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Procedia Environmental Sciences 4 (2011) 209–217

Procedia
Environmental Sciences

Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter

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Received date September 30, 2010; revised date January 30, 2011; accepted date January 30, 2011

Abstract

A reliable method able to separate and quantify Sb(III) and Sb(V) species by ion chromatography - inductively coupled plasma - mass spectrometry (IC-ICP-MS) was applied to PM samples from brakes, major source of antimony in coarse particles, and to atmospheric PM₁₀ and size segregated samples. For brake samples we obtained recovery percentages of the IC-ICP-MS vs. ICP-MS analysis close to 100%. In PM samples the two inorganic species were detected only in the coarse fraction. The low recovery percentages obtained for fine particles suggest the presence of nano-particles aggregates in the analysed solutions, which are retained by the chromatographic column.

© 2011 Published by Elsevier BV Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).*Keywords:* Airborne particulate matter; antimony; nano-particle aggregates; size-segregated samples; ion chromatographic separation.

1. Introduction

Antimony is an emerging element of environmental concern because of its alarming concentration increase observed during the last years [1-3]. This is due to the current extensive industrial use of antimony, e.g. antimony compounds are employed in the production of glassware and ceramics, in brake linings and in electronic components. Recently, a high number of studies about the environmental relevance of this element have been published, even though many questions about its chemistry remain unanswered [4].

It is known that the oxidation state influences the physiological and toxicological behavior of antimony, as well as of other elements (e.g. As). Just like As, Sb(III) is more toxic than Sb(V) and Sb₂O₃ is considered suspected of being carcinogenic in humans by the International Agency for Research on Cancer (IARC) [5].

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Antimony is generally released to the atmosphere in the form of particulate matter (PM); it is the trace metal at highest concentration in urban atmospheres and in the major cities of the world its enrichment factor in coarse particles has shown a high increase [6-9]. It is well known that the study of atmospheric particle size distribution may give information about particle formation pathways and particle sources [10, 11]. Sb is contained into brake pads in the form of Sb_2S_3 , used as a lubricant to reduce vibrations and to improve friction stability, and is released into the environment during breaking. This process constitutes the main source of Sb in the coarse fraction of PM. Forest fires, volcanic eruptions and waste incineration are the main sources of Sb in the fine fraction of PM [12-14]. A comparison of the size distribution of Sb in rural [15] and urban [10-11,16] atmospheres is reported in Figure 1. As expected, at rural sites Sb is present mainly in particles with an aerodynamic diameter (AD) < 1 μm , while at urban sites Sb is present both in the fine and the coarse mode.

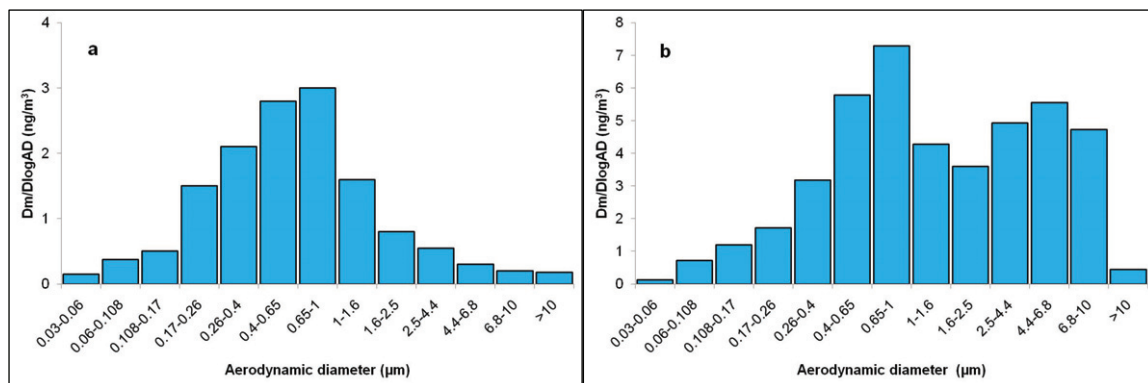


Figure 1: Size distribution of Sb in a rural area (a) and in a urban area (b).

Generally, all the studies regarding the separation between Sb(V) and Sb(III) in environmental matrices have been carried out by using hyphenated techniques. In aquatic matrices, these studies revealed a prevalence of Sb(V) due to aquatic microorganisms converting Sb(III) to Sb(V) [17].

To our knowledge, the identification and the quantification of the antimony species in real samples of atmospheric particulate matter has been attempted only in a few research works. Zheng et al., using an HPLC-ICP-MS method, detected the predominance of the Sb(V) form [18-21]. On the contrary, Smichowski et al. [22], by means of an ultrasound probe-assisted fast extraction followed by HPLC-HG-AFS analysis, detected both Sb forms in PM_{10} samples. Recently, Iijima et al. [23] applied a HPLC-ICP-MS method to PM samples collected by a multi-stage impactor. Their results showed that Sb(III), produced by brake abrasion, is predominant in the coarse fraction while Sb(V) is distributed in both fine and coarse particles. In addition, these Authors found non-negligible amounts of an unknown antimony species in the fine extracted fraction.

The aim of the present work is the application of a new fast analytic method for the determination of Sb(III) and Sb(V) to different PM samples. The method is based on the efficient ultra-sound assisted extraction of antimony from PM and on the determination of Sb(III) and Sb(V) by ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS). It has been applied to PM_{10} filters and to size-segregated PM samples collected at an urban site. Furthermore, in order to assess the distribution of the two Sb species in the major source of Sb coarse particles, the analytical separation was applied to brake pads dust obtained by mechanical abrasion.

2. Experimental

2.1 Particulate matter sampling procedure

Bulk dust samples were obtained from three kinds of brake pads (powdered by abrasion), from the brake linings of a car and from the dust deposited on the side of an urban road close to the PM sampling site. Three samples were obtained for each kind of dust. Before the analysis, all dust samples were sieved (inox Retsch) to get particles lower than 63 μm in size.

Fifteen pairs of equivalent PM₁₀ samples were collected for 48 h on 47 mm diameter PTFE membranes (1 mm pore size; PALL Corporation, U.S.A.) at a traffic site in the urban area of Rome, Italy. A dual-channel sampler (Hydra, FAI-Instruments, Fontenuova, Rome - Italy), a sequential instrument able to sample on two independent channels, was used for this study; it was configured with a single PM₁₀ head, compliant with the EN12341 standard and operating at a flow rate of 2.3 m³ h⁻¹; incoming air was then divided between the two channels, obtaining two equivalent PM samples. The performance of the method was assessed by applying the procedure to pairs of equivalent real PM₁₀ samples, as suggested in UNI EN 14902 [24].

At the same site, a 13-stage low-pressure impactor (DLPI, DEKATI Ltd., Tampere, Finland) was run during a period of 15 days. The instrument operates at the flow rate of 10 L min⁻¹ and at the pressure of 100 mbar under the last impactor stage. The nominal values for the equivalent aerodynamic 50% cut-off diameters of the stages are: 10, 6.8, 4.4, 2.5, 1.6, 1.0, 0.65, 0.40, 0.26, 0.17, 0.108, 0.060, and 0.030 µm. PTFE membranes, 25 mm diameter, (ALBET, Barcelona, Spain) were used as substrates on the collection plates of the impactor.

2.2. Analytical procedure

All the samples were placed in polyethylene tubes and extracted in ultrasonic bath (Falc Instruments, Treviglio (Bg), Italy). A tailor-made rotating device assured the homogeneity of the ultrasonic irradiation. A solution of ethylenediaminetetraacetic acid (EDTA) and potassium hydrogen phthalate (KHP) was employed to extract Sb from the samples. The extraction efficiency (see Table 1) of this solution was evaluated as percent recovery of extractable Sb/total Sb, obtained by microwave-assisted acid digestion in HNO₃/H₂O₂ [25]. All the reported results refer only to the Sb fraction that is extractable in mild conditions, as the acidic digestion needed to obtain a quantitative Sb recovery would have altered the distribution of the Sb species in the sample.

The extracted solutions were filtered by using a cellulose nitrate filter (Millipore, 25 mm diameter, 0.45 µm pore size) and analyzed both by inductively coupled plasma-mass spectrometry (ICP-MS) to determine total extractable Sb concentration, and by ion chromatograph (IC) coupled to ICP-MS to determine Sb(III) and Sb(V) concentration. The IC employed was a Metrohm mod. 761 Compact (Metrohm, Origgio (Va), Italy) equipped with a 100-µl loop and an anion exchange column (Metrosep Supp 5, 150 mm, particle size 5 µm); the ICP-MS was a Varian 810 (Mulgrave, Australia). Working conditions are reported in Table 1. More details about the optimization of the experimental conditions are described in ref. [26].

Table 1: Summary of the experimental condition used for the analyses.

Extraction solution	2.5 ml EDTA 5 mM/KHP 0.5 mM at pH 4.5. Sb efficiency extraction: 75±3% Extraction time: 20 min
Ion Chromatography (IC) conditions	Isocratic elution Flow rate: 0.7 mL/min Total elution time: 6 min;
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) conditions	Nebulizer: cross-flow Varian Micromist RF forward power: 1,200W Plasma Ar flow rate: 15.0 L min ⁻¹ Auxiliary Ar flow rate, 1.20 L min ⁻¹ Nebulizer Ar flow rate, 1.090 L min ⁻¹ Data acquisition mode: time resolved analysis Isotope monitored: ¹²¹ Sb

Figure 2 briefly summarizes the application of the method: all the extracted samples were divided in two aliquots: one was analyzed by ICP-MS to obtain total extractable Sb concentration and the other one was injected in the chromatographic column and analyzed by ICP-MS to obtain the concentration of the two inorganic Sb species. In this work the recovery percentage of IC-ICP-MS vs. ICP-MS was evaluated comparing the sum of the measured concentrations of Sb(III) and Sb(V) with the direct measurement of total extractable Sb.

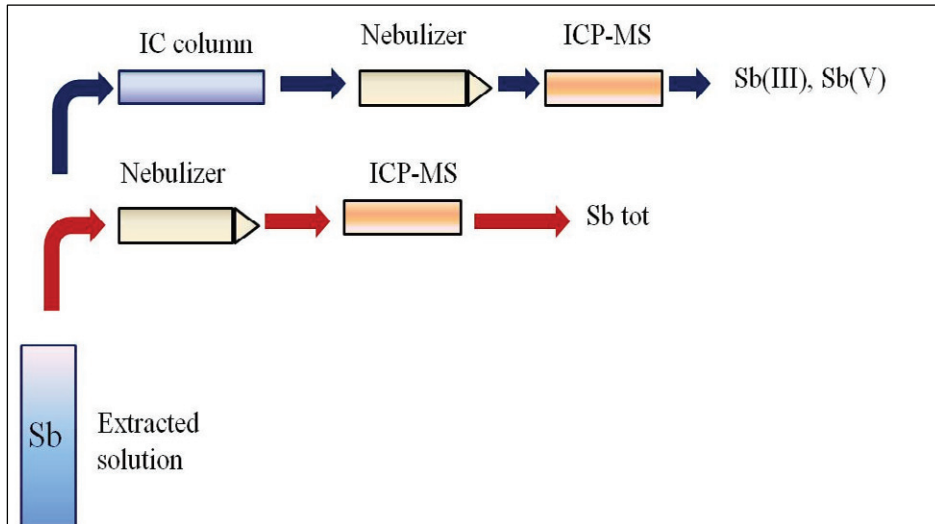


Figure 2: Scheme of the method for the determination of total extractable Sb, Sb(III) and Sb(V).

The instrumental limit of detection (LOD_{instr}), the limit of detection of the atmospheric concentration, the analytical repeatability and the linearity range of Sb(III) and Sb(V) determinations are reported in Table 2.

Table 2: Analytical parameters of Sb(III) and Sb(V) separation in standard solutions.

Instrumental limit of detection (LOD_{instr})	2 $\mu\text{g/L}$
Limit of detection for atmospheric concentrations	0.1 ng/m^3 for PM_{10} samples 0.02 ng/m^3 for size-segregated PM samples
Analytical repeatability (50 $\mu\text{g/L}$ standard solution)	3%
Linearity range	5–100 $\mu\text{g/L}$

3. Results and Discussion

3.1. Application to PM samples from brakes

Being vehicular traffic the main urban source of antimony in coarse particles (release from brake pads and road dust re-suspension [27]), we first applied the method to dust samples obtained by abrasion of two different types of new brake pads, by collection from a car braking system and by collection of road dust.

For these samples the recovery was close to 100%, indicating that coarse particles produced by brake pad abrasion and road dust re-suspension contain extractable Sb almost totally in the inorganic forms Sb(III) and Sb(V). The chromatograms of the analyzed samples, reported in Figure 3, show that Sb(III) is the predominant form in brake pads, as a consequence of Sb_2S_3 use in blendings, while Sb(V) is predominant in dust from brake linings and in road dust. Among the three type of samples, dust from brake pads abrasion showed the highest total Sb concentration, while it decreased in dust from the car braking system and much more in road dust (which includes different contributes such as soil and brake linings).

Comparing our data with the results of brake pad dust analyses reported in a recent paper of Iijima et al. [23], a substantial equivalence of the total extractable Sb amount was found, while Sb(III) and Sb(V) concentrations were rather different. This is probably due to the fact that in our case brake pad samples were obtained by cold abrasion

while in the case of [23] they were generated by using a brake dynamometer and simulating typical urban driving conditions. These results seem to indicate that the conversion of Sb(III) to Sb(V) is mainly driven by the temperature reached by the pad during the braking process.

An unidentified peak (retention time: 2.8 min) was observed in some of the chromatograms. This peak, detected also in some PM₁₀ samples, is responsible of very small Sb concentrations and its identification will deserve further investigations.

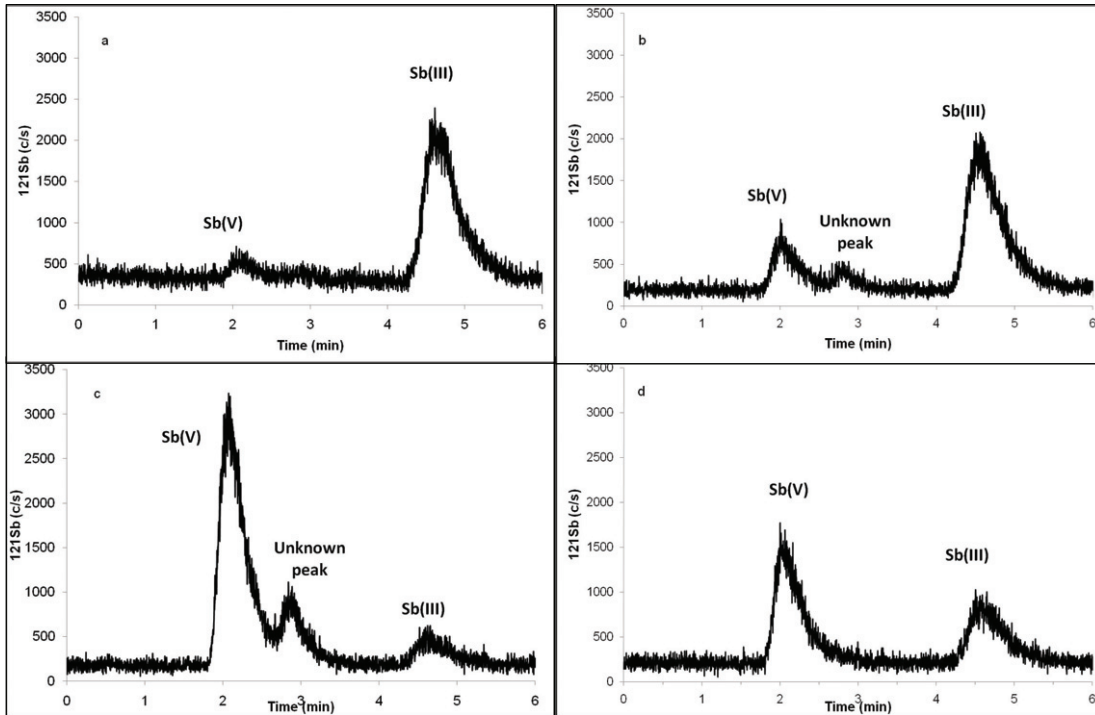


Figure 3: Separation of Sb(III) and Sb(V) by IC-ICP-MS in different samples: a-b) two different types of brake pads, c) dust from a car braking system d) road dust.

3.2. Application to real PM samples

The procedure was then applied to fifteen PM₁₀ sample pairs: in most samples both Sb(III) and Sb(V) species were detected. It is worth considering that in some cases Sb(III) concentration exceeded Sb(V) and that the ratio Sb(III)/Sb(V) ranged from 0 to 1.5. This variability may be either a consequence of the daily variation of PM concentration, due to different emission sources contribution, or a result of the possible oxidative conversion of Sb(III) to Sb(V).

In order to study the spontaneous oxidative conversion between the two species in atmosphere, as a result of aging processes, three pairs of equivalent PM₁₀ samples were subjected to different storage conditions. Briefly, one sampled filter was kept in sealed containers at 5°C in the absence of natural light, while the other one was exposed to daylight and ambient air for ten days. We report in Figure 4 the chromatograms of two equivalent PM₁₀ samples: the difference between exposed and unexposed sample is negligible, suggesting that in atmosphere the oxidation of Sb(III) is insignificant, in contrast with the results from other environmental matrices [17].

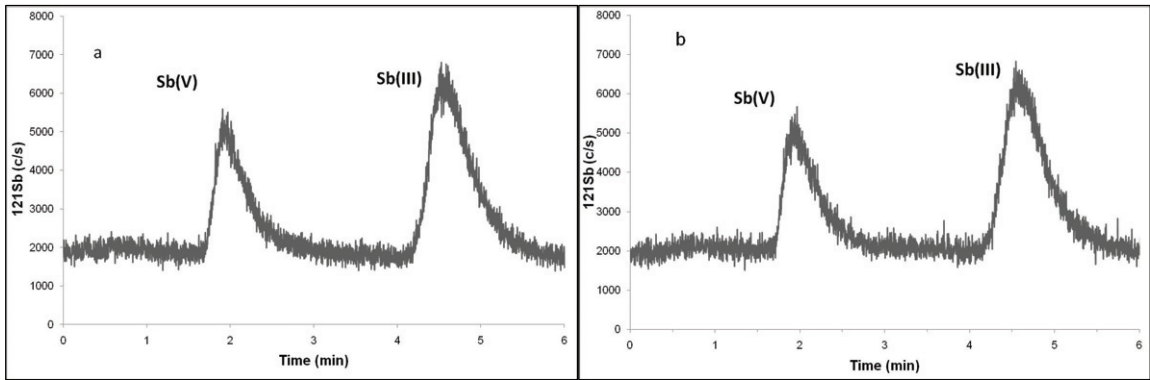


Figure 4: Determination of Sb(III) and Sb(V) by IC-ICP-MS in two members of a PM₁₀ pair: one kept in the dark and refrigerated (a) and the other one exposed to ambient air and natural light.

As described in the experimental section, the extracted solutions were separated in two aliquots: one analyzed by ICP-MS and the other one by IC-ICP-MS. Comparing the sum Sb(V)+Sb(III) determined by IC-ICP-MS with the total extracted Sb concentration determined by ICP-MS, we obtained highly variable recovery percentages, ranging from 10% to 70%. On the other hand, the repeatability of the results from filter pairs was satisfactory (percent difference lower than 20%). The concentrations of total extractable Sb, Sb(III) and Sb(V) in atmospheric PM₁₀ samples are graphically reported in Figure 5.

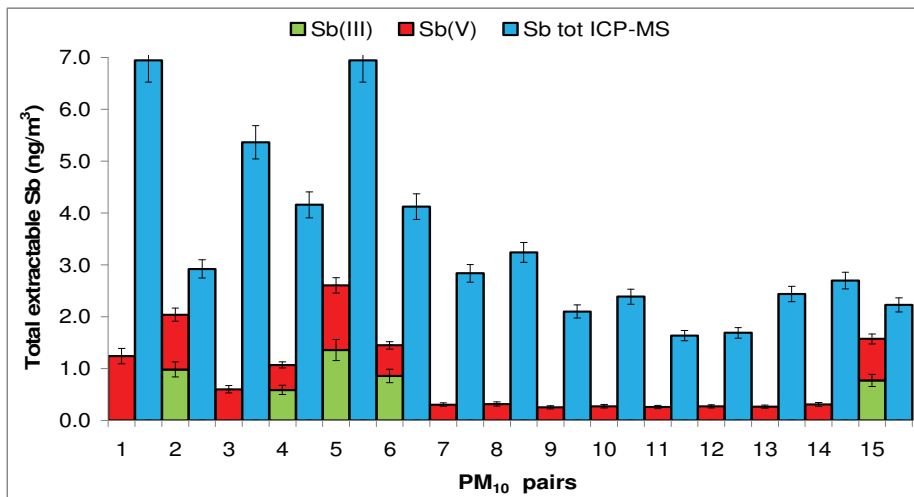


Figure 5: Determination of total extractable Sb (light blue bar), Sb(III) (green bar), Sb(V) (red bar) in fifteen real PM₁₀ pairs. Error bars indicate the difference between the two members of each PM₁₀ equivalent sample pair.

The presence of other soluble Sb forms was excluded by carrying out other experimental trials in different chromatographic elution conditions and extraction conditions: none of these changes influenced the results.

To obtain more information about the different behavior of total extracted Sb and Sb(III)–Sb(V) forms, the method was applied to size-segregated samples collected by a 13-stages impactor. The study of Sb dimensional distribution, reported in Figure 6, shows very different results: total extractable Sb showed a typical bimodal pattern, while Sb(III) and Sb(V) were almost exclusively in the coarse mode.

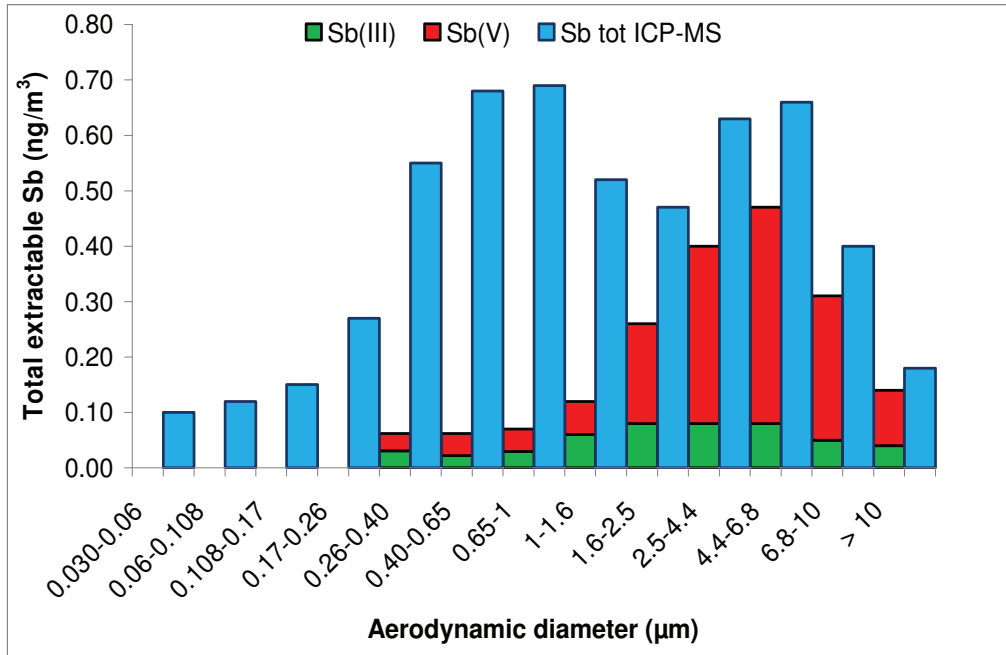


Figure 6: Size distribution of total extractable Sb (light blue bar), analysed by direct ICP-MS, and Sb(V) (red bar) and Sb(III) (green bar) analyzed by IC-ICP-MS.

The overall recovery percentages of the IC-ICP-MS vs. ICP-MS analysis were comparable to the results obtained from PM₁₀ samples. However, this recovery was below 10% for fine particles and increased up to about 80% for coarse particles. It can be noted that the size distributions obtained by ICP-MS and IC-ICP-MS are very different and the values from ICP-MS analysis show a typical bimodal pattern [10-11,16], while Sb(III) and Sb(V) are almost completely in the coarse mode particles.

As most of the sources contributing to the atmospheric fine fraction of Sb may be considered also responsible for nano-particles emission [28], we checked the existence of Sb-containing solid nano-particles suspended in the extracted solutions. The ultrasound assisted extraction, in fact, could reasonably break up nano-particles aggregates; then, during the filtration with the 0.45 µm membrane, the smaller aggregates would pass through the filter pores. In the case of direct ICP-MS analysis nano-particles and small aggregates would then be able to reach the plasma torch, allowing the measurement of the total Sb content; in the case of IC-ICP-MS analysis, instead, they would be retained by the chromatographic column, allowing the measurement of water-soluble Sb species only. This mechanism could explain the low recovery obtained for the fine fraction of Sb.

The presence of suspended nano-particles in the filtered solution was confirmed by light scattering measurements (Zetasizer NanoZS, Malvern Instruments, England). Further confirmation was obtained by using membranes having different porosity for the filtration step. Five equivalent pairs of PM₁₀ samples were extracted and filtered with a 0.45 µm membrane; then one aliquot was analyzed with ICP-MS and IC-ICP-MS, while another one was stored at 5 °C for 48 h and then filtered again on a 0.22 µm membrane before analysis. In the results of this experiment, reported in Figure 7, show that a relevant decrease in total Sb concentration detected by ICP-MS was observed when the 0.22 µm filtration was applied. The acid digestion of 0.22 µm filters demonstrated that the observed difference was due to the presence of Sb-containing solid particles on the filter. It is worth noting that the smallest nano-particles aggregates are certainly able to pass through the 0.22 µm pores as well, and this justifies the persistence of a low recovery of IC-ICP-MS vs. ICP-MS measurements also after the filtration at 0.22 µm.

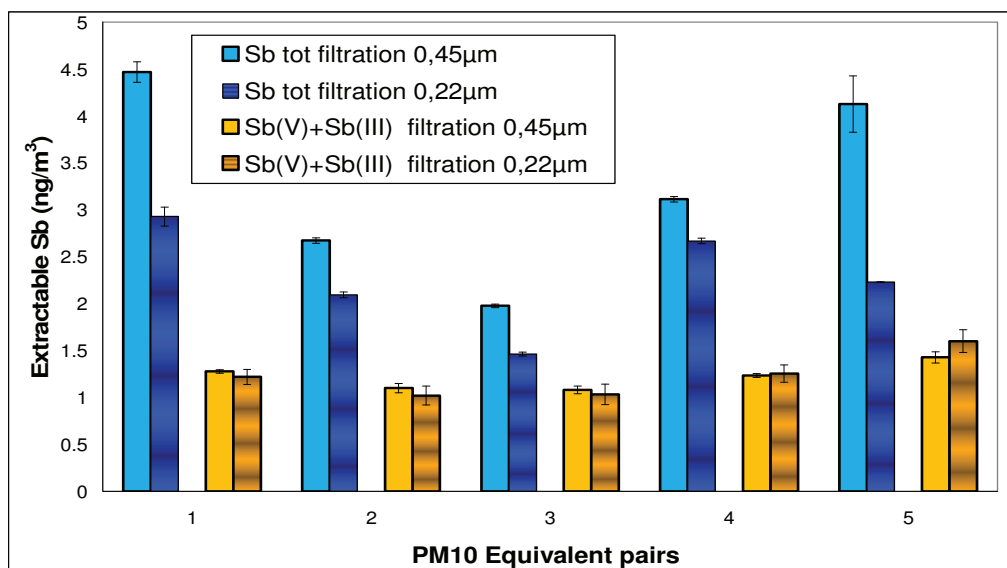


Figure 7: Comparison of the results obtained by ICP-MS and IC-ICP-MS analysis (average Sb concentrations with error bars) of the extraction solution of five PM₁₀ pairs filtered with membranes of different porosity.

4. Conclusions

The method described in this paper, fast and easily applicable to intensive monitoring campaigns, allows the analysis of the two main inorganic forms of extractable antimony 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 analyses of PM₁₀ samples collected at an urban site showed that 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 indicate that a relevant fraction of the total extracted Sb in particles having aerodynamic diameter < 1µm (fine fraction of PM) is in the form of solid nano-particles suspended in the solution. The nano-particles contribution may be easily estimated as the difference between ICP-MS and IC-ICP-MS analysis.

The aggregation state of these nano-particles seems to be easily altered when they are suspended in the water solution; a similar behaviour could be hypothesized when the aggregates are in contact with biological fluids and their health effect would then deserve further investigations.

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