

Quantification of carbonate carbon in atmospheric aerosol by means of ATR (Attenuated Total Reflection) spectroscopy and a multivariate calibration method

P. Fermo¹, A. Piazzalunga^{1*}, F. Tuccillo¹, L. Brambilla¹, F. Mazzei², P. Prati²

¹Dep. Inorganic, Metallorganic and Analytical Chem., University of Milan, Via Venezian 21, 20133, Milan, Italy

*Now: Dep. of Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126, Milan, Italy

²Dipartimento di Fisica and INFN, University of Genova, via Dodecaneso 33, 16146, Genova, Italy

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Particulate matter (PM) carbonaceous fraction contains organic carbon (OC), elemental carbon (EC) as well as 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 some 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).

PM10 atmospheric aerosol samples came from Massa Carrara, one of the most famous place in Italy where marble is quarried. The samples were collected on a daily basis (24 hours) along the road followed by the trucks transporting marble rocks from the pit to the sea. PTFE filters were used and characterized for their elemental composition by means of ED-XRF. PM10 concentration on average was $34.6 \mu\text{g}/\text{m}^3$ and calcium showed quite high values being on average $17.3 \mu\text{g}/\text{m}^3$. Therefore a contribution of the marble pit and/or marble transportation as significant PM sources cannot be ruled out.

In this work CaCO_3 was determined by infrared spectroscopy in ATR (Attenuated Total Reflection) mode. This approach, more effective than IR spectroscopy in transmission mode, has already been used in the literature for the quantification of PM organic fraction (Ghauch *et al.*, 2006).

In order to quantify CaCO_3 amount by ATR technique, a multivariate calibration method has been employed. For this purpose the program TQ ANALYST 8.0 by Thermo Fisher Scientific was employed. The regression algorithm is PLS (Partial Least Square). The use of chemometric techniques for quantification of some species in PM samples by IR spectroscopy has been already used (Coury *et al.*, 2008) but not for the determination of carbonate content since CaCO_3 infrared most intense absorption (at about 1420 cm^{-1} and due to CO_3^{2-} stretching mode) is interfered by the presence of both ammonium sulphate and nitrate. Because of this superposition we investigated only the region center at 871 cm^{-1} which correspond to CO_3^{2-} bending.

Suitable standards were prepared mixing known quantities of calcium carbonate with nujol, which is

normally used as a diluting matrix when IR spectra are acquired. In order to obtain for the standard mixtures ATR spectra comparable with those registered for PM samples, the standards were deposited on the diamond crystal, covered with a PTFE filter and then pressurized and scanned as for the ambient samples.

The calibration curve, obtained analyzing 15 standards, has a fit of $R^2=0.99$ and a RMSEC (root mean square error of calibration) of 0.69. Since the model efficiency is based on its performance in prediction (in this case the ability to estimate unknown CaCO_3 concentrations in aerosol samples), a validation procedure was applied giving a model Performance Index of 91.3%.

In order to validate the method based on ATR-FTIR, portions of the same PM10 samples have been analyzed by means of IC (Ion Chromatography) following a procedure recently suggested in the literature (Jankowski *et al.*, 2008).

A very good agreement between the two methods has been obtained. Furthermore it has been demonstrated that there is a contribution to PM due to the marble caves even if calcium is not present only as calcium carbonate (on average 50% of Ca is in the form of CaCO_3). This evidence has been confirmed also by SEM-EDX (Scanning Electron Microscopy – Energy Dispersion X-ray spectroscopy) analyses carried out on some of the filters where the presence of calcium carbonate together with calcium silicates and calcium sulphate has been pointed out.

In conclusion the method here proposed is an alternative to IC analysis and offers an advantage since it allows to analyze directly carbonate content which is not indirectly derived from the ions balance.

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