

ACCOUNT of an innovative procedure for the assessment of inorganic particles and mineral phases in the PM₁₀

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Abstract - *a modus operandi* to move on suitable support for morphological, chemical and mineralogical characterization under scanning Electron Microscopy equipped with Energy dispersive spectroscopy (SEM/Eds) of the inorganic component of PM₁₀, collected on depth filters routinely used by the Environmental Protection agencies (in Italy A.R.P.A.) for the air quality assessment, is described. The proposed methodology has been tested on six membranes, sampled according to the EN 12341/99 procedure, in areas characterized by natural and anthropogenic sources of Particulate Matter. First outcomes prove that the methodology, allowing the morphological-chemical and mineralogical characterization of the particles, may be a useful tool for the Environmental Protection agencies to detect the contribution of the natural background and of the anthropogenic sources to the air pollution.

Riassunto - nel seguente lavoro viene descritto un *modus operandi* per la caratterizzazione chimica-morfologica-mineralogica, utilizzando la Microscopia Elettronica a scansione con annessa sonda in dispersione di Energia (SEM/Eds), della componente inorganica del PM₁₀, raccolta su supporti quotidianamente utilizzati dalle agenzie di Protezione ambientale (A.R.P.A.). il metodo prevede il trasferimento di tale componente dal supporto utilizzato per la raccolta e l'analisi gravimetrica su una membrana più adatta

all'esame SEM/Eds. La metodologia proposta è stata testata su sei campioni raccolti secondo la procedura EN 12341/99 e provenienti da differenti aree caratterizzate da PM sia di origine naturale che antropica.

I primi risultati dimostrano che la metodologia, permettendo la caratterizzazione morfo-chimica delle particelle inorganiche aerodisperse, può costituire un veloce ed efficace supporto per le agenzie di Protezione ambientale anche per individuare il contributo delle sorgenti naturali e delle attività antropiche all'inquinamento atmosferico.

Key words: PM₁₀; inorganic particles; SEM/EDS; EN 12341/99 procedure; filter substrates.

Introduction

The increase of air pollution is one of the most important issues due to the outcome on the human health, and the European law requires the monitoring of the Particulate Matter (PM) (Directive 2008/50/EC). Recent studies on PM₁₀ (Particulate Matter with aerodynamic diameter less than 10 µm) emphasize that the airborne fine particles are a multiphase system, which undergo many chemical-physical modifications especially because of their heterogeneous composition (Willis *et al.*, 2002; Casuccio *et al.*, 2004; Senlin

et al., 2007). depending on their origin, in fact, particles can differ in shape and physical state: e.g. condensation aerosol is generally liquid and exhibits spherical shapes, whereas particles from natural sources are solid and show irregular morphology (Posfai and Molnàr, 2000). in this last category, there are many mineral particles that may be involved in chemical transformations, adsorption of metals and/or gases as well as act in a synergistic way in their effects on the human health (Fubini and areán, 1999; senlin *et al.*, 2007). investigations about the mineral component of the PM₁₀ result therefore essential to obtain information about the chemical-physical properties of the Particulate Matter. For example, there is not enough information on the potential risk of asbestos at low amounts, like for environmental exposure, taking into account that the world Health organization does not report a threshold below which there is no risk for asbestos and fibrous mineral exposure (wHo, 1986). similarly to asbestos, the transition metals, frequently present in the urban area, may play a significant role on the human health (willis *et al.*, 2002).

PM₁₀ is usually monitored by high volume devices, collecting the suspended material onto glass fibers filters or fused silica membranes (norton and gunter, 1999) (usually named "quartz membranes") and measuring with gravimetric analysis the concentration of suspended PM₁₀, defined as the total mass of the PM₁₀ per cubic meter of air, within 24 hours (dM 25/11/1994; Cd 80/779/EEC; directive 2008/50/EC).

by this way only the weight of the suspended materials without information about the ratio between organic and inorganic components is obtained. Moreover, the European Community is recently showing an increasing interest in assessing the chemical characterization of the different components of the PM (directive 2004/107/EC; d.lgs. 152/2007; d.lgs. 120/2008), as well as in a more detailed investigation

about the natural background (directive 2008/50/EC). so, increasingly attention is devoted to the analytical techniques suitable for detecting morphology and chemical composition of single aerosol particles.

The described study aimed to elaborate a simple and not expensive methodology to perform the characterization of the inorganic phases in the PM₁₀, with particular attention to the potentially toxic particles (e.g. asbestos and metals), using scanning Electron Microscopy, equipped with Energy dispersive spectroscopy - sEM/Eds. Moreover, considering that the local Environmental Protection agencies (a.r.P.a) collect the PM₁₀ on depth filters like quartz, actually fused silica, or glass fibers supports (En 12341, 1999), a procedure allowing the micro-analyses of the airborne inorganic particles starting from these types of substrates was worked out.

it should be remarked that fused silica and glass fiber supports exhibit several disadvantages when analyzed under sEM/Eds:

- a) their depth prevents a good conductivity of the samples;
- b) a detailed morphological and micro-analytical identification of the particles entrapped in the depth of the filter is avoided;
- c) the chemical components of the filters are si, na, al, K, Ca, o and ba in traces; these elements may be present also in the chemical composition of the inorganic particles in the PM and the interpretation of Eds micro-analyses may be difficult.

in an effort to overcome these issues, a procedure has been elaborated to remove the solid components of the PM from the original filter and deposit them onto a polycarbonate support, more suitable for the morphological and chemical characterization of the inorganic particles under sEM/Eds. since the carrier liquid used and the solid phases re-deposition can imply a solubilization/loss of particles (willis *et al.*, 2002), this study does not claim to provide a

quantitative assessment of the inorganic material, but only to offer a representative inorganic/mineralogical composition occurring in the PM, discerning among different inorganic species and trying to give an apportionment source.

The procedure, starting from the glass fiber filters, has been tested on four PM₁₀ samples collected on the above cited glass supports. In a further step, to test the contribution of different filters types to the identification of the inorganic particles, the same procedure was applied also on two samples collected onto fused silica fiber filters.

MaTErIaLS and METhods

The chemical characterization of the inorganic solid portion of PM₁₀ was carried out on six membranes collected in Alessandria Province - NW of Italy, all of them sampled according to the EN 12341/1999 procedure. Four of the six samples examined - labeled hereafter MiC, soI, sTa and C - were gathered using a high volume sampler TisH Environmental, inC - TE6070v model, working with constant flow of atmospheric air suction, corresponding to 1.1 m³/min within 24 hours and collecting the PM₁₀ material onto a glass fiber filter, 20.3 x 25.4 cm in size.

The sampled area is characterized by the presence of an important industrial complex, a former waste landfill, several transport infrastructures and it is interested by heavy vehicular traffic. In particular, two samples (MiC and soI) were collected at about 100 m from two factories with the highest environmental impact in the studied area; the sample sTa was collected at about 10 m from a road characterized by a high vehicular traffic; C sample, placed in the studied area but far from specific anthropic activities, is representative of the environmental background. The four samplings were carried out during the same period.

At first, on each sample a gravimetric analysis

was carried out, weighting the filter before and after the sampling at 20 ± 1°C and relative humidity 50 ± 5%. The weighted mass of PM₁₀ was related to the volume of sampled air.

After, the filters were processed in order to remove the inorganic particles from the depth filter and to transfer them on a polycarbonate membrane, whose chemical composition does not interfere with the chemicals forming the airborne inorganic particles. The few data reported in literature suggest sonication of the original filter in acetone (Willis *et al.*, 2002), but by this way, in addition to the released inorganic particles entrapped in the filter, an high amount of glass fibers from the original support were found onto the polycarbonate surface. Moreover, an effect on the particles forming aggregates may be produced by the sonication. After several attempts, the best result was obtained without sonication of the samples and following the subsequent steps:

a) a portion of the filter was cut (about 1.5 cm x 4.5 cm) and dipped into a test tube with filtered acetone for 20 min; after, the filter was moved up-down into the solution for 10 min. The same procedure was repeated twice. By this operation the release of the inorganic particles into the solution was strongly promoted;

b) the membrane was taken away from the solution and the acetone centrifuged twice for 10 minutes at 4000 rpm each. A pellet of the inorganic particles on the bottom of the test tube, separated from the synthetic fibers detached from the support and suspended into the supernatant, was formed;

c) the supernatant was removed from the test tube, the pellet re-suspended in de-ionized water and filtered onto a polycarbonate membrane, porosity of 0.4 µm and diameter of 25 mm;

d) finally, the polycarbonate filter was glued onto a sEM aluminum pin-stub by adhesive type and carbon coated for observation in high vacuum.

The chemical, mineralogical and morphological

characterization was carried out by a variable Pressure scanning Electron Microscope (vP-SEM, IEO 1450 model), equipped with Energy dispersive spectrometer (oxford instruments, inCa EnErgy model). The SEM/Eds analyses were performed at 20 kv, 2000 magnification along 100 microscopic fields. The elemental composition of each observed particle/fibers was determined; the identification of the different phases was carried out by comparison of the registered Eds spectra with those reported by literature (severin, 2004; Iowers and Meeker, 2005).

in order to test the variability in the number/chemical characteristic of the analyzed particles, for each filter two aliquot parts of the sample were prepared following the described procedure and studied subsequently. The error percentage in the different clusters considered and detected during subsequently sessions on the same range of analyses is reported in TABLE 1.

since in the area under study could be present potentially toxic airborne inorganic fibers, such

as asbestos (gunter, 1994), particular care was addressed to the chemical characterization of each fiber observed under SEM. The presence of residual fibers from the original glass fiber supports on the polycarbonate membranes, due to the similarity of the elemental composition (si, na, al, Ca), accounted for a problem. To solve this difficulty, for each microscopic field, an elemental spatial distribution of Mg, Fe - chemical elements characteristics for asbestos - and si - common for both types of fibers - was carried out using the Eds two-dimensional mapping function. Moreover, several tests were previously performed using well know asbestos fibers widespread onto the filter in order to verify the possibility of identifying different types of inorganic fibers by this function. when a potential asbestiform phase was detected by the elemental mapping, different spot micro-analyses were accurately performed, and a size determination was carried out to check its breathability - length (L) > 5 µm, diameter (d) < 3 µm, (L/d) > 3, as defined by the European law (directive 2003/18/EC).

in a second time, the elaborated procedure was checked on two samples, named hereafter urb1 and urb2, collected by means of a TECORA skypost, Hv model, supporting the fused silica filters of 47 mm in diameter. urb1 was collected in a central zone of a town, about 10 m from the main road; urb2 was sampled in an outskirt area of the same town, far-away about 1 km from the same road.

TABLE 1

Percentages of particles ascribed to the different inorganic phases observed in the sample C and analyzed in subsequent sessions. The variability is also reported. The serpentines are considered separately from the other phyllosilicate minerals in order to highlight the possible presence of chrysotile, regulated as "asbestos" by the Law (Directive 2003/18/EC).

CLUSTERS % DATA error

Phyllosilicates	24.7	+/-6.5
serpentines	4.3	+/-3.0
Feldspars	4.3	+/-1.0
Calcite	11.8	+/-3.0
vitreous particles	26.8	+/-5.5
Man-made compounds	3.2	+/-2.4
Metal-rich particles	0.2	+/-1.0
siO ₂	0.1	+/-1.0
nd	24.6	+/-10.5

RESULTS and discussion

The standard filters used for high volume sampling, as shown in Fig. 1, are constituted by a close net of long and thin fibers, whose chemical components, determined under SEM/Eds, are si, na, al, K, Ca, o and ba in traces, similar to those constituting the mineral phases, potentially present in the PM. Moreover, many airborne particles may be entrapped in the

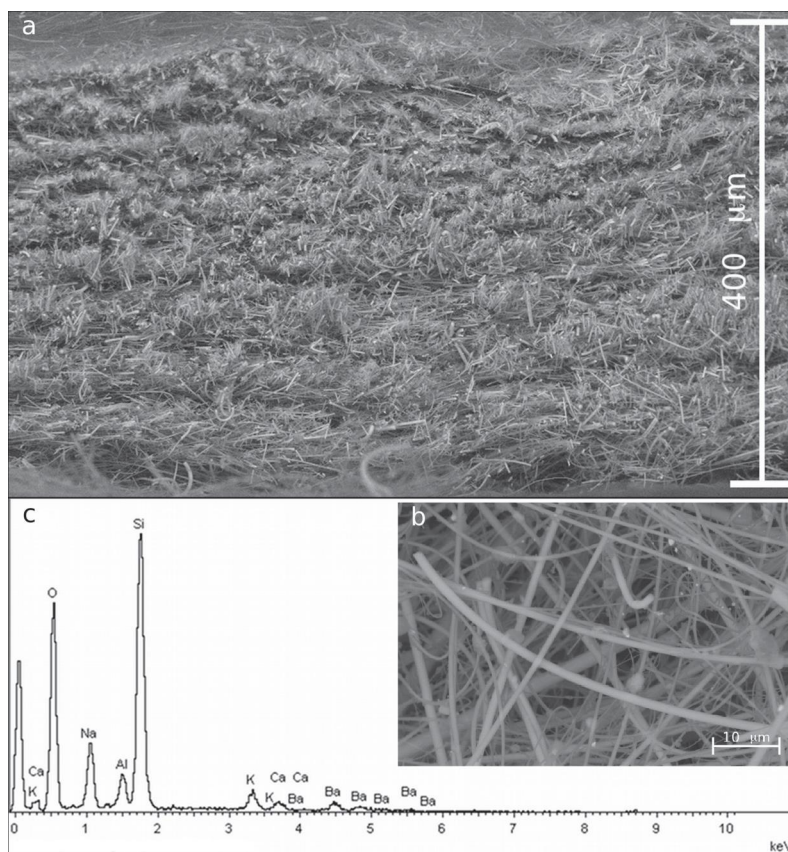


Fig. 1 - a) sEM microphotograph of the cross section of a glass fiber filter. b) sEM image at 3000 M of the surface of the glass fiber filter, where some particles entrapped close to the glass fibers are seen. c) Eds spectrum of a glass fiber filter showing its characteristic chemical composition of si, o, na, al, K, Ca and ba.

filter wool and for them the sEM/Eds analysis is prevented. as seen in Fig. 2, by applying to a filter the methodology described previously, the inorganic materials occurring in the PM₁₀ appear widespread in a monolayer onto polycarbonate membranes. also when several glass and fused silica fibers, liberated from the original supports, were present onto the polycarbonate membranes, they result easily distinguishable from the PM₁₀ particles (Fig. 2).

as described previously, for each sampling two aliquot parts for each filter were prepared

separately and observed under sEM/Eds. The error percentage in the different clusters considered and detected during subsequent sessions on the same range of analyses is reported in TABLE 1. in the following of the work, we discuss the results grouping the analyzed particles, as that seen in Fig. 3, in the clusters reported in TABLEs 2 and 3. For some particles/fibers the Eds spectra were too complex and a gross identification is proposed: “vitreous particles” when si, o and low amounts of al were detected; “calcium-rich particles”,

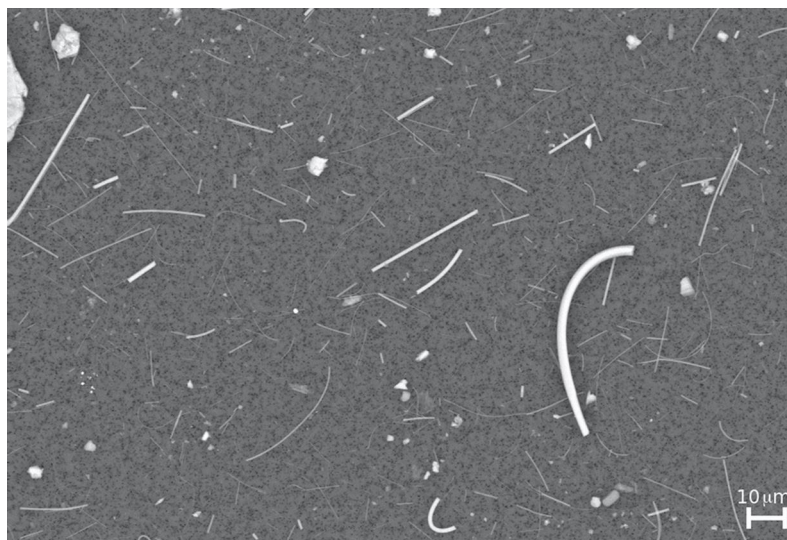


Fig. 2 - backscattered sEM image at 500 M of the deposited material (sample C) onto a polycarbonate membrane after the procedure described in the work. both the inorganic particles and the glass fibers are detected onto the surface in a monolayer, it is therefore possible to analyze each particle/fiber by Eds.

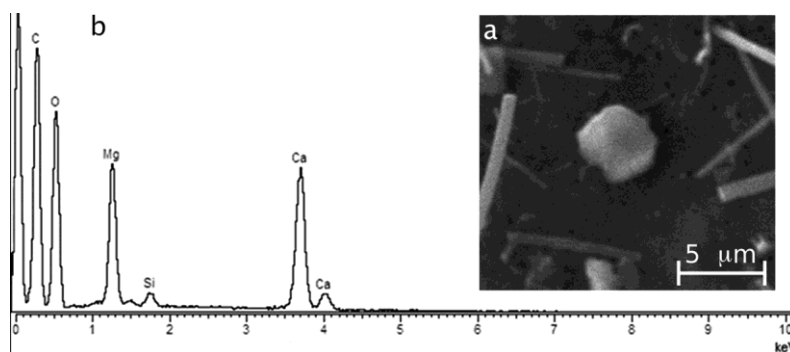


Fig. 3 - a) secondary electron SEM image of an isodiametric particle in the sample so1. b) Eds spectrum of the particle in a): the elemental composition - Mg, Ca, C, o - allows identifying dolomite. si may be ascribed to the glass fibers surrounding the particle.

when Ca and other minor elements like si, al were determined, “metal-rich particles”, when an heavy metal, such as Fe, Cr, Pb, Zn was the major element identified; “man-made compounds”, when the chemical composition and the morphological aspect were not ascribable to a natural phase. in addition, to

verify the presence of chrysotile, regulated as “asbestos” phase (directive 2003/18/EC), the serpentines, magnesium rich phases, were considered separately from the other phyllosilicate minerals and distinguished from them on the basis of the relative intensities of si and Mg peaks on the Eds spectra. For the

Table 2

The inorganic particles identified by SEM/EDS in the samples collected with glass fiber supports grouped in eleven clusters. The values are reported as percentages. Serpentine is considered separately from the other phyllosilicate minerals in order to highlight the possible presence of chrysotile, regulated as "asbestos" by the Law (Directive 2003/18/EC). The gravimetric values of the different samples studied are also reported.

	SOI	STA	MiC	C
grAViMeTriC MeASure in µg/m³	31	16	40	41
CIUSTerS %				
Phyllosilicates	37.1	40.0	33.3	24.7
serpentine	10.1	2.5	16.7	4.3
Feldspars	2.9	7.5	3.3	4.3
dolomite	1.4	-	-	-
Calcite	-	-	-	11.8
vitreous particles	17.1	12.5	23.3	26.8
Man-made compounds	5.7	7.5	3.3	3.2
Metal-rich particles	5.7	20.0	5.1	0.2
TiO ₂	-	-	3.3	-
SiO ₂	1.4	-	1.7	0.1
nd	18.6	10.0	10.0	24.6

particles showing a potential asbestos chemical composition, Fig. 4, a size determination was also performed to check their breathability (directive 2003/18/EC).

Finally, in the nd (not determined) were grouped all the inorganic particles/fibers from which a reliable identification by the micro-analysis was prevented.

As seen on Table 2, in the samples collected originally on glass fiber filter (sTa, soI, MiC and C) eleven different inorganic groups were identified. six inorganic species - phyllosilicates, serpentine, feldspars, dolomite, calcite and SiO₂- can be ascribed either to natural sources or to anthropogenic activities involving removal or transformation of natural soils/sediments. The vitreous particles, man-made compounds, metal-rich particles and TiO₂ are more likely connected to anthropogenic sources. it is interesting to note

Table 3

Gravimetric values (in µg/m³) and inorganic species identified (in percent) in the samples collected with fused silica fiber supports. Serpentine is considered separately from the other phyllosilicate minerals in order to highlight the possible presence of chrysotile, regulated as "asbestos" by the Law (Directive 2003/18/EC).

	UrB1	UrB2
grAViMeTriC MeASure in µg/m³	92	101
CIUSTerS %		
Phyllosilicates	12.9	24.4
serpentine	3.2	4.9
Feldspars	3.2	4.8
Metal-rich particles	32.3	12.2
barium sulfate	11.3	4.9
Calcium-rich particles	22.6	29.3
nd	14.5	19.5

that some inorganic compounds have been detected only in specific samples. as an example, titanium dioxide (TiO₂), Fig. 5, phase ascribing to anthropogenic source, was detected only in MiC, from an area characterized by the presence of an important factory. other species, as metal-rich compounds, were detected in high percentages in sTa, sampled at about 10 m from a main road, therefore they may be correlated to high vehicular traffic. Calcite, shown in Fig. 6, was identified only in sample C, corresponding to a rural area; in fact it may be a mineral constituting the natural soils. on the other hand, also norton and gunter (1999) determined in their PM₁₀ samples about 5-10 % of calcite, feldspars and micas as mayor phases and small amounts of amphiboles; all these phases were ascribed to a natural source. it is not therefore surprising to detect in the airborne the minerals constituting the natural soils/sediments of the examined areas.

Considering now the gravimetric values and the inorganic phases detected in the different specimens, it is interesting to compare samples

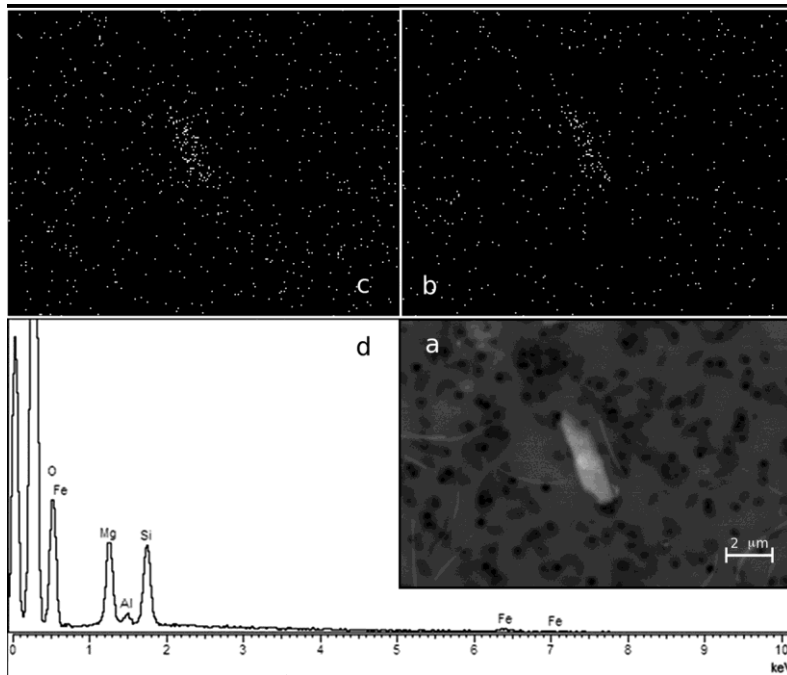


Fig. 4 - a) sEM image of an elongated particle in the sample C. b) and c) are the elemental mappings of Mg and si respectively of the area shown in a). The map of Mg and si allowed distinguishing this elongated particle from those from the glass filter. d) Eds spectrum of the elongated particle shown in a); its chemical composition - Mg, si, o and small amount of Fe- identifies serpentines; C rises from the polycarbonate substrate.

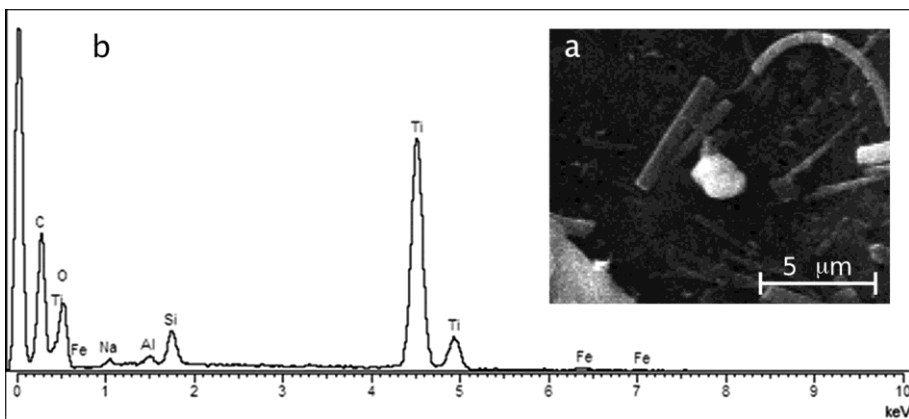


Fig.5 - a) secondary electron sEM image of an isodiametric particle in MiC. b) Eds spectrum of the particle in a) identified as titanium dioxide. The presence of si, al and na in traces is a consequence of the presence of glass fibers in the analyzed area close to the particle.

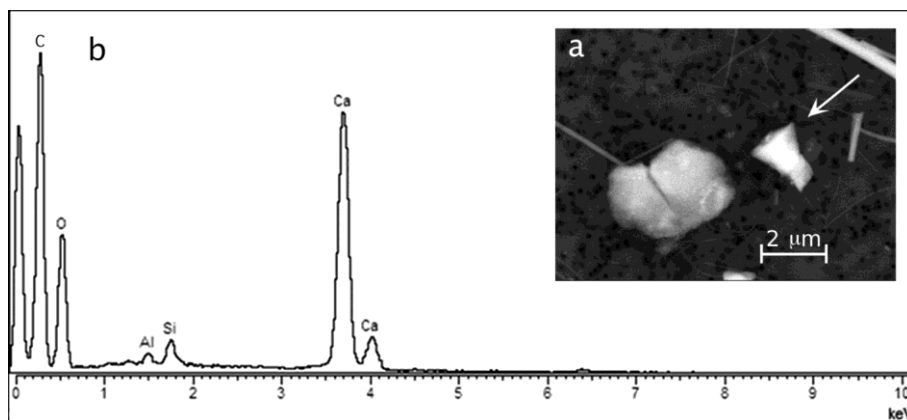


Fig. 6 - a) backscattered sEM image of two particles in the sample C. b) EDS spectrum of the particle indicated by an arrow in a) and identified as calcite by its elemental composition - Ca, C and O. Si and Al rise from the glass fibers, close to the analyzed particle.

MiC and C. They are characterized by comparable gravimetric values (40 and 41 $\mu\text{g}/\text{m}^3$ respectively), but by different inorganic phases (Table 2): in MiC, phyllosilicates, serpentines, metal-rich compounds are the most frequently determined phases, whereas in C calcite is the mineral identified in highest amount. The sample sTa, with the lowest gravimetric values (16 $\mu\text{g}/\text{m}^3$), has the highest amount of metal-rich particles. This means that particles potentially toxic for human health can be present in significant amounts even in samples characterized by low gravimetric values.

in all the studied samples the detected particles appear mainly isodiametric, as demonstrated by their mean size of length, diameter and length/diameter ratio, Table 4.

The data until now described can be compared with those obtained using TECORA skypost, Hv filters, constituted by fused silica, of 47 mm in diameter, sampled in areas of a small town, urb1 and urb2. at first, it is important to emphasize that the fused silica, constituting the sampling membrane, shows a higher release of the constituting fibers on the polycarbonate support, making more difficult the sEM/EDS

data interpretation. in any case urb1 and urb2 appear, with respect to the samples described previously, characterized by a more pronounced homogeneity in the inorganic phases detected, Table 3. on these filters, phyllosilicates, serpentines and feldspars may be ascribed either to natural sources or to anthropogenic activities (involving removal or transformation of natural soils/sediments) whereas metal-rich particles, as that shown in Fig. 7, and barium sulfate to anthropogenic sources. The presence of barium sulfate is not surprising when we consider that a factory producing this compound is operative in the area; for calcium-rich particles a well defined origin cannot be proposed. also on these samples the particles appear mainly isodiametrics, smaller in urb1 than in urb2 (Table 5).

Considering the gravimetric values of the two samples, 92 e 101 $\mu\text{g}/\text{m}^3$ in urb1 and urb2 respectively, both exceed the limits provided by the European law (directive 2008/50/EC); moreover the percent of particles ascribing to anthropogenic source appears particularly high. in fact in both samples an atypical presence of barium sulfate is detected and calcium-rich and metal-rich particles show considerable percents.

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Table 4

Mean size of the particles (L= length, d=diameter, L/d= aspect ratio) for each inorganic species identified in the samples collected on glass filters. The error for the measures is 0.2 μm . Serpentine are considered separately from the other phyllosilicate minerals in order to highlight the possible presence of chrysotile, regulated as "asbestos" by the Law (Directive 2003/18/EC).

	SOI			STA			MiC			C		
	l μm	d μm	l/d	l μm	d μm	l/d	l μm	d μm	l/d	l μm	d μm	l/d
Phyllosilicates	7.1	4.2	1.7	6.9	4.6	1.5	7.5	5.2	1.4	6.7	4.2	1.7
serpentine	5.7	3.9	1.5	6.4	3.2	2.0	6.3	3.9	1.6	6.7	4.1	1.9
Feldspars	11.6	5.3	2.0	3.1	2.4	1.3	6.7	4.9	1.4	4.3	2.6	1.6
dolomite	4.5	4.5	1.0	-	-	-	-	-	-	-	-	-
Calcite	-	-	-	-	-	-	-	-	-	4.3	3.6	1.2
vitreous particles	5.3	3.6	1.5	6.3	2.7	2.1	6.2	3.8	1.6	4.8	3.5	1.4
Man-made compounds	16.6	12.8	1.4	3.5	2.7	1.2	17.8	14.1	1.2	6.3	3.8	1.6
Metal-rich particles	3.9	2.6	1.5	3.4	2.0	1.4	2.8	2.2	1.3	3.9	2.9	1.3
TiO ₂	-	-	-	-	-	-	2.7	2.7	1.0	-	-	-
siO ₂	26.2	17.2	1.5	-	-	-	5.6	4.9	1.1	14.2	6.3	2.3

ConClusions

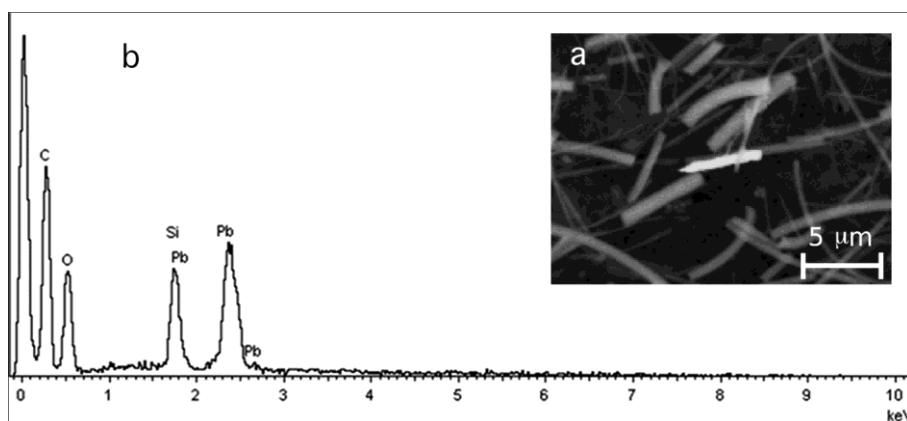


Fig. 7 - backscattered SEM image of an elongated metal-rich particle in urb1 b) Eds spectrum of the particle in a) showing important bands produced by Pb X-ray scattering; si and o are due to the fused silica fibers rising from the original support and close to the metal-rich particle.

TABLE 5

Mean size of the particles (L = length, d =diameter, L/d = aspect ratio) for each inorganic species identified in the samples collected on fused silica filters. The error for the measures is $0.2 \mu\text{m}$. Serpentine is considered separately from the other phyllosilicate minerals in order to highlight the possible presence of chrysotile, regulated "asbestos" by the Law (Directive 2003/18/EC).

	UrB1			UrB2		
	1 μm	d μm	L/d	1 μm	d μm	L/d
Phyllosilicates	6.8	6.1	1.1	8.5	6.3	1.2
serpentine	11.1	6.3	1.8	5.5	2.7	2.1
Feldspars	4.9	4.1	1.2	9.8	6.6	1.6
Metal-rich particles	4.8	2.9	1.9	13.1	14.8	1.3
barium sulfate	3.0	2.3	1.4	8.2	5.3	1.6
Calcium-rich particles	3.1	2.2	1.4	9.5	6.4	1.3

The methodology elaborated during this study proved suitable for chemical, mineralogical and morphological characterization under sEM/Eds of the inorganic particles in PM_{10} , starting from filters routinely used by the Environmental Protection agencies for monitoring the air quality. since the transfer of the particles from the original filters to the support more suitable for sEM/Eds study was a step necessary for analyzing particles, entrapped in the close net of the fibers forming the original filters, the data exposed in this work cannot be considered quantitative. nevertheless, information useful for the Environmental Protection agencies on the phases more frequent in the PM_{10} collected under different environmental conditions and in several areas can be obtained. in fact, our study on samples from different critical situations - two factories with high environmental impact, a road characterized by a heavy vehicular traffic and an urban area - and sampled using two different membranes (fused silica and glass fibers) allowed:

a) to observe easily particles/fibers constituting the PM_{10} sample avoiding interferences of the

material from the original support;

b) on the basis of the Eds chemical analysis, to assign the different observed particles to the inorganic/mineral phase;

c) to propose an apportionment of the detected phases to different sources, either natural or anthropogenic and match this data with the gravimetric analyses; as an example the sample sTa is characterized by a gravimetric value below the law limits, but at the same time shows the highest fraction of particles from anthropogenic sources proving that potentially toxic particles can be in significant amount also in samples with low gravimetric value;

d) to exclude the presence of fibrous breathable phases ascribing to asbestos in the studied area.

The proposed methodology turns out therefore reliable, cheap and fast for obtaining reproducible information about the chemical, morphological and mineralogical characteristics of suspended inorganic particles in the PM_{10} - useful also for the Environmental Protection agencies. Certainly, other studies are necessary to improve the methodology, but at the moment it appears reliable to analyze the filters every day sampled

by the Environmental Protection agencies to control the air quality, without further *ad hoc* sampling.

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