Abstract: PM10 samples were collected simultaneously at three representative areas (central city, industrial area and rural clean air). Their morphology and elemental composition were determined by scanning electron microscopy coupled with energy analysis (SEM-EDS). The particles were classified into groups based on morphology and elemental composition.

Keywords: SEM-EDS, morphological and chemical characterization, single particle analysis.

1. INTRODUCTION

The use of Scanning Electron Microscope (SEM) has found application in the field of particulate air pollution for several years, its use has helped the study of particle morphology and single particles chemical composition. In fact, the simultaneous characterization of both physical-chemical and morphological parameters of a complex mixture of organic and inorganic particulate matter is one of the major aspects for the characterization and identification of emission sources that contribute to particulate concentrations in the atmosphere [1]. The particles collected on filters show a large number of shapes and sizes [2-5]. Neglecting this morphological variety couldn’t help to adequately consider the effects of many processes, such as the absorption of volatile molecules of air and water, particles chemical reactivity and their origin. Many studies have looked at individual characterization of single particles [6, 7]. Electron microscopy is a useful tool that allows the characterization of individual aerosol particles by going beyond the limitations imposed by a bulk chemical analysis [8, 9] that provide us a full characterization of a particulate filter without any single particles data. The aim of this work were to chemical and morphological characterize the particulate matter sampled in three site of central Italy. This also allowed to gather information on the main aerosol sources acting on the studied area.

2. EXPERIMENTAL EQUIPMENT AND SITE

The particulate matter was sampled at three stations located along the Tyrrhenian coast: the first sampling station was placed in a city park, the second station was placed in a site of industrial interest and the third station in a rural site. All three sites are located at a distance of 0.5 km from the sea and are approximately equidistant from each other: the urban park is located 5.5 km from the industrial site which is about 4 km from the rural site.

The particulate matter was collected by samplers Hydra Dual Channel, using a sampling flow of 2.3 m³/h. Sampling was carried out at 6 hours (14:30 to 20:30; 24/07). The filters used are polycarbonate membrane, particularly suitable for analysis by SEM, with a diameter of 47 mm and a porosity of 0.8 microns.

In order to carry out morphological and chemical analyses of the single particles, SEM images have to show particles well separated from each other and, moreover, the presence of particle clusters, which can be generated during a long time sampling, have to be minimized. In order to choose the best sampling condition filters sampled in each site for 24, 12 and 6 hours have been observed by sem. SEM images of particles sampled in the yard site are shown in Figure.

This site presents an higher amount of PM10 than the other sites and it is due to the construction activity in this site, so its SEM images of PM show an higher amount of particles and clusters than the other site images. 6 hours sampled filters were choose because they present distinct particles and because the number of clusters is reduced in comparison to filters sampled for 12 and 24 hours. In this work filters sampled from 12:30 to 18:30 were analysed. In order to study the atmospheric particles sampled in the same
In order to obtain detailed SEM images for an accurate determination of morphological parameters, the image definition and the area of the particles are essential. Considering that in scanning electron microscope the lateral resolution is often on the order of 100-200 nm for atmospheric aerosol particles with low contrast (i.e., particles from combustion processes) and that microanalysis of particles with diameter less than 0.6 µm give signals not statistically distinguishable from background, then, fixed five values of magnification, particles with defined area and diameter were analysed for each values. The selected magnification of SEM images and the relative analyzed particle dimensions are: particles of area between 72.3 and 289.4 µm$^2$ (which corresponds to 9.6-19.2 µm diameter respectively) have been observed with a magnification of 600x, particles area between 18.1 and 72.3 µm$^2$ (4.8 - 9.6 µm diameter) with a magnification of 1200x, particles area between 4.5 and 18.1 µm$^2$ (2.4 - 4.8 µm diameter) with a magnification of 2500x, particles area between 1.13 and 4.5 µm$^2$ (1.2 - 2.4 µm diameter) with a magnification of 5000x and than particles area between 0.28 and 1.13 µm$^2$ (0.6 - 1.2 µm diameter) have been observed with a magnification of 10000x. These selected magnifications allow to analyse the chemical and morphological parameters of particles in the entire particle size range considered (with a continuous area and diameter range, 0.28 - 289.4 µm$^2$ and 0.6 - 19.2 µm respectively).

In order to obtain a representative data set, the minimum number of particles to be observed was 400 [10] for each sample: an adequate choice of the number of observed particles guarantees a more representativeness of samples. For the systematic analysis of particulate, the operational settings of the SEM were: Low Vacuum 0.7 torr, beam voltage 30 Kv; Acquisition time 100 Lsec; Working distance 10 nm.

3. PARTICLES CLUSTERS AND MORPHOCHEMICAL CHARACTERIZATION

Examining SEM images and the spectrum of the single particles these were distinguished and labelled as: particles of aluminosilicate (AlSi); particles rich in calcium (Ca); carbonaceous particles of biological origin (Cb); soot particles (carbon particles from incomplete combustion of organic matter) (Cs); cenosphere (Cc); salts of sodium chloride (Cl); sulfates (Sc); metal particles (Me); spherical particles of iron (Fe); various (particles without a characteristic spectra) (Va).

Aluminosilicate (45.1% of particles): these particles are composed primarily of feldspar (Si, Al, Ca or Si, Al, K) and clay (Si, Al or Si, Al, Fe), their origin is mainly crustal, but they can also come from erosion of building products and road dust. Other elements are present in minor concentration in the aluminosilicate particles and they are Na, Mg, Ti, Mn, Ni and Zn. Within the family of aluminosilicates some crustal particles rich in Si (principally quartz) are included, for the similar origin. These particles mainly present an angular shape, ranging from polyhedral to sharp one. Calcium-rich particles (21.7% of particles): in this cluster particles with a high concentration of calcium are included. They are calcium carbonate, calcium oxide and particles with minor concentration of elements such as Al, K and Si. These particles can be related to crustal source and they can belong to yard activities such as lime production and the use of cement. These particle are present in the whole studied size range and they show a greater Roundness than the aluminosilicates. Biological carbon (4.8% of particles): biological particles (pollen, spores and plant fragments) show an high content of carbon and oxygen, and sometimes they are characterized by minor content of elements such as Na, Mg, P, K and Ca. They are characterized by regular and symmetrical shapes, ranging from spherical to elliptical shape.

Soot (7.2% of particles): these particles are an agglomeration of carbon particles resulting from incomplete combustion of organic matter, they are characterized by 80% - 96% of carbon in relationship to the physical-chemical condition of combustion. They are originated from combustion of burning oil, gasoline, diesel, fuel oil, paraffin, butane; they are, therefore, an important tracer of vehicular traffic.

The structure of soot particles are strictly related to their age, in fact their shape range from a linear to a more and more branched structure, where the first one is related to a newly formation soot and the second one to an advanced agglomeration. Furthermore this type of particles is characterized by an higher value of Fractal Dimension (average value of 1.16 ± 0.07) than the other particles families (AlSi 1.10 ± 0.04, Ca 1.08 ± 0.03, Cb 1.08 ± 0.04, Cc 1.08 ± 0.04, Cl 1.07 ± 0.03, Fe 1.06 ± 0.01, Me 1.07 ± 0.02, Sc 1.10 ± 0.04). Cenosphere (0.7% of particles): these particles are carbonate and they are originated from incomplete combustion processes of diesel and fuel oil. These particles present a minor amount of S and metals such as V, Ni, Fe, Ti. They are characterized by a spherical shape.

Salts of sodium chloride (3.5% of particles): these particles consist essentially of Na and Cl, sometimes traces of Mg, K, Ca and S are detected. NaCl particles are mainly due to marine aerosols. Calcium sulfate (1.7% of particles): these particles are originated by acid-base neutralization reactions in atmosphere and by deterioration of building’s surface, composed of CaCO$_3$ (marble and limestone), and it is due to reaction with sulfur compounds in the atmosphere. Calcium sulfate is also used for the production of cement and it is a secondary product of desulphurisation of flue gas. The shape of these particles is typically symmetrical and elongated, even if there are irregular examples of particles, too. Metal (7.5% of particles): these are particles with an high metal content such as Fe, Zn, Ti, Cu, Mn and Cr. They are originated by different sources depending on the metal content: particles containing mainly Fe, for example, can be of crustal origin, but may also come from human activities such as industrial processes, abrasion of metallic materials and traffic-related sources.
**Spherical particles of iron** (0.4% of particles): These particles consist exclusively of iron oxide. Their size ranges between 0.2 and 2 µm and they present a peculiar morphology, in fact they are characterized by a perfect sphericity indicating their smelting iron origin or metallurgical activities in general. They are characterized by shape factor (Roundness) of 0.9 ± 0.13 and Fractal Dimension of 1.06 ± 0.01.

**Various** (6.9% of particles): these are particles without a characteristic spectra with the presence of low analyta signals. Moreover, it has to be pointed out that analyzing the size of the particles they present the smallest values. The absence of characteristic spectra for these particles is mainly due to a instrumental limit of technique for particles with diameter less the 0.6 µm. Than the amount of elements is underestimated for small particles, compared to a particle of the same composition but larger. So particles classified as 'various' are characterized by low weight percentages of the investigated elements and their classification turns out to be difficult.

The sites are characterized as in the following graph:

![Figure 2) Distribution of particles in the industrial site.](image)

![Figure 3) Distribution of particles in the rural site.](image)

Analyzing the obtained data they show that:
- The cluster of aluminosilicates was more abundant in the industrial site, mainly due to the construction material and the suspended dust caused by vehicular traffic within the yard, during the daytime period.
- The calcium-rich particles were more abundant in the industrial site than in the urban site and than in the rural site. This trend was compatible with the possible origin of the particles found: erosion of soil and rocks but also the use of building materials containing cement.
- Biological origin particles were particularly evident in the rural site and in the city park, even if the biogenic contribution varies with the seasons and it is linked to the plant activity.
- Cenosphehers were present essentially in the urban site, characterized by a more vehicular traffic pollution.
- Chlorides were due to the proximity of the sea.
- Soot particles, which is due mainly to motor of vehicle or combustion, were more abundant in the city even if they were present in all the sites: this means that also the other two sites are influenced by anthropogenic activities.
- The iron spherical particles are present in low amounts in all types of site;
- Metal particles were more abundant in the urban and rural site; they included both particles of probable crustal origin (mainly oxides of Fe) and particles of anthropogenic origin.
- Sulfates were present in the industrial and urban site but insignificant in the rural site.

**5. ACKNOWLEDGMENTS**

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**6. REFERENCES**


