Characterization of atmospheric particulate matter by thermal analysis

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INTRODUCTION

One of the most important problems for air quality management is the pollution from fine particulate matter, PM10 and PM2.5. Particulate Matter (P.M.) is one the most important pollutant monitored for the air quality assessment and in particular PM10/PM2.5 have direct effects on human health. This pollutant deals with a wide range of sources either anthropogenic, natural or "secondary", as well as with climatological and meteorological phenomena [Schnelle-Kreis 2001, Lunz 2001]. Many research studies have shown that the composition of the PM10/2.5 is very different, depending on the monitoring site [Paoletti 2001].The complex mixture of inorganic and organic compound dealing with the particulate matter composition is one of the main aspects either for their characterization or for the sources emissions apportionment. Carbonaceous materials make up a large fraction, sometime dominant, of ambient particles and depending on their nature it is possible to distinguish the emitting sources, either primary or secondary ones. The carbonaceous fraction is composed of elemental carbon (EC) also called Black Carbon (BC) (graphitic carbon mostly emitted by combustion processes) and organic carbon (OC) (a mixture of hydrocarbons and oxygenates compounds) can be emitted either directly from sources (primary OC) or formed in ambient air. The long range transport phenomena and the consequential interaction of the aerosols with the atmospheric chemistry is, at the present time, one of the main research topics. The emitted soot particles (EC) through coagulation, condensation of aerosol organic compounds and cloud processing change their chemical composition. The complex mixture of OC carbon is constituted of hundreds of organic compounds of different types (aliphatic, PAH etc.) and they also interact with the organic atmospheric chemistry. The researchers were trying to identify the main constituents of this pollutant and the biggest work is now focusing on the identification of molecular constituents and potential tracers that will possibly explain the various sources contributions.
Many techniques are implemented to analyze the collected particles either for the identification of the amount of carbonaceous constituents or for the speciation of the organic components [Fraser et al. 2002, Chow et al. 1993]. Some techniques for the determination of elemental and organic carbon are accepted by the USEPA but the results of recent round robin tests show very high uncertainty in the experimental results[Puxbaum et al. 2001].
The first tests of the characterization of the PM by thermogravimetric balance (TGA), coupled with FTIR, are presented. The aim of this activities is to developed a method to characterize either the ambient air particles or the directly emitted ones, in particular from combustion processes.

PARTICULATE MATTER INVESTIGATION

The complex research work of studying the particulate matter nature, either for air quality monitoring or for the emission characterization, in particular referring to the combustion processes, needs a detailed and methodological approach. In figure 1 all the steps are shown: in our research activities we focused on six main topics: the sampling, the analysis, the

evaluation and elaboration of the air quality data, the meteorological characterization, the emission inventory and the dispersion models. All these phases are strictly correlated one to each other. Firstly, starting from the monitoring of the air quality and the acquisition of meteorological parameters that after appropriate elaboration can well describe the type of pollution of the interesting site.

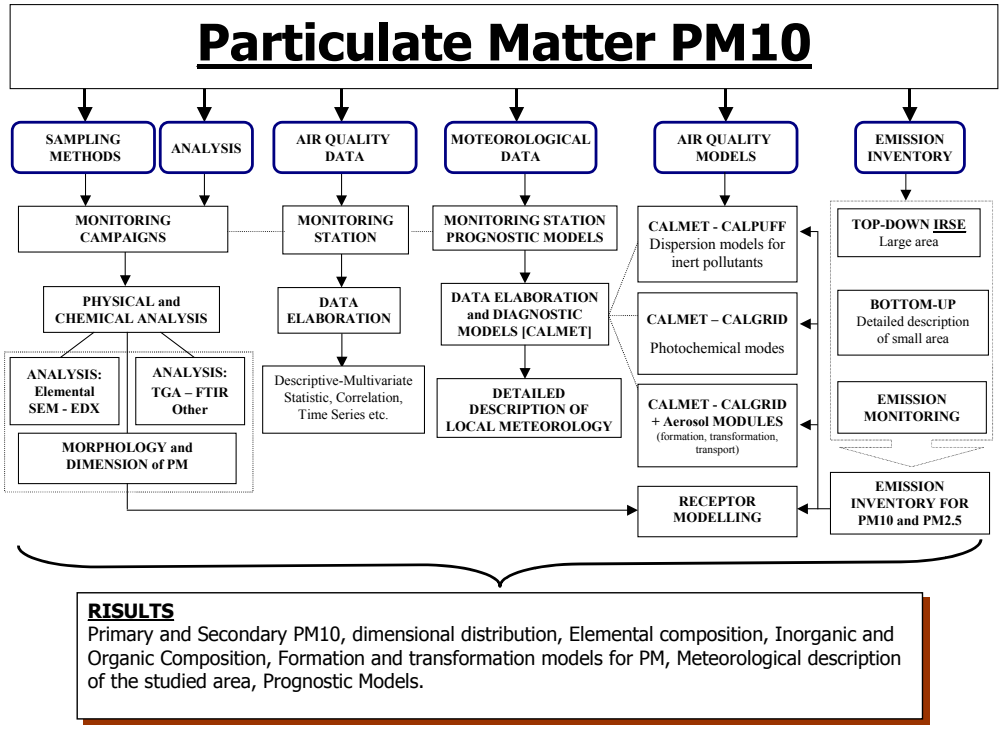

Figure 1 Methodological approach to the study of particulate matter.

Secondly, the emission inventory estimation is one of the main steps for air quality management due to the apportionment of source contribution; for this purpose it is important to use new and detailed emission factor. Then, the sampling and analysis of the PM10 are necessary to characterize the particles by chemical and physical points of view. The last phase is the modeling one, used to estimate how the emission scenarios together with meteorological condition, deal with the pollutant concentration in air.

EXPERIMENTAL

Sampling

Sampling techniques used for characterization of PM are very different concerning to the type of the chemical and physical analysis that should be done. We used either high volume sampler (HVS), Andersen GMW Instruments, with operating flow rate of 1.13 m^3/min and low volume sampler (LVS), Tecora TCR, with sampling head USEPA-cfr part.50 for PM10 and USEPA Wins impactor for PM2.5, with operating flow rate of 16.7 liter/min.

For collecting the aerosols samples we used quartz fiber filters Ø47 mm diameter and 210x240 mm quartz filter paper used with the two different particulate matter samplers. We also used POLICARBONAT PC40 AOX filter Ø47 mm, Ø0.4 μm pore diameters with the LVS. These two types of filter media were used for chemical speciation of the particulate matter: the quartz fiber filters were used, due to their inert behavior, for thermal analysis ant the polycarbonate filters for the morphological and dimension analysis. With the HVS sampler we performed 24 hr a day and of 27 m^3 of air sampling and with the LVS we

collected the particles for 15 minutes every 2 hr during 24 hr for a total amount of 2 m^3 of air.

Analysis

The polycarbonate filters were analyzed with scanning electron microscope SEM-EDX, Jeol 6100, equipped with Oxford ISIS EDX System. This technique allows to analyze the particulate matter with various magnification x100 to x50.000, with very high resolution and to store digitalized images. Those images are then elaborated with an image analysis software, Image-Pro® Plus, for the dimensional and morphological analysis. This software allows to identify up to 20.000 particles on each samples [100μm^2] and measured for their dimensions and shapes characteristics. By the EDX system, X-ray mapping of the following elements were possibly detected on the policarbonate filters: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, Br and Pb. Post processing of image analysis was performed to correlate chemical and dimension results.

Thermogravimetric (TG) data are obtained using a Netzsch STA 409/C thermoanalyzer. Typical sample weights of 15 mg to 30 mg are employed, depending on the pollutant concentration in air the PM weights varies from 3 mg to 0.4 mg. Experimental runs are carried out using a purge gas flow (60 ml/min) either of air or nitrogen. FTIR measurements are carried out using a Bruker Equinox 55 spectrometer equipped with DTGS and MCT detectors. TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during TG runs are carried out coupling the FTIR spectrometer to the Netzsch TG. FTIR measurements are carried out with a MCT detector in a specifically developed low volume gas cell (8.7 ml) with a 123 mm path-length, heated at a constant temperature of 250°C. A new thermoanalyzer, TA instruments 500, was utilized for the test run. This new analyzer allows to carry out more sensible measurement due to the low values of the weight loss that should be done (10^1 μg - 10^3 μg).

RESULTS AND DISCUSSION

The particulate matter samples used for this investigation were collected in Pisa in two different monitoring sites, an urban station and a rural station. The sampling was performed during two weeks one in February 2003 and the other in March 2003. The sampling were done for 24 hr per day and for seven days per week. In figure 2 an image is shown of the PM10 collected with the LVS and used for the elemental and morphological analysis.

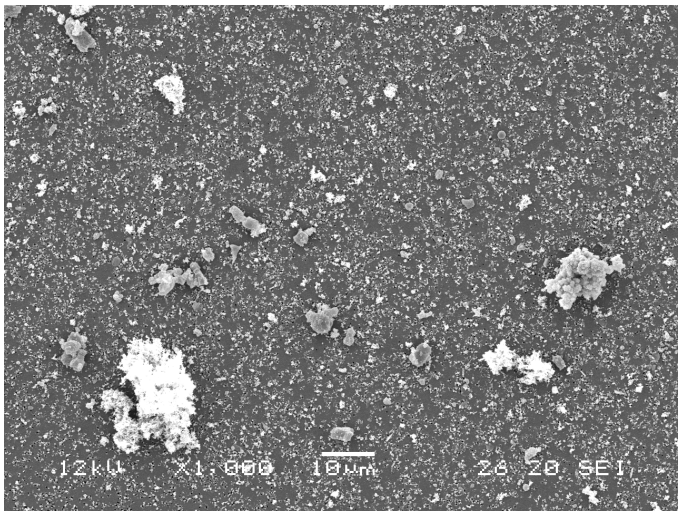

Figure 2 Particulate matter PM10 on polycarbonate filter by SEM analysis.

In table 1 preliminary results of the thermal characterization of the PM10 were reported. The main differences in the weight loss changes were related to the evolution of the organic matter present in the particles. The first step is due to the presence of moisture and then the light and heavy organic compound up to the soot particles. These results allow to identify the OC and EC fraction of the analyzed samples that were important components used for the source apportionment of the emissions, as previously said. The scanning tests were performed in air with an heating rate of 10°C/min up to 960°C followed by 20 minutes of isotherm.

Sample N°	*PM10 concentration [$\mu g/m^3$]*	*Weight loss PM10 [wt %]*				
		100°C	450°C	750°C	n.d.	Total
10SC	90	5.2	47.5	14.3	33	70.2
2SC	91	4.1	40.3	10.7	44.9	66.6
1SB	47	6.4	49.3	5.3	46.5	69.6

Table 1 Results of the thermal characterization of the PM10

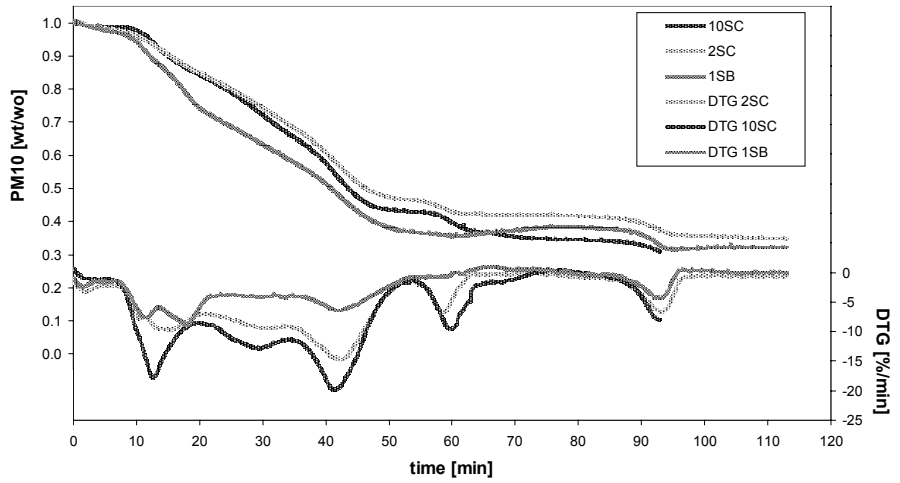

Figure 3 PM10 analyzed with TGA [HR: 10°C/min time: 960°C + isothermal run 20 min]

So far the behaviors shown in figure 3 have been detected. Studying the DTG several peaks during the weight loss tests were identified. Those peaks can be correlated firstly to the moisture release (100°C) and then to the various steps (450°C-500°C, 750°C-800°C) for volatile materials and combustion processes. The main steps to compute the organic and elemental carbon as far as their operative definitions are 450°C and 750°C. Different tests with inert gas and heating programming are now studied to upgrade the tests performances.

REFERENCES

1. Fraser M.P., Yue Z.W., Tropp R.J., Kohl S.D. and Chow J.C.: Atmospheric Environment 36: 5751-5758 (2002)
2. Schnelle-Kreis J., Gebefügi I., Welzl G., Jaensch T. and Kettrup A., *Atmospheric Environment* 35(1), S71-S81 (2001)
3. Lutz M., Lenschow P., Abraham H.-J., Kutzner K., Preuβ J.-D., Reichenbacher W.: *Atmospheric Environment* 35(1), S23-S33 (2001)
4. Puxbaum H., et al.: *Atmospheric Environment* 35, 2111-2121 (2001)
5. Paoletti L., De Berardis B.: *The Science of the Total Environment* 292, 265 (2001)