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A study of uniformity of elements deposition on glass fiber filters after collection of airborne particulate matter (PM-10), using a high-volume sampler

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Abstract

A study was conducted to evaluate the homogeneity of the distribution of metals and metalloids deposited on glass fiber filters collected using a high-volume sampler equipped with a PM-10 sampling head. The airborne particulate matter (APM)-loaded glass fiber filters (with an active surface of about 500 cm^2) were weighed and then each filter was cut in five small discs of 6.5 cm of diameter. Each disk was mineralized by acid-assisted microwave (MW) digestion using a mixture of nitric, perchloric and hydrofluoric acids. Analysis was performed by axial view inductively coupled plasma optical emission spectrometry (ICP OES) and the elements considered were: Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Ti and V. The validation of the procedure was performed by the analysis of the standard reference material NIST 1648, urban particulate matter. As a way of comparing the possible variability in trace elements distribution in a particular filter, the mean concentration for each element over the five positions (discs) was calculated and each element concentration was normalized to this mean value. Scatter plots of the normalized concentrations were examined for all elements and all sub-samples. We considered that an element was homogeneously distributed if its normalized concentrations in the 45 sub-samples were within ±15% of the mean value ranging between 0.85 and 1.15. The study demonstrated that the 12 elements tested showed different distribution pattern. Aluminium, Cu and V showed the most homogeneous pattern while Cd and Ni exhibited the largest departures from the mean value in 13 out of the 45 discs analyzed. No preferential deposition was noticed in any sub-sample.

Keywords: Airborne particulate matter; PM-10; Glass fiber filters; Homogeneity of metal deposition; Inductively coupled plasma-optical emission spectrometry

1. Introduction

High-volume samplers using glass fiber filters have been widely used for suspended particulate matter (SPM) collection in a number of contaminated areas [1–3] because of their high collection efficiency for particulates and low resistance [4] even when they may contain relatively high levels of some trace elements as impurities [5].

The determination of elements in airborne particulate matter (APM) collected on filters is usually performed by selecting only a part of the filter for subsequent leaching or digestion. In some cases, a disc is cut from the central part but the homogeneity of elements deposition on glass fiber filters have been little studied to assess if this procedure is correct. In the framework of a project focused on the effect of industrial activities, Pöykiö et al. [6] studied the homogeneity deposition of Cd, Cr, Cu, Fe and Ni on glass fiber filters collected using a high-volume sampler. ICP OES was used for Cr, Cu and Fe determination and graphite furnace atomic absorption spectrometry (GF AAS) for Cd and Ni. From the six samples studied, the results indicated that Cr, Cu, Fe and Ni were not necessarily uniformly distributed over the glass fiber filters. Larger variations where exhibited by Ni and Fe while the depositions of Cr and Cu were comparatively more uniform. The deposition pattern of Cd could not be determined as the concentrations in the selected filters were very low. For Cd and Pb, Zdrojewski et al. [7] reported a non-uniform distribution these elements on glass fiber filters using high-volume samplers.

A comparative study [8] aimed to evaluate the performance of three analytical techniques namely, inductively coupled plasma

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optical emission spectrometry (ICP OES), anodic stripping voltammetry (ASV) and instrumental neutron-activation analysis (INAA) for the determination of Cd, Fe and Pb in airborne particulate matter showed that the correlation coefficient for results from ICP OES and ASV was better than for each of these methods with respect to INAA. It was attributed to a non-homogeneous deposition of the APM on the different filter position by the high-volume sampler, and to differences between the specific weights of the various parts of the filter used.

The aim of our study was to evaluate if the deposition of metals and metalloids on glass fiber filters collected using a high-volume sampler equipped with a PM-10 sampling head is or not homogenous and to clarify whether there exists a preferential deposition pattern.

This study is part of a national project funded by the Agencia de Promoción Científica y Tecnológica (Agency for Scientific and Technological Development) of Argentina aimed to quantifying metals and metalloids in urban suspended particulate matter as well as identifying their sources.

2. Experimental

2.1. Instrumentation and reagents

A Perkin-Elmer (Norwalk, CT, USA) ICP Optima 3100 XL (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer provided with a model AS 90 autosampler was used for trace elements determination. Instrumental details and operating conditions are summarized in Table 1.

A MLS-2000 (Milestone-FKW, Sorisole, Bergamo, Italy) microwave (MW) apparatus equipped with 10 Teflon-PFA (perfluoroalkoxy) vessels was used to digest the samples.

Deionized distilled water (DDW) was produced by a commercial mixed-bed ion-exchange system Barnstead (Dubuque, IA, USA) fed with distilled water. All reagents were of analytical grade. Hydrochloric, nitric and perchloric acids (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards. Commercially available 1000 mg l^{-1} standard solutions (Merck) of the elements analyzed were used. Diluted working solutions were prepared daily by serial dilutions of those stock solutions. All samples and standards were stored in polyethylene bottles (50 ml) or Falcon® tubes.

Table 1
Instrumental characteristics and settings for ICP OES

Instrument	Perkin-Elmer optima 3100 XL
Forward rf power	1300 W
Frequency of rf generator	40 MHz (axial view)
Coolant gas flow rate	15 l min^{-1}
Auxiliary gas flow rate	0.5 l min^{-1}
Sample gas flow rate	0.8 l min^{-1}
Solution delivery	1.0 ml min^{-1}
Automatic sampler	Perkin-Elmer AS90
Nebulizer	Cross-flow with scott type expansion chamber
Polychromator	Echelle grating, cross-dispersed, wavelength range (nm): 165–403
Detector	Segmented-array charge coupled device
Measurement mode	Continuous nebulisation
Signal processing mode	3 pixels peak area
Background correction	Two points
Wavelengths (nm)	Al, 308.215; As, 188.979; Cd, 228.802; Cr, 267.716; Cu, 324.742; Fe, 238.204; Mn, 257.610; Ni, 232.003; Pb, 217.000; Sb, 206.836; Ti, 337.279; V, 290.880

2.2. Sample collection

Airborne particulate matter samples were collected on ash-free-fiber-glass filters (8 × 10 in., ADVANTEC, GB100R, 0.6 μm nominal rating) with a high-volume air sampler (SIBATA, HV 1000F) with a PM-10 sampling head. The sampling flow rate used was 1000 l min^{-1} and the average total sampling time was 24 h to achieve a concentration of trace metals sufficient for their quantification. The average air volume collected daily was 1440 m^3. Each filter was placed in a clean polyethylene bag during transport and storage. The glass fiber filters were heated in a vacuum drying oven at 110–120 °C for 120 min prior to use. The filters were weighed (after moisture equilibration) before and after sampling to determine the net particulate mass gain. Filter conditioning environment during the 24 h equilibration period included controlled temperature with less than ±3 °C and constant relative humidity within ±5%. Filters were stored in clean containers under refrigeration after weighing.

To analyze the homogeneity of element deposition, we selected filters from different monitoring campaigns that had been carefully archived in our laboratory. These campaigns were undertaken in urban and industrial settings under different emission patterns and meteorological conditions. Five out of the nine samples analyzed were collected in urban sites in the cities of Campana, San Nicolás and Buenos Aires (Argentina). Campana and San Nicolás are cities of ∼100,000 inhabitants holding considerable industrial activities that include large steel mills, petrochemical refineries and other industrial facilities [9,10]. The metropolitan area of Buenos Aires, which is composed by the city itself and 24 neighboring districts is a megalopolis with about 14 million people and a traffic density of 1.5 million vehicles per day [1]. The rest of the filters were collected at four monitoring sites inside one of the largest steel mills of Argentina, located in the city of Campana. These samples provided a wide range of element concentrations for our investigation. In this way, we have avoided assessing homogeneity patterns under a narrow variability range.

Operation, treatment and handling of samples and data validation were carried out according to quality assurance and quality control (QA/QC) guidelines of the World Health Organization [11].

2.3. Sample treatment

For our study, each archived filter loaded with airborne particulate matter (with an active surface of about 500 cm^2) or blank filter was cut in five small discs of 6.5 cm of diameter and their

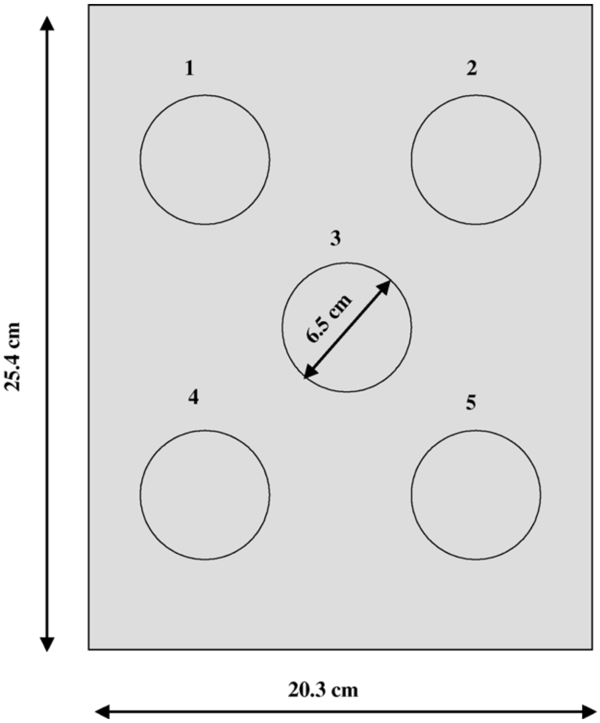

Fig. 1. Pattern of sub-sampling. Position of discs (1–5), cut from each glass fiber filter.

weights recorded. Fig. 1 illustrates the position of the five discs (1–5) cut from glass fiber filters. The five discs (together) had an area equivalent to a half filter. Pieces were carefully placed into a reaction vessel and a mixture of 5 ml of HNO_3, 2 ml of HF and 2 ml $HClO_4$ was added to the samples, which were then allowed to undergo overnight digestion. Samples were finally subjected to microwave-assisted acid digestion in a microwave oven. The digestion cycle adopted is detailed in Table 2. The entire cycle was repeated three times and 1 ml of HF was added before each cycle started. After digestion, the resulting solution was evaporated and the residue dissolved with 5 ml of 0.1 mol l^{-1} HCl. Samples were dried again and dissolved with 25 ml of 0.1 mol l^{-1} HCl. About 250 mg of the certified reference material NIST SRM 1648 (urban particulate matter) were weighed onto a blank filter and subject to the same treatment as for the samples.

Table 2
Main steps of the digestion procedure for filters loaded with APM

Reagents	5 ml of concentrated HNO_3, 2 ml of concentrated HF and 2 ml of concentrated $HClO_4$	
Step	MW power (W)	Time (min)
Digestion cycle[a]		
1	250	5
2	0	5
3	400	5
4	0	5
5	600	5

[a] Three cycles were carried out in total and 1 ml of HF was added before each new cycle started.

Table 3
Detection limits of ICP OES measurements after pre-treatment of discs loaded with particulate matter

Element	LODs in solution (ng ml^{-1})	LODs in air (ng m^{-3})
Al	9.9	0.17
As	4.3	0.07
Cd	0.6	0.01
Cr	9.7	0.16
Cu	1.8	0.03
Fe	6.4	0.11
Mn	1.2	0.02
Ni	3.0	0.05
Pb	3.0	0.51
Sb	3.4	0.06
Ti	5.8	0.10
V	6.5	0.11

2.4. Sample analysis

Inductively coupled plasma optical emission spectrometry was employed in the determination of metals and metalloids in airborne particulate matter collected in glass fiber filters. This technique can be applied to different matrices after a suitable dissolution procedure and is characterized by extended dynamic concentration range (four to six orders of magnitude), is multi-elemental in nature and possess high sensitivity and appropriate detection power.

For ICP OES determinations, multi-elemental calibrants were prepared from 1000 $\mu g\, l^{-1}$ standard solutions of the individual elements in 0.1 mol l^{-1} HCl. Calibration curves were obtained with matrix matched calibration standards.

2.5. Blanks, detection limits and precision

Filters used to collect aerosol samples are not free from impurities. The concentration of trace metals was also measured by ICP OES in solutions of filters that were treated as the filters loaded with particles to establish a baseline. The blank was a reagent + beaker + filter blank and the concentrations of metals and metalloids measured were subtracted to the ICP OES measurements of real samples. These average concentrations were: Al, 0.63 mg l^{-1} (equivalent to 11 ng m^{-3}), Cu, 0.09 mg l^{-1} (equivalent to 1.6 ng m^{-3}), Fe, 2.88 mg l^{-1} (equivalent to 40 ng m^{-3}).

Using optimized conditions, analytical figures of merit including, detection limit and precision of replicate measurements were established. Detection limit was calculated following the IUPAC rules on the basis of 3σ criterion for ten replicated measurements of the blank signal. Limits of detection in solution and in air are set forth in Table 3. The relative standard deviations (R.S.D.s) for the 12 elements evaluated are in general in a more than satisfactory interval (4.2–10.9%) considering the complexity of the matrix analyzed.

2.6. Validation of measurements of trace elements

Table 4 illustrates the results of the determination of analytes evaluated in the certified reference material NIST 1648 (urban

Table 4
Accuracy test: analysis of the standard reference material NIST 1648 (urban particulate matter) by ICP OES

Element	Certified	Found[a]
Al (%)	3.42 ± 0.11	3.39 ± 0.15
As ($\mu g\,g^{-1}$)	115 ± 10	111 ± 6
Cd ($\mu g\,g^{-1}$)	75 ± 7	72 ± 5
Cr ($\mu g\,g^{-1}$)	403 ± 12	381 ± 27
Cu ($\mu g\,g^{-1}$)	609 ± 27	615 ± 28
Fe (%)	3.91 ± 0.10	3.89 ± 0.15
Mn ($\mu g\,g^{-1}$)	786 ± 17	784 ± 23
Ni ($\mu g\,g^{-1}$)	82 ± 3	85 ± 6
Pb (%)	0.655 ± 0.008	0.645 ± 0.05
Sb ($\mu g\,g^{-1}$)	45	65 ± 4
Ti (%)	0.40	0.34 ± 0.05
V ($\mu g\,g^{-1}$)	127 ± 7	121 ± 8

[a] Two set of replicates, each set consisting of ten measurements. Data enclosed in brackets are non-certified values, only indicatives.

particulate matter) as determined by ICP OES. The overall picture turns out to be satisfactory, especially if we considered the complexity of the matrix analyzed. Even when Sb is a non-certified element, the recovery obtained (65 $\mu g\,g^{-1}$ versus 45 $\mu g\,g^{-1}$) was high. No convincing explanation could be found for this high recovery and similar results were obtained in a previous paper [1].

3. Results and discussion

As the filters selected for this study belong to different monitoring campaigns undertaken in urban and industrial settings under different emission patterns and meteorological conditions, the concentrations of each element in the different filters analyzed vary within at least one order of magnitude. This can be appreciated in Table 5, where Ti is the only element whose concentrations varied within a narrow range. On the other hand, large variations were observed for As, Cd, Cu and Sb.

Table 5
Range of measured concentrations in the different sub-samples of the filters selected for the study

Element	Minimum	Maximum
Al	3700	9875
As	0.18	49.8
Cd	0.08	2.55
Cr	0.78	5.78
Cu	2.65	378
Fe	120	2250
Mn	1.43	40.1
Ni	0.23	3.75
Pb	4.8	100
Sb	0.23	295
Ti	21.3	37.8
V	0.93	3.75

Element concentrations are expressed in μg.

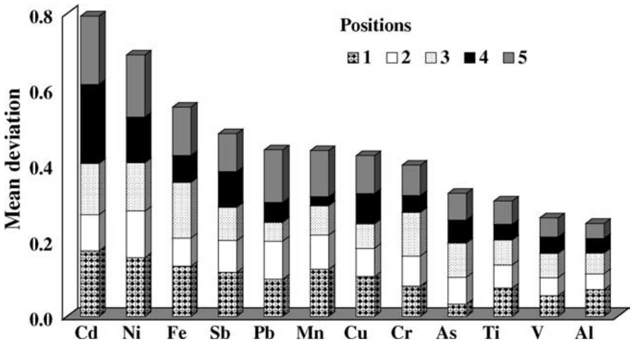

Fig. 2. Distribution of elements in the five positions. Values plotted correspond to the mean deviation per position defined according to Eq. (3).

To assess the element deposition pattern, we considered, for each filter k of the nine selected for the study, the measured concentration of each element i in each disc (position) j, X_{ijk}, and defined the normalized concentrations, $\hat{X}_{ijk}$, as follows:

$$\hat{X}_{ijk} = \frac{X_{ijk}}{\bar{X}_{ik}} \tag{1}$$

$$\bar{X}_{ik} = \frac{1}{5}\sum_{j=1}^{5} X_{ijk} \tag{2}$$

where, i: corresponds to each measured element ($k = 1$–12); j: corresponds to each position (disc cut from each filter) ($k = 1$–5); k: corresponds to the filters considered for the study ($k = 1$–9); $\bar{X}_{ik}$: is the average concentration of element i for the five discs taken from filter k.

Fig. 2 illustrates the variability of element concentrations in the five positions considered. Mean deviation, D_{ij}, in each position was calculated according to Eq. (3) and represents, for all filters considered, the average of the deviations of the normalized concentrations with respect to one.

$$D_{ij} = \frac{1}{9}\sum_{k=1}^{9} |\bar{X}_{ijk} - 1| \tag{3}$$

Although the plot should not be considered as a cumulative representation, Fig. 2 gives an overall picture showing that the largest variations were for Cd > Ni > Fe > Sb. Similar overall variations within an intermediate range were observed for Cr, Cu, Mn and Pb while the elements with the lowest variations were for As > Ti > V > Al. The larger variations for Ni and Fe as well as similar variations for Cu and Cr are compatible with the results reported previously by Pöykiö et al. [6]. Also the variability observed for Cd is compatible with the results reported by Zdrojewski et al. [7]. Cadmium (positions 1, 4 and 5) and Ni (positions 1 and 5) are the only elements with mean deviations higher than 0.15. This pattern distribution was observed for practically all the filters analyzed. The non-uniform distribution of these two elements on the filters could be attributed to differences in particulate size distribution of the metals. Another feature arising from the pattern shown in Fig. 2 is that there is no preferential position for the deposition of the elements on the filter and that it is more dependent on the element.

Figs. 3 and 4 illustrate the normalized concentrations (Eq. (1)) of all elements in the five positions considered. Aluminum, Ti

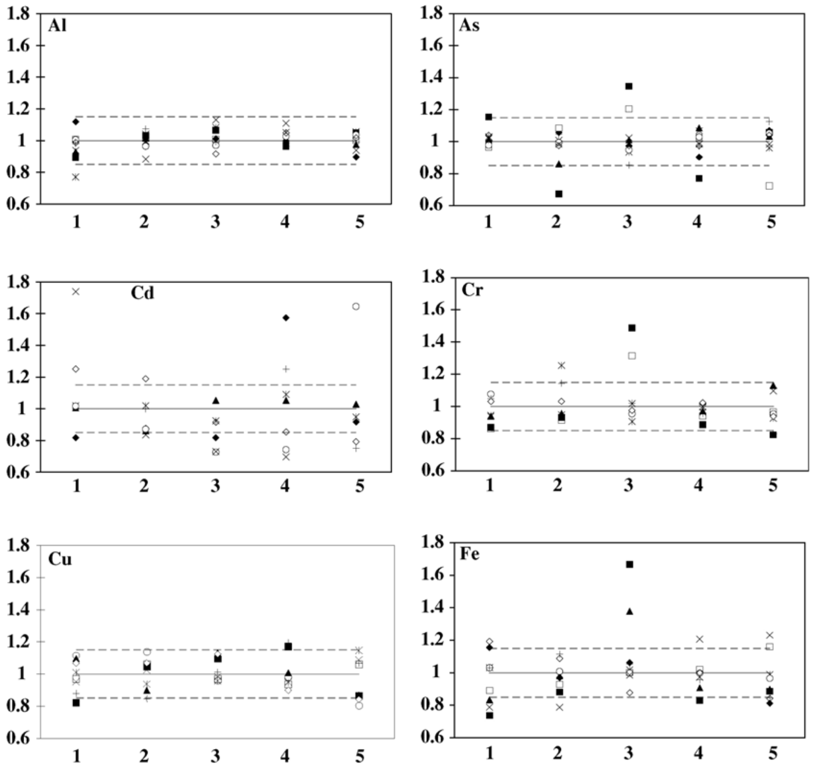

Fig. 3. Normalized concentrations vs. position (1–5) for Al, As, Cd, Cr, Cu and Fe. Normalized concentrations were calculated according to Eq. (1).

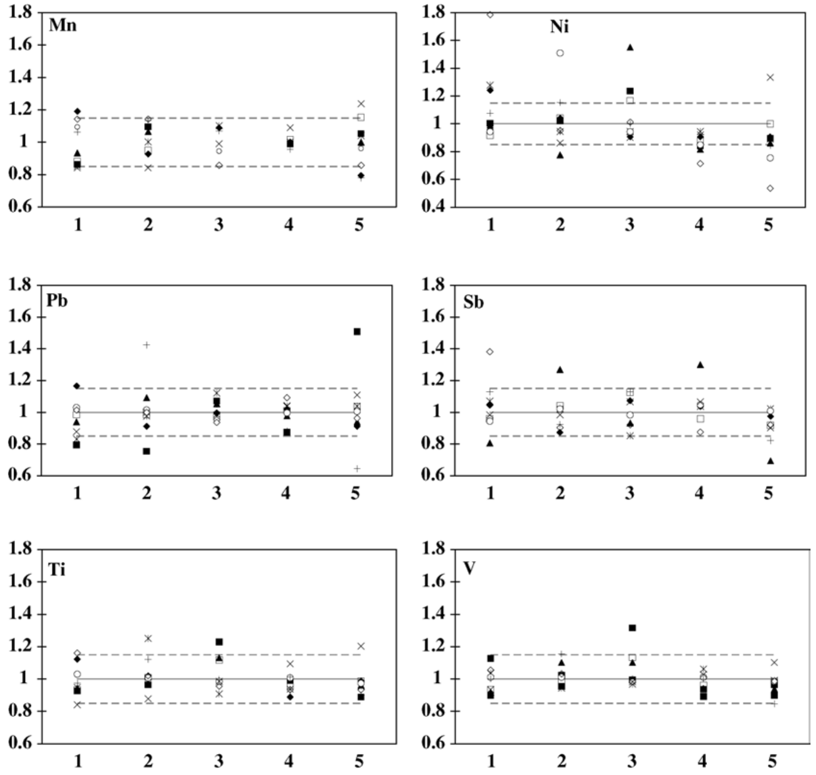

Fig. 4. Normalized concentrations vs. position (1–5) for Mn, Ni, Pb, Sb, Ti and V. Normalized concentrations were calculated according to Eq. (1).

and V showed the most homogeneous pattern. The distribution of these elements was compatible with a comparatively narrow range of concentrations (Table 5) and it was independent of their concentration levels. However, in general terms, no correlation was found between the range of concentrations measured and the distribution pattern observed, for instance, as the comparatively low variability exhibited while its concentration range was relatively wide (0.18–49.8 μg).

4. Conclusions

The results of this study show that Cd and Ni exhibited the largest departures from the mean value in 13 out of 45 discs analyzed. This could indicate that the distribution of both elements was not uniform when high-volume air samplers were used for suspended particulate matter collection. For this reason, it is recommended that a homogeneity test be a part of the customary quality assurance/quality control procedures when only a portion of the total filter is used for multi-elemental analysis of SPM. No tendency to a preferential deposition pattern was noticed in any position (sub-sample) even when a wide range of concentrations were present in the filters analyzed.

Aluminum, Ti and V showed the most homogeneous pattern. The distribution of these elements was compatible with a comparatively narrow range of concentrations and it was independent of their concentration levels.

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