered.

6. Conclusions

6. Conclusions

The main conclusions of the thesis are:

1. A new method for Sb extraction in PM samples has been developed, based on the use of microwave radiation (operated at 90 W during 3-6 min) with a 0.05 mol l^{-1} $NH_2OH{\cdot}HCl$ solution. The analysis of the extracts was performed by coupling high performance liquid chromatography (HPLC), hydride generation (HG) with atomic fluorescence spectrometry (AFS). Extraction by microwave radiation was compared to ultrasound probe extraction.

The proposed extraction method for Sb speciation in atmospheric particulate matter based on microwave extraction represents a suitable alternative to ultrasound probe extraction. It has additional advantages in comparison to ultrasound probe method. The first one is that it is suitable for samples with rather low concentration of Sb. A second advantage is the easy and safe use of the microwave oven compared to the ultrasound probe, which produces a high frequency and disrupting noise during its operation that can be harmful and a possible health hazard for the operator. Overall, the extraction time with microwave radiation is in the same range as the ultrasound probe, although a little bit longer (6 min compared to reported 3 min).

2. The proposed extraction method has been applied to PM10 samples of Cordoba and Granada, collected from 4 monitoring stations of different categories: one corresponds to urban background (Lepanto station in Cordoba), two to traffic influence (Alnasir station in Cordoba and Granada Norte in Granada) and one to industrial influence (Parque Joyero station in Cordoba).

Sb speciation analysis of the samples indicated a different distribution of Sb(V) and Sb(III) depending on the type of monitoring station. At the industrial station Sb(V) reached 85-88% (Parque Joyero) while at the urban station (Lepanto) Sb(V) was between 74-77%.. At the traffic station of Al Nasir Sb(V) was 73%, higher that the observed Sb(V) observed in Granada Norte (64-69%). This later result indicates the influence of the industrial source on the other monitoring stations of Cordoba. These results show that Sb speciation can be a useful geochemical tracer to identify anthropogenic sources.

3. It has been performed a thorough revision of the state of the art of As in atmospheric particulate matter, considering analytical steps such as sampling, sample treatment, and analysis of both total and speciation at different particle size has been performed. Sample digestion of the collecting media of PM for total As has been described, indicating proposed and established procedures that use acids or mixtures of acids aided with different heating

procedures. The most common detection techniques are summarized and compared (ICP-MS, ICP-OES and ETAAS), as well those techniques capable of direct analysis of the solid sample (PIXE, INAA and XRF).

For As speciation, mild aqueous extractants are employed, usually in a single extraction step, although sequential extraction procedures have been also described. The common procedure for As speciation analysis is the combination of a separation technique (HPLC and to a minor extend also GC) with atomic spectroscopy detectors (AAS, AFS and ICP-OES) or mass spectrometry (ICP-MS). Intermediate steps that use hydride generation or cold trap are also employed in As speciation analysis. Results about total As and As speciation analysis around the world have summarized, indicating the study area, levels or arsenic, size fraction of PM and analytical methodology employed.

4. A study about the air quality of Huelva, located nearby on the largest Cu-smelter in Europe, has been performed for the period 2001-2015. The trends of SO_2 and geochemical pattern of PM2.5 and PM10 were studied. Three periods were selected: prior (2001-2008), during (2009-2013) and after (2014-2015) the implementation of emission abatement technology (wet electrofilters, bag filters and lime injection) by this large industrial facility.

A high As concentration is the main geochemical anomaly in PM of Huelva. In the period 2001-2008, prior to the implementation of current high efficient emission controls in this industry, high levels of sulphide-related elements (As, Se, Cd , Sn, Pb and Bi) were recorded, which resulted in the repeatedly exceedances of the EU annual target value of As concentration of 6 ng m^{-3}. In the latest period 2014-2015, a -50% reduction or higher was observed for these elements, which in the case of As resulted in mean concentration of 2.8 ng m^{-3} in PM10. A similar behavior was observed for PM2.5 samples. However, there are still sporadic (less intensity) As and SO_2 pollution episodes.

Furthermore, As speciation analysis of PM10 and PM2.5 samples with HPLC-HG-AFS has point out that As is present mainly as As(V) (>90%) in relation to As(III) (<10%). The trend in the studied period indicates a, reduction in the proportion of As(V) in PM10 from 97% in 2010 to 90% in 2014. This reduction in the percentage of As(V) is due to a decrease of the concentration of As(V), not to an increment of As(III). Nevertheless, episodes with a high As(III) proportion are still registered.

6. Conclusiones

Las principales conclusiones de la tesis son:

1. Se ha desarrollado un nuevo método de extracción para la especiación de Sb en muestras de PM, basado en el uso de radiación de microondas (operado a 90 W durante 3 minutos) con una disolución $NH_2OH{\cdot}HCl$ 0.05 mol l^{-1}. El análisis de los extractos se realizó mediante acoplamiento de cromatografía líquida de alta resolución (HPLC), generación de hidruros (HG) y espectroscopia de fluorescencia atómica (AFS). Se comparó la extracción con microondas con la extracción por sonda de ultrasonidos.

El método propuesto de extracción que emplea microondas representa una alternativa adecuada a la extracción por sonda de ultrasonidos. Tiene además varias ventajas adicionales, como son ser adecuada para muestras con bajas concentraciones de Sb, uso fácil y seguro en contraposición con el ruido de alta frecuencia que produce la sonda de ultrasonidos. De manera general, el tiempo de extracción mediante radiación de microondas está en el mismo rango que la sonda, aunque es algo superior (6 minutos frente a 3 minutos).

2. El método propuesto de extracción se ha aplicado a muestras de PM10 de Córdoba y Granada, obtenidas de 4 estaciones de muestreo de varias categorías: una corresponde a fondo urbano (estación de Lepanto en Córdoba), dos a estaciones con influencia de tráfico (estación de Alnasir en Córdoba y de Granada Norte en Granada) y una estación con influencia industrial (Parque Joyero en Córdoba).

Los resultados de los análisis de especiación de Sb mostraron una distribución de Sb(V) and Sb(III) que dependía de la estación de muestreo. En la estación industrial el Sb(V) alcanzó un 85-88% (Parque Joyero) mientras que en la estación urbana (Lepanto) el Sb(V) representó entre 74-77%. En la estación de tráfico de Alnasir la proporción de Sb(V) fue del 73%, superior a la observada en la estación de tráfico de Granada Norte (64-69%). Este último resultado indica la influencia de la fuente industrial en las otras estaciones de muestreo de Córdoba. Los resultados obtenidos muestran que la especiación de Sb puede ser un trazador geoquímico útil para identificar fuentes antropogénicas.

3. Se ha realizado una revisión bibliográfica detallada sobre As en material particulado atmosférico, considerando diferentes etapas del proceso analítico, como son el muestreo y el análisis tanto del As total como el análisis de especiación de As referido a distintos tamaños de partícula. Se ha descrito los procedimientos de toma y digestión de la muestra para la determinación del As total, indicando procedimientos establecidos y propuestos

que usan ácidos o mezclas de ácidos, en combinación con diferentes maneras de calentamiento. Se han resumido y comparado las diversas técnicas de detección más comunes (ICP-MS, ICP-OES y ETAAS), así como aquellas técnicas de análisis directo de las muestras sólidas (PIXE, INAA y XRF).

En el caso del análisis de especiación se emplean extractantes acuosos, generalmente en una única etapa de extracción, aunque también se han descrito esquemas de extracción secuencial. El procedimiento de análisis más común combina una técnica de separación (principalmente HPLC y en menor grado GC) con detectores de espectroscopia atómica (AAS, AFS y ICP-OES) o espectrometría de masas (ICP-MS). Se suelen emplear también etapas intermedias en el análisis, como la generación de hidruros o la trampa fría. La revisión bibliográfica realizada considera también un resumen de determinación de As total y especiación de As en muestras en diversas partes del mundo, indicando la zona de estudio, niveles de As, tamaño de partícula de PM y metodología analítica empleada.

4. Se ha realizado un estudio de la calidad del aire en Huelva, que está situada junto a uno de las mayores fundiciones de Cu de Europa. El periodo estudiado fue 2001-2015, considerando la tendencia en los niveles de SO_2 y la composición geoquímica de PM2.5 y PM10. Se seleccionaron tres periodos de estudio: antes (2001-2008), durante (2009-2013) y después (2014-2015) de la aplicación de medidas correctoras de emisiones (electofiltros húmedos, filtros de manga e inyección de cal) por parte de esta instalación industrial

La principal anomalía geoquímica del PM de Huelva es una alta concentración de As. En el periodo 2001-2008 registraban altas concentraciones de elementos asociados a los sulfuros que se emplean como materia prima en la fundición de cobre (As, Se, Cd, Sn, Pb y Bi), con el resultado de concentraciones de As superiores al valor anual establecido por la Unión Europea, de 6 ng m^{-3}. En el último periodo 2014-2015, se observó una reducción del 50% o mayor para dichos elementos, que en el caso del As supuso un valor medio de 2.8 ng m^{-3} en PM10. Un comportamiento similar se obtuvo para las muestras de PM2.5. A pesar de las mejoras, todavía se registran en Huelva episodios menos intensos tanto de As en PM como de SO_2.

Los estudios de especiación de As en PM10 y PM2.5 mediante HPLC-HG-AFS mostraron que el As se encuentra mayoritariamente como As(V) (>90%) en relación con el As(III) (<10%). La tendencia del periodo estudiado indica una reducción en el porcentaje del As(V) en PM10 del 97% in 2010 a 90% en 2014. Esta reducción se debe a una disminución de la concentración de As(V), no a un aumento en la del As(III), aunque todavía se registra episodios con alta proporción de As(III).

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