

Methodology to determine carbonate carbon from Thermal Optical Transmittance measurements

M. R. Perrone¹, A. Piazzalunga² and M. Prato³



¹ CNISM, Physics Department, University of Salento, Via Arnesano, 73100 Lecce, Italy (perrone@le.infn.it)
² Department of Environmental Science, University of Milano Bicocca, 20126 Milano, Italy
³ Department of Pure and Applied Mathematics, University of Modena and Reggio Emilia, Modena, Italy

Carbonate carbon (CC) is often not considered in atmospheric aerosol chemistry studies which comprise the measurement of elemental carbon (EC) and organic carbon (OC). The reason for this may be its low contribution to fine particle mass in most area along with the difficulties in its analytical determination in atmospheric aerosol collected on filter matrices.

However, the CC fraction in particulate matter may not be negligible if high concentrations of mineral dust, either natural (natural erosion, sand storms) or originating from street abrasion or construction sites are present.

We have implemented a methodology to determine CC, OC and EC levels from Thermal Optical Transmittance (TOT) measurements on ground collected samples without pre treating the samples with HCl fumes.

Methodology

We have used the sample pretreatment with HCl fumes to identify the CC contribution to the flame ionization detector (FID) signal from TOT measurements.

The time evolution analysis of the FID signal before (black line) and after (grey line) the treatment with HCl fumes, has revealed that the CC peak may occurs within the 220-250 s time interval and that it is characterized by a full-with-at-half-maximum $\Delta t^* = 25\pm 3$ s

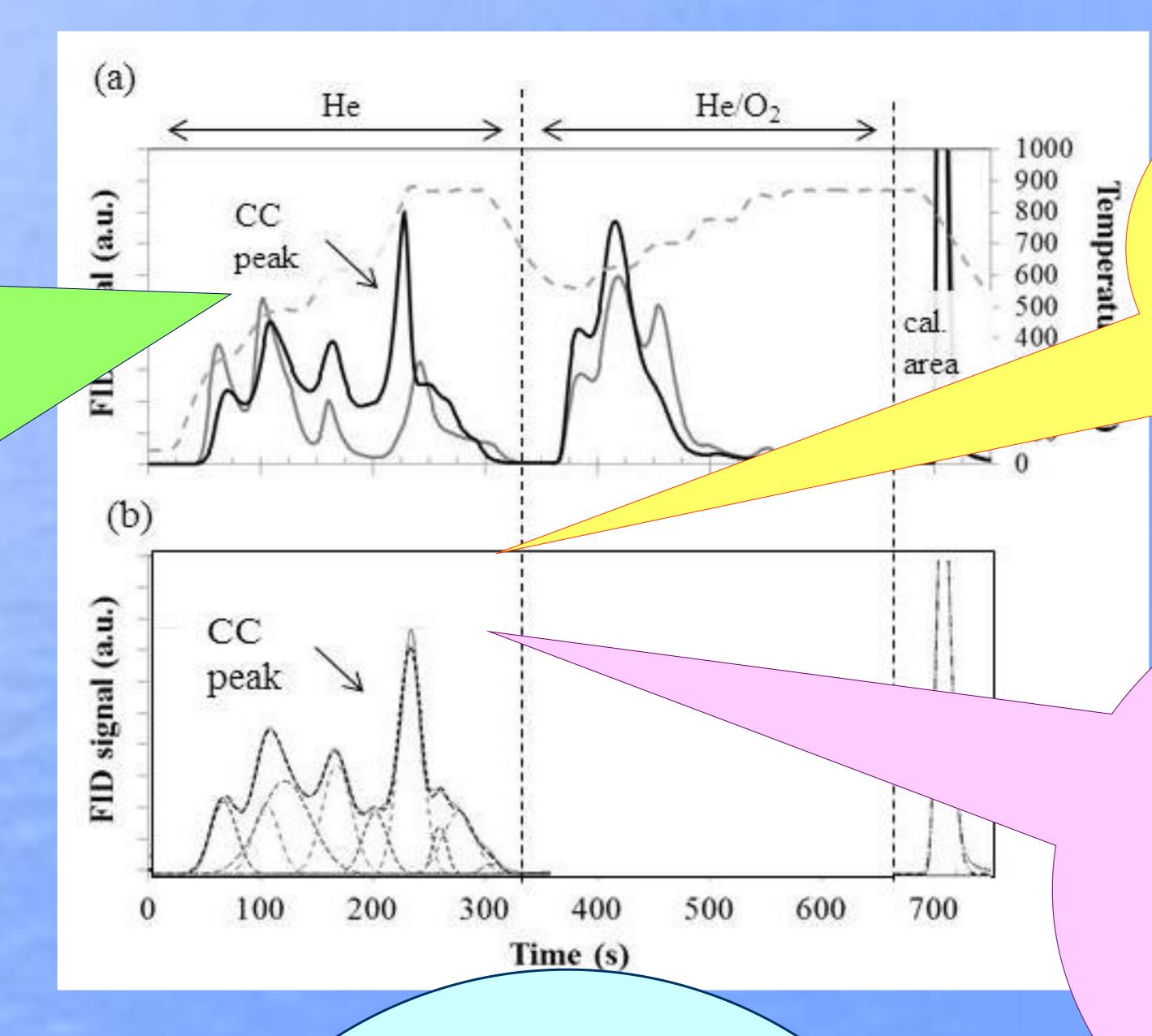
Results

■ EC

TSP

■ OC

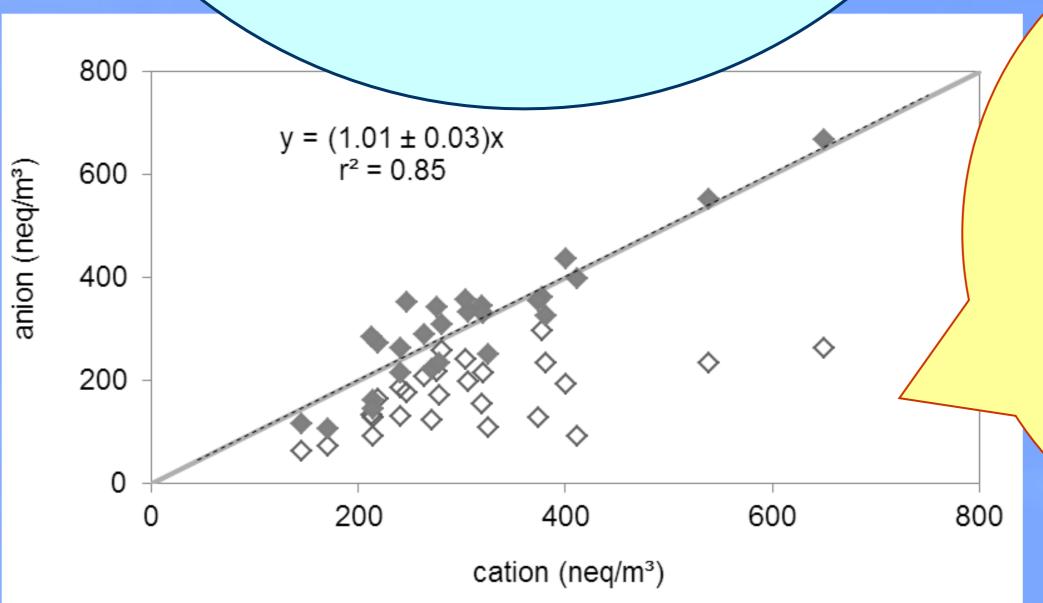
· CC



EC, OC, and CC have been measured in 26 TSP and PM2.5 randomly selected samples, which have been collected over southeastern Italy in 2007.

The CC/OC mass ratio varies within the 0.02 - 0.4 and 0.02 - 0.2 range in TSP and PM2.5 samples, respectively.

Hence, OC levels can be quite overestimated in TSP and PM2.5 samples if the CC contribution to the FID signal is not accounted for.



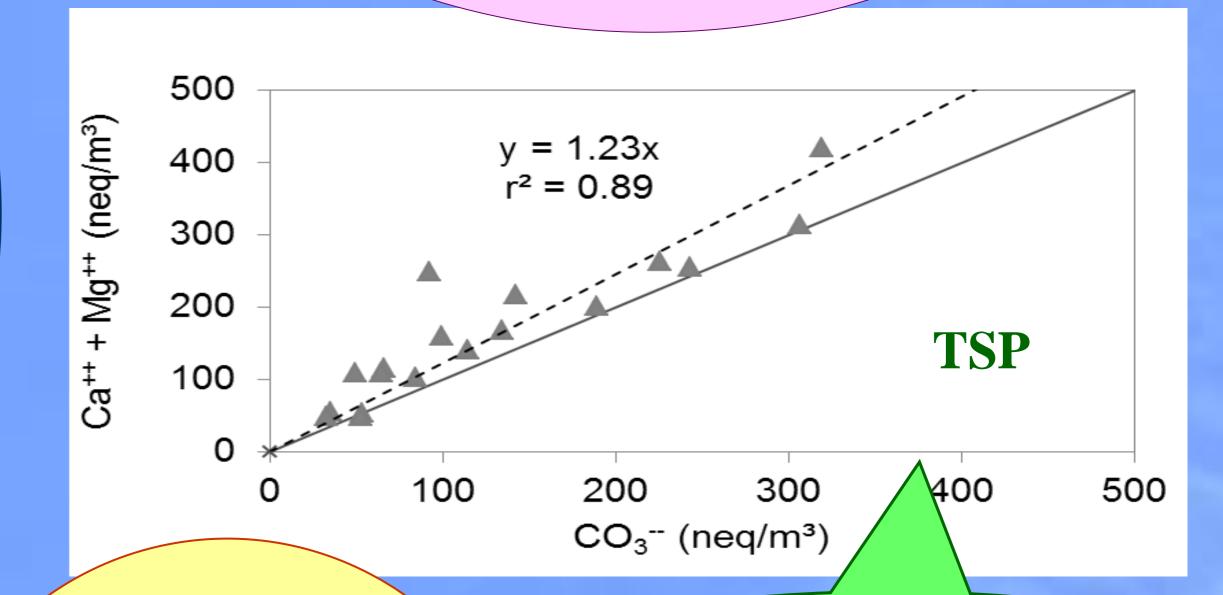
The FID signal has been represented as a weighted sum of Gaussian functions:

$$S(t) = \sum_{i} a_{i} \exp[-(t-t_{i})^{2}/2\sigma_{i}^{2}]$$

where a_i, t_i, and σ_i represent amplitude, peak-time and standard deviation of the Gaussian function i.

We have assumed that the CC volatilization contributes to the FID signal with a pulse which can be fitted by a Gaussian function with the peak at a time t_i (within the 220-250 s time interval) and a full-width-at-half-maximum $\Delta t_i = 25\pm3$ s.

Then, we have calculated the Gaussian function area ascribed to the CC volatilization and the area of the calibration signal, to quantify CC levels.



Scatter plot of the sum of anions versus the sum of cations in TSP samples.

Open diamonds refer to data points when CO_3^{2-} is not accounted for.

 CO_3^{2-} is mainly neutralized by Ca^{2+} and Mg^{2+} .

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