Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: ElnetPLS model for statistical selection of relevant absorption bands for OC predictions

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Organic carbon (OC) is a major component of atmospheric particulate matter (PM), which has been associated with increased morbidity and mortality, climate change and reduced visibility. Typically OC concentrations are measured using thermal methods such as thermal-optical reflectance (TOR, Chow et al., 2007) from samples collected on quartz filters. However, TOR measurements are destructive and relatively expensive.

We aim at reducing the operating costs of large air quality monitoring networks by estimating TOR OC concentrations using Fourier transform infrared (FT-IR) of ambient samples collected on Teflon (PTFE) filters. This analysis technique is inexpensive, non-destructive and fast. It uses PTFE filters, which are commonly used in PM monitoring networks for gravimetric mass and elemental analysis. Moreover, many quantities of interest such as functional group composition can be quantified from the same FT-IR spectra (Ruthenburg et al., 2014; Takahama et al., 2013).

We present a statistical approach to identify the most relevant infrared absorption bands that allow us to make quantitative predictions of TOR OC using FT-IR spectra. For this purpose, we estimate TOR OC concentrations using a sparse calibration model that combines elastic net regularization and partial least square regression (ElnetPLS). This calibration model excludes unnecessary wavenumbers from infrared spectra during the model building process, permitting identification and evaluation of the most relevant vibrational modes of molecules in complex aerosol mixtures associated with reported TOR OC concentrations.

In this work, we have used the FT-IR absorbance spectra, and TOR OC concentrations collected in the Interagency Monitoring of PROtected Visual Environment (IMPROVE) network (USA) in 2011 at seven sites (six rural and one urban). Dillner and Takahama (2015) used this dataset to predict TOR OC concentrations using the full spectra (2784 wavenumbers).

The ElnetPLS model that uses samples collected in all the sites (first row in Fig. 1) has similar model performance (bias = -0.01 μgm^{-3}, error = 0.12 μgm^{-3}, norm. error = 16% and R^2 = 0.95) of the full wavenumber model (Dillner and Takahama, 2015) while requiring only 13 wavenumbers associated with carbonyl groups (1740-1735 cm^{-1} and 1707-1702 cm^{-1}), and with primary amines and benzene rings (1598-1595 cm^{-1}, Shurvell, 2002). We further discuss variations in selected absorption bands according to calibration models built for urban and rural sites (second and third rows in Fig.1).

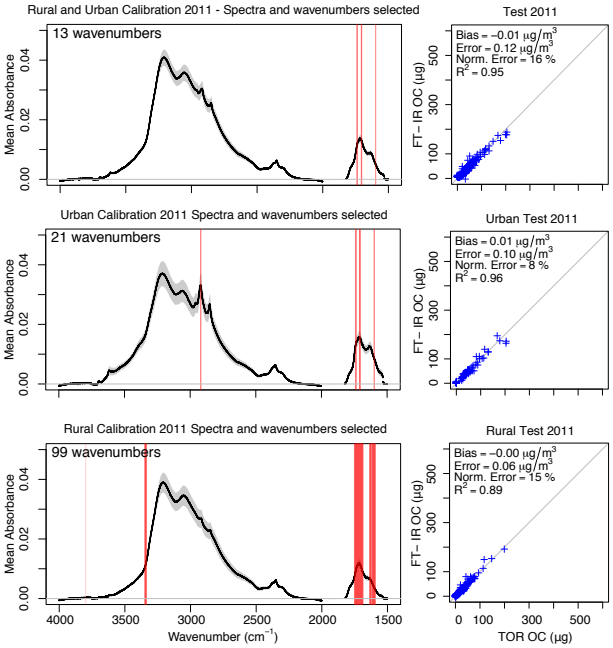

Figure 1. Left column: mean spectra (grey area represents the 95% confidence intervals), and wavenumbers selected (red lines). Right column: scatter plots and performance metrics between FT-IR OC and TOR OC. Concentration units of μgm^{-3} for bias and error are based on the IMPROVE nominal volume of 32.8 m^3.

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