Quantification of carbonate carbon in atmospheric aerosol by means of FT-IR spectroscopy and a multivariate calibration method

P. Fermo[1] , F. Tuccillo[1], L. Brambilla[1], E. Cuccia[2], F. Mazzei[2], D. Massabò[2], P. Prati[2], R. Vecchi[3], C. Paganelli[3], A. Piazzalunga[4]

[1]Dep. Inorganic, Metallorganic and Analytical Chem., Università degli Studi di Milano, Via Venezian 21, 20133, Milan, Italy
[2]Dept. of Physics and INFN, University of Genova, via Dodecaneso 33, 16146, Genova, Italy
[3]Dept. of Physics, Università degli Studi di Milano,Via Celoria 16, 20133, Milan, Italy
[4]Dep. of Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126, Milan, Italy

andrea.piazzalunga@unimib.it
paolo.prati@unige.it

Quantification of Carbonate by means of FT-IR spectroscopy

The analytical methodology here proposed for Carbonate Carbon (CC) quantification and based on FT-IR spectroscopy is reported in figure 2.
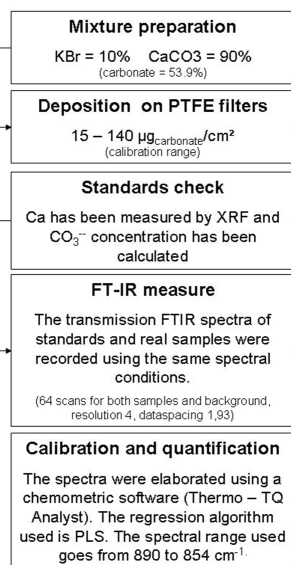

Mixture preparation
KBr = 10%   CaCO3 = 90%
(carbonate = 53.9%)

Deposition on PTFE filters
15 – 140 $\mu g_{carbonate}/cm^2$
(calibration range)

Standards check
Ca has been measured by XRF and CO_3^{--} concentration has been calculated

FT-IR measure
The transmission FTIR spectra of standards and real samples were recorded using the same spectral conditions.
(64 scans for both samples and background, resolution 4, dataspacing 1,93)

Calibration and quantification
The spectra were elaborated using a chemometric software (Thermo – TQ Analyst). The regression algorithm used is PLS. The spectral range used goes from 890 to 854 cm^{-1}.

figure 2

TQ analyst performance

First derivatives were considered to minimize the baseline differences between the spectra and a smoothing with Savitzky – Golay filter (based on 7 data points, polynomial order 3) was applied in order to better evidence the peaks which were partially masked by the spectrum noise
On X axis of the calibration curve the real concentrations of carbonate are reported, whereas on Y axis the concentrations calculated from algorithm using the FT-IR spectra are shown. The difference between calculated and actual concentration values goes from 2.47 to - 3.70 µg/cm². The correlation coefficient is 0.999
The obtained calibration curve shows low errors both in calibration and in prediction.
•RMSEC (Root Mean Square Error of Calibration) 2.26
•RMSEP (Root Mean Square Error of Prediction) 0.350

References
Koulouri E. et al., (2008) Atmospheric Environment 42, 6542-6550
Fermo P. et al., (2006) Chemical Engineering transaction vol. 10, 203-208,

Carbonate Carbon in the particulate matter

Particulate matter (PM) carbonaceous fraction contains organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC). The contribution of inorganic carbon is often neglected because its concentration is generally low and, moreover, there is not a reference analytical method for its quantification.
Nevertheless in same cases, where a specific source of carbonate is present (mineral dust, street dust re-suspension, concrete plant, etc.), this fraction must be determined (Jankowski et al., 2008).

figure 1

Results

The Carbonate concentration measured by FT-IR (figure 3) shows the same time trend and the same concentration of Calcium measured by ED-XRF.
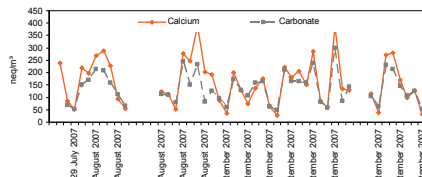

figure 3

The CaCO3 average concentration over the whole period is 6.8 ug/m³ but during working days it shows an increase (8.4 ug/m³ as average value).
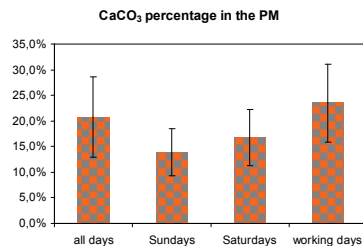The percentage of calcium carbonate of the total PM is reported in figure 4.

figure 4

Ion Chromatography Analysis

In the anions analysis water is the most common solvent used for extraction (Fermo et al. 2006), but carbonate compounds have very low solubility in this solvent. Jankowski et al. (2008) suggest to use Methane Sulfonic Acid (MSA) to have a complete dissolution of all anions. This method is more laborious because it requires a double extraction, one for anions and one for cations.
Nevertheless, in order to test the possibility of obtaining a complete dissolution of carbonate compounds in water, a subset of 10 samples has been analyzed using the two different solvents (water and MSA). As shown in figure 5, water dissolves completely the carbonate compounds.
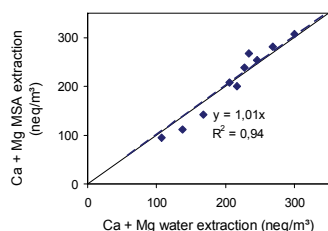

figure 5

Samplig site and methodology

PM10 was sampled at Massa Carrara (see Figure 1), one of the most famous place in Italy where marble is quarried. The samples were collected for two months in summer 2007 on a daily basis (24 hours) along the road covered by the trucks transporting marble rocks form the pit to the harbour. PTFE filters were used and characterized for their elemental composition by means of Energy Dispersive – X Ray Fluorescence (ED-XRF), the ionic composition of some samples was determined by Ionic Chromatography (IC). PM10 average concentration was 34.6 µg/m³ and calcium showed quite high levels being on average 3.2 µg/m³. However, it is difficult to single out the contribution of the marble pit and/or marble transportation to PM10 levels.

Jankowski et al., (2008) calculate carbonate concentrations using the ionic balance (IB). To validate our method (by FT-IR) we have compared our results with the values obtained by IB.

Ionic balance

$$[(Na^+ + NH_4^+ + K^+ + Mg^{++} + Ca^{++}) - (Cl^- + NO_3^- + SO_4^{--})]$$
$$vs.$$
$$CO_3 \text{ (by FT-IR)}$$

The comparison between the two approaches shows that the CaCO3 concentrations calculated by IB are higher than those by FT-IR. This is probably due to to the absence of methane sulfonic compounds and mono and di-carbossilic short chain organic acids not determined in this work (Koulouri et al. 2008). The first one represents a significant component of marine aerosol while organic anions, especially oxalate, can be an important portion of ionic compounds in particulate matter (Jankowski et al., 2008).
This is confirmed by the anion deficit when in the IB we introduce the carbonate measured by FT-IR (figure 7). In our case ammonium is completely balanced by nitrate and sulfate while the molar ratio between Na$^+$ and Cl$^-$ is 3,5±1,8.
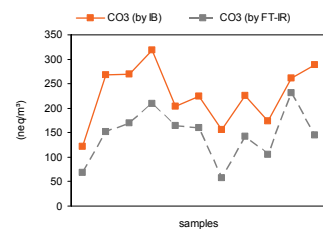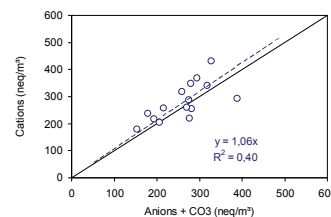

figure 6

figure 7

Conclusion

FT-IR technique followed by a chemometric approach is useful to quantify the carbonate concentration in particulate matter samples.
Marble pits and/or marble transportation are significant PM sources in the considered, quite peculiar, area. During the working days the carbonate calcium accounts for a significant part of PM10 mass (up to 20.8%). A more robust identification and quantification of PM10 sources in the area is in progress based on receptor models.
The carbonate compounds are completely soluble in water and it has been demonstrated that the extraction with MSA is not necessary.
For a complete ionic balance it is necessary to measure some species (Koulouri et al., 2008) because, in sites like Massa Carrara affected by advection of air masses coming from the sea , could be a significant portion of PM mass.