

Methodology to determine carbonate carbon from Thermal Optical Transmittance measurements

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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. Carbonate particles are expected to significantly contribute to the Mediterranean PM mainly during the intrusion of air masses from North Africa. 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. Some thermal-optical methods have recently been used to determine carbonate carbon, along with different organic fractions and EC and it has been shown that the interference of CC with the signal of EC or OC may lead to overestimations of either of these two carbon fractions during thermal-optical analysis (Karanasiou et al., 2010). The use of a sample pretreatment with HCl fumes to eliminate CC prior to the thermal analysis is suggested to avoid the interference by carbonate particles. We have used the sample pretreatment to identify the CC contribution to the flame ionization detector (FID) signal from TOT measurements and implement a numerical procedure to determine CC, EC, and OC levels. The time evolution analysis of the FID signal before and after the treatment with HCl fumes of TSP and PM2.5 samples, has revealed that the CC peak may occur within the 220-250 s time interval and that it is characterized by a full-width-at-half-maximum (FWHM) $\Delta t^* = 25 \pm 3$ s, in accordance with previous studies. 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 the time t_i (within the 220-250 s time interval) and the FWHM width $\Delta t_i = 25 \pm 3$ s, to determine CC levels. In particular, we have calculated the Gaussian function area ascribed to the CC volatilization and the area of the calibration signal, to quantify CC levels in the analyzed PM samples. This calculation has been carried out through a fitting procedure, in which the FID signal is represented as a weighted sum of Gaussian functions, $S(t)$, through an algorithm implemented by ourselves in Matlab[®]. In fact, we have assumed that $S(t)$ can be represented by the following relationship:

$$S(t) = \sum_{i=1}^N a_i e^{-(t-t_i)^2/2\sigma_i^2} \quad (1)$$

where a_i , t_i and σ_i represent amplitude, peak-time and standard deviation of the Gaussian function i and N represents the total number of Gaussian functions. The FID signal has at first been interpolated with cubic splines to obtain a straightforward calculation of its first and second derivatives. Then, through the analysis of the second derivative minima we have automatically identified the number N of Gaussian functions composing $S(t)$. A FWHM $\Delta t_i = 25 \pm 3$ s has been imposed to the Gaussian function ascribed to CC, in accordance with experimental results. We have assumed that CC level uncertainties are mainly due to the uncertainties of the parameters defining the Gaussian function fitting the CC volatilization signal. The implemented technique has been tested by determining CC, OC, and EC levels in 26 TSP and PM2.5 samples which have simultaneously collected over south-eastern Italy, in the Central Mediterranean. We have found that uncertainties on CC levels vary from 0.1% up to 9% and from 0.2% up to 20% in TSP and PM2.5 samples, respectively. It has also been shown that OC levels may be quite overestimated mainly in the coarse fraction, if the CC contribution is not accounted for. Figure 1 shows as an example Ca^{2+} and CO_3^{2-} levels (calculated from CC concentrations) in the 26 analyzed TSP samples. The good correlation between Ca^{2+} and CO_3^{2-} levels support the reliability of the implemented technique: carbonate-containing mineral dust is often associated with calcium. The anion deficit defined as an excess of positive charge, which is often found in Mediterranean PM samples, has been used in some Mediterranean studies to infer and estimate carbonate mass concentrations.

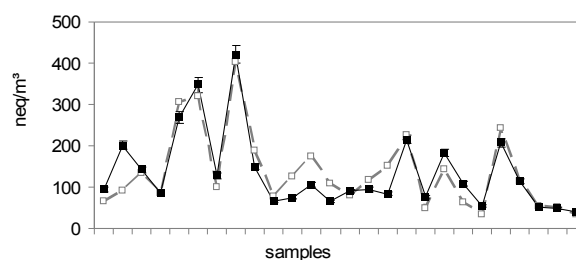


Fig. 1 Ca^{2+} (full boxes) and CO_3^{2-} (open boxes) levels (neq/m^3) in the 26 analyzed TSP samples

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Karanasiou et al., Atmos. Meas. Tech. Discuss., 3, 5375-5409, 2010.