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Comparison of methods for the quantification of the different carbon fractions in atmospheric aerosol samples

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Atmospheric carbon consists of: organic carbon (OC, including various organic compounds), elemental carbon (EC, or black carbon [BC]/soot, a non-volatile/light-absorbing carbon), and a small quantity of carbonate carbon. Thermal/optical methods (TOM) have been widely used for quantifying total carbon (TC), OC, and EC in ambient and source particulate samples. Unfortunately, the different thermal evolution protocols in use can result in a wide elemental carbon-to-total carbon variation. Temperature evolution in thermal carbon analysis is critical to the allocation of carbon fractions. Another critical point in OC and EC quantification by TOM is the interference of carbonate carbon (CC) that could be present in the particulate samples, mainly in the coarse fraction of atmospheric aerosol. One of the methods used to minimize this interference consists on the use of a sample pre-treatment with acid to eliminate CC prior to thermal analysis (Chow et al., 2001; Pio et al., 1994).

In Europe, there is currently no standard procedure for determining the carbonaceous aerosol fraction, which implies that data from different laboratories at various sites are of unknown accuracy and cannot be considered comparable. In the framework of the EU-project EUSAAR, a comprehensive study has been carried out to identify the causes of differences in the EC measured using different thermal evolution protocols. From this study an optimised protocol, the EUSAAR-2 protocol, was defined (Cavali et al., 2009).

During the last two decades thousands of aerosol samples have been taken over quartz filters at urban, industrial, rural and background sites, and also from plume forest fires and biomass burning in a domestic closed stove. These samples were analysed for OC and EC, by a TOM, similar to that in use in the IMPROVE network (Pio et al., 2007). More recently we reduced the number of steps in thermal evolution protocols, without significant repercussions in the OC/EC quantifications.

In order to evaluate the possibility of continue using, for trend analysis, the historical data set, we performed an inter-comparison between our method and an adaptation of EUSAAR-2 protocol, taking into account that this last protocol will possibly be recommended for analysing carbonaceous aerosols at European sites. In this inter-comparison we tested different types of samples (PM2,5, PM2,5-10, PM10) with large spectra of carbon loadings, with and without pre-treatment acidification. For a reduced number of samples, five replicates of each one were analysed by each method for statistical purposes.

The inter-comparison study revealed that when the sample analysis were performed in similar room conditions, the two thermo-optic methods give similar results for TC, OC and EC, without significant differences at a 95% confidence level. The correlation between the methods, DAO and EUSAAR-2 for EC is smaller than for TC and OC, although showing a coefficient correlation over 0,95, with a slope close to one. For samples performed in different periods, room temperatures seem to have a significant effect over OC quantification.

The sample pre-treatment with HCl fumigation tends to decrease TC quantification, mainly due to the more volatile organic fraction release during the first heating step. For a set of 20 domestic biomass burning samples analyzed by the DAO method we observed an average decrease in TC quantification of 3,7 % in relation to non-acidified samples, even though this decrease is accompanied by an average increase in the less volatile organic fraction.

The indirect measurement of carbon carbonate, usually a minor carbon component in the carbonaceous aerosol, based on the difference between TC measured by TOM of acidified and non-acidified samples is not a robust measurement, considering the biases affecting his quantification.

The present study show that the two thermo-optic temperature program used for OC and EC quantification give similar results, and if in the future the EUSAAR-2 protocol will be adopted the past measurement of carbonaceous fractions can be used for trend analysis. However this study demonstrates that the temperature control during post-sampling handling is a critical point in total OC and TC quantification that must be assigned in the new European protocol.

References:
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