Elemental and Organic Carbon: the starting point

The European Directive 2008/50/CE and its Italian transposition (DLgs 155/2010) have introduced the Organic and Elemental Carbon (OC-EC) on PM2.5 filters sampled in rural sites, aiming at collecting sufficient information to characterize the background levels.

At the same time, since one of the general objectives of the Lombardy Region is to obtain information and knowledge on ambient air quality as a basis for identifying the measures to be taken to combat pollution, to better comply with the Directive it was predisposed the Supersite Project. Within this project they have been identified "Special Sites", or stations to meet specific regulatory requirements; "Supersites", or stations in which are activated measurements of air quality parameters with high frequency, relevant to the achievement of specific objectives; "stations deepening", or sites identified for specific and intensive campaigns as a support to the information collected with continuity in the other stations.

For the above reasons, ARPA Lombardia has acquired the proper tools in order to perform the necessary depth of expertise.

Here the analysis performed with the purpose of choosing the analytical protocol to be adopted for carrying out the analysis of OC-EC has been discussed.

OC and EC have, at present, only an operational definition, namely: OC is defined as the fraction of total non-inorganic carbon volatilized or pyrolyzed to a specific protocol; EC is defined as the fraction of non-inorganic carbon in the sample of PM , characterized by its non-volatility, according to a specific protocol thermo-optical and it evolves from the sample just to oxidation.

For the determination of the carbonaceous component of the particulate deposited on the filter, ARPA Lombardia features a device based on the thermo-optical method, or TOT/TOR (Thermal-Optical Transmittance/Reflectance): the carbonaceous components of PM are volatilized, oxidized and then quantified on basis of the signal of the CO_2 released, appropriately corrected by the refractory components that can form in the process. The determination of the OC-EC deposited on the ambient air filter is regulated by the CEN/TR 16264:2011.

Because temperature in the analysis phase can be very high, quartz fibre filters should be used. Since this type of array can produce artefacts, or may present intrinsically an amount of organic substances, they must be suitably treated before being sampled. The pre-treatment consists of a passage in a muffle furnace at 600°C for about two hours. After this treatment, filters may be weighed and used on gravimetric samplers.

To quantify the content of OC and EC of a filter, it is used the principle of desorption and oxidation at temperatures well defined. The signal transmittance and/or reflectance (based on the model of the instrument) is used to correct what is called "charring effect" or the production of pyrolytic carbon during the first temperature ramp that goes to overlap to the signal of the final EC, through the issuance of EC secondary.

A precision tool is used to select a fragment of area well defined (punch from 1.5 cm²) from the filter sampled and weighed, and then placed on a support that is inserted into the oven of the instrument. In this first phase (Phase 1, inert carrier gas), the heating takes place in a helium atmosphere, without oxygen, and the temperature increases up to the first maximum (typically from 550°C to 900°C, according to the protocol applied), allowing the volatilization of OC and the consequent emission of pyrolytic carbon (PC). In the second phase (Phase 2, oxidative carrier gas) to the atmosphere of helium is added to an oxygen percentage and the temperature drops to 500-600°C before starting a second temperature ramp that reaches 800-900°C. In Phase 2, the EC and the PC are oxidized to CO_2. All gases which evolve from the punch during the first two phases are brought into a furnace of manganese dioxide where organic vapors are oxidized into CO_2. The CO_2 can be directly detected by a detector or mixed with hydrogen and conducted into an atmosphere of helium through a heated nickel catalyst which reduces the CO_2 into methane. The methane is then measured using a FID.

The function of the laser transmittance and/or reflectance is to correct the production of PC from OC that can be produced during Phase 1: if not taken into account, it could likely be underestimated and overestimated the concentration of OC to EC. The correction can be carried out thanks to a continuous control signal reflectance and/or transmittance of the laser beam: when there is the production of charring in Phase 1, the signal generally decreases and then increased when the whole PC is oxidized (split-point). From here on, all the carbon that evolves is considered EC. As the particulate matter can penetrate into the filter during the analysis, the concentration value of the OC and EC may change between the signal in transmittance and the reflectance. Conversely, this effect does not affect the determination of total carbon (TC), whose signal has no dependence with the processing mode in transmittance and/or reflectance.

Currently four protocols have been adopted to set the operating parameters (exposure time and temperature) that perform such analyzes (Table 1).

	NIOSH-Like		NIOSH-5040		IMPROVE		EUSAAR2	
Step	T (°C)	t (s)	T (°C)	t (s)	T (°C)	t (s)	T (°C)	t (s)
He1	310	60-80	250	60	120	150-580	200	120
He2	475	60	500	60	250	150-580	300	150
He3	615	60	650	60	450	150-580	450	180
He4	870	90	850	90	550	150-580	650	180
He	No heating	50					No heating	30
He/O_2 1	550	45-60	650	30	550	150-580	500	120
He/O_2 2	625-650	45-60	750	30	700	150-580	550	120
He/O_2 3	700	45-60	850	30	800	150-580	700	70
He/O_2 4	770-775	45-60	940	120			850	80
He/O_2 5	870-890	110-165						

Table 1 – Protocols adopted by CEN/TR 16243:2011 (E).

The legislation has not yet given an indication of the protocol to be used. The scientific community is moving on the choice between two protocols among the four in the table: the NIOSH-Like and EUSAAR2.

Before making a choice of action, we selected a great number of filters of PM10 sampled in Milan-Pascal (from 26th November 2012 to 10th January 2013, for a total of 46 filters) to apply both protocols. Figure 1 shows on the left the daily concentrations of total carbon (TC = OC + EC) determined with both protocols, compared with the average daily PM10 and, on the right, the TC correlation between the two protocols applied.

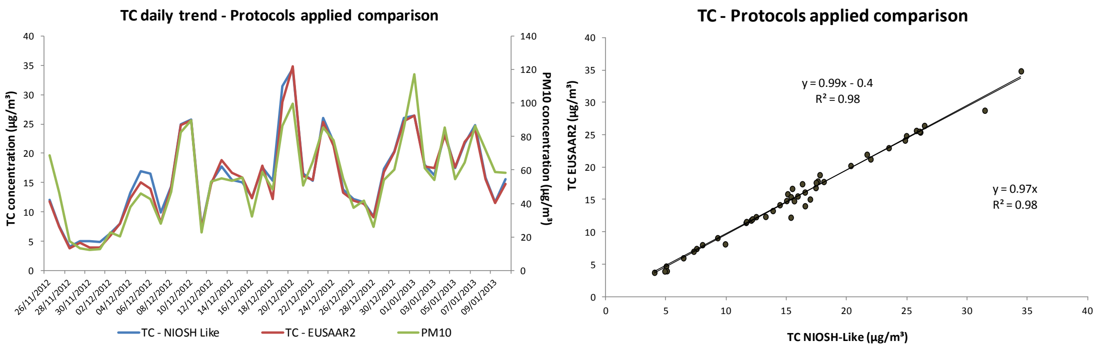

Figure 1 –TC and PM10 daily trend (left side) and correlation between two applied protocols on TC (right side).

If you focus on the determination of total carbon, the two protocols appear to be entirely comparable, showing a good correlation (m=1, R^2=0.98), consistent with the previous discussion. As the legislation requires the determination of the OC and of EC and not only of the TC, ,the graphs of Figure 2 show the correlations made on determinating OC and EC by applying the two protocols NIOH-Like and EUSAAR2 and considering both the signal, transmittance and reflectance.

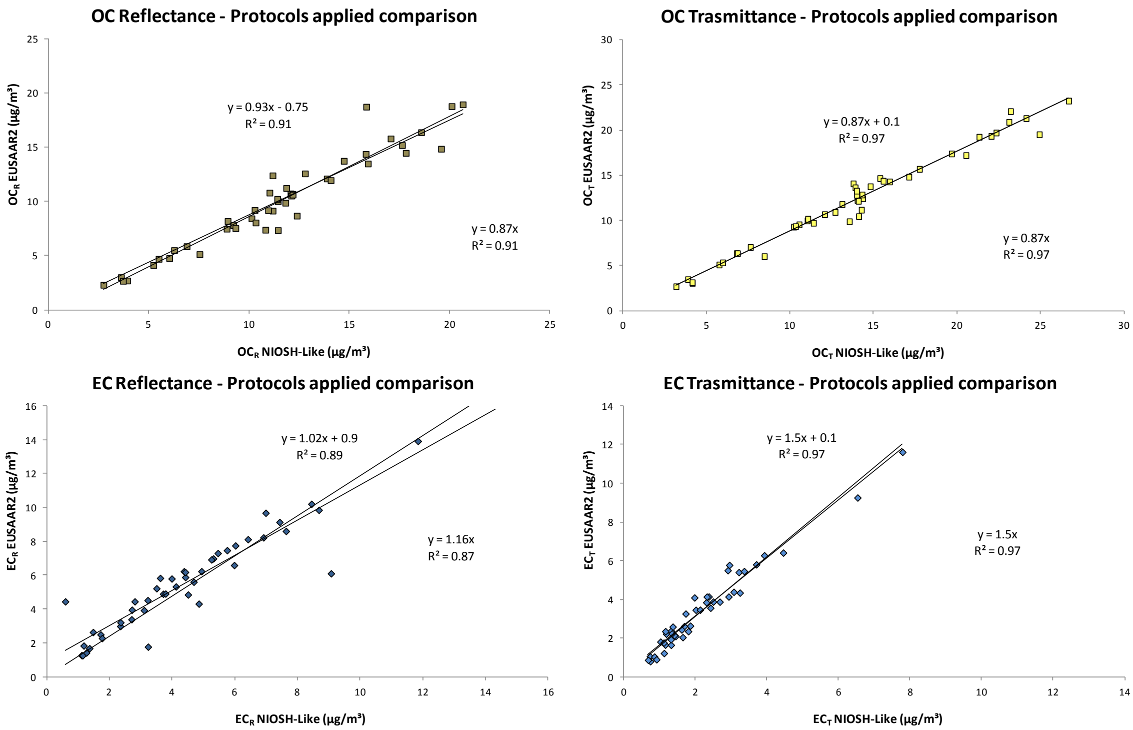

Figure 2 –OC(up) and EC (down) correlations between two protocols applied, and referred to Reflectance (left) and Trasmittance (right) signals.

Analysis of the correlations shows firstly a lower dispersion of data whereas the signal transmittance with respect to reflectance; in addition, since the reflectance signal is only used by the last available version of this type of tools, to be able to have available data always comparable with the literature, the first choice has been to use the concentration detected by the signal transmittance.

By the same signal (Transmittance), the application of the two protocols shows a difference of about 13% on the determination of the OC and, instead, 34% on the determination of EC.

To make an objective choice about the protocol to be applied on our filters, for the purpose of comparability on measurements at the various sites, it was made the analysis of the thermograms. In Figure 3,the thermograms are shown as example concerning the application of the two protocols, on the same sample, PQ271, referred to 22th December 2012.

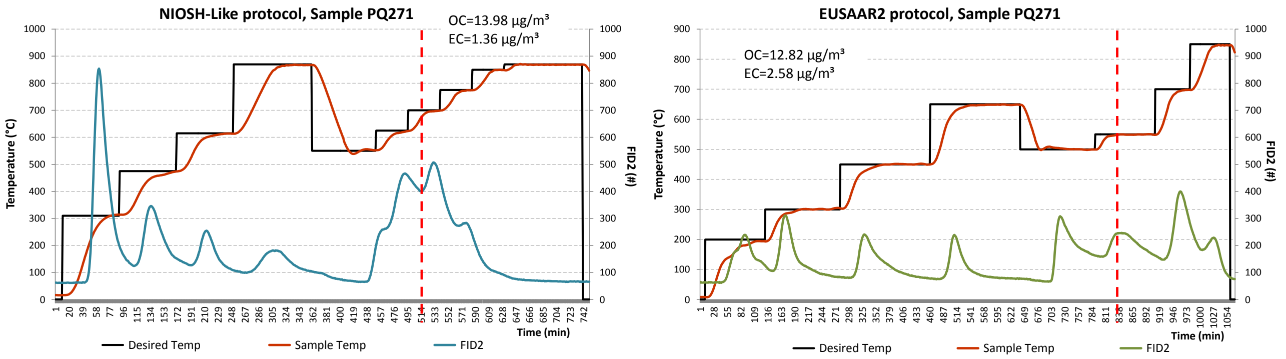

Figure 3 –Thermogram analysis of the sample PQ271: NIOSH-Like on the left and EUSAAR2 on the right side.

Thermograms show a better recognition of the first phase of the split-point of the graph on the left. In addition, the higher temperature set in the NIOSH-Like protocol for the achievement of the first ramp favors the emission of a signal net (peak of OC). This is not seen in the thermogram relating to protocol EUSAAR2: during phase 1, because of the lower set temperature (200°C compared to 310°C), it has greater production of PC. This is reflected in the concentration results for this sample (Table 2).

PQ271	NIOSH-Like	EUSAAR2
OC (μg/m³)	13.98	12.82
EC (μg/m³)	1.36	2.58

Table 2 – Results related to PQ271 sample, with two protocols applied.

As expected and given by the magnitudes involved, the increased production of PC occurs in an underestimation of the value of OC by about 8%, offset by an overestimation of the EC value of about 47%.

From literature (Piazzalunga et al., 2011 and references cited therein) is known that the formation of PC is also favoured by the presence of soluble organic compounds in the particulate and therefore a better quantification of EC can be done by removing such compounds, for example by washing with pure water.

This technique can not be used for everyday analysis as onerous; however, experimental tests have shown that the use of protocols such as the high temperature NIOSH-Like, minimizes the differences between the results of a sample subjected to analysis with and without washing, compared the use of a protocol that operates at lower temperatures as the EUSAAR2.

For all these reasons it has been decided that, where there are no specific indications, ARPA Lombardia in the analysis of particulate organic fraction through thermo-optical method will use the parameters established by the Protocol NIOSH-Like.

Centro Regionale Monitoraggio della Qualità dell'Aria
Ufficio Progetti Speciali

Cristina Colombi Vorne Gianelle