EC/OC comparison exercise with same thermal protocols after temperature offsets correction

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The department of Air Quality of Public Health Service Amsterdam has been organizing laboratory comparison exercises for the past few years on thermal-optical elemental carbon / organic carbon (EC/OC) analysers. To our knowledge, all laboratory comparisons performed in Europe up to 2012 considered results derived from different protocols applied per participant, usually NIOSH (Birch & Cary, 1996) or EUSAAR2 (Cavalli et al., 2010), limiting comparability of the performance of each laboratory. The scope of the 2012 comparison exercise was to evaluate results based on an identical, to the extent possible, instrument set-up for all participants. By definition the same protocol should then be applied. Yet, the debate over NIOSH and EUSAAR2 is still ongoing in Europe and a selection of one out the two would have been complex. As an alternative, we decided for the use of both protocols by each participant, providing additional information that could point out possible differences between the two protocols.

Each protocol facilitates several thermal steps and instrument-specific deviations of the desired temperature can alter the sample treatment and bias the analysis result. Since the introduction of a temperature calibration kit by the analyser manufacturer (Sunset Laboratory Inc, OR, US) in early 2012 it is possible to overcome these deviations. All participants agreed on performing the calibration and compensating for the temperature offsets before the comparison exercise analysis.

A total of 20 1.5 cm^2 punches, derived from 5 PM sampled quartz filters, and two sucrose standard solutions were delivered to each of the 17 participants. Duplicate analyses per filter and triplicate per solution were performed applying each protocol. Next to the EC and OC concentrations, raw data and thermograms were provided and additional analysis factors were investigated, namely, split time, transit time, pyrolytic carbon, temperature offsets and thermal peaks distribution. All analyses were performed on transmittance mode (TOT) while the majority of participants also provided reflectance (TOR) results.

In the comparison of EUSAAR2 derived thermograms (Figure 1), notable differences were observed in peak distribution, especially after the 4th, suggesting possible pre-oxidation on a number of analysers. The split point separating EC from OC fell in a range of about 100 seconds. Similar observations were made on the respective NIOSH thermograms. Figure 2 shows all paired EC results for EUSAAR2 and NIOSH indicating that reported EC concentrations may vary for

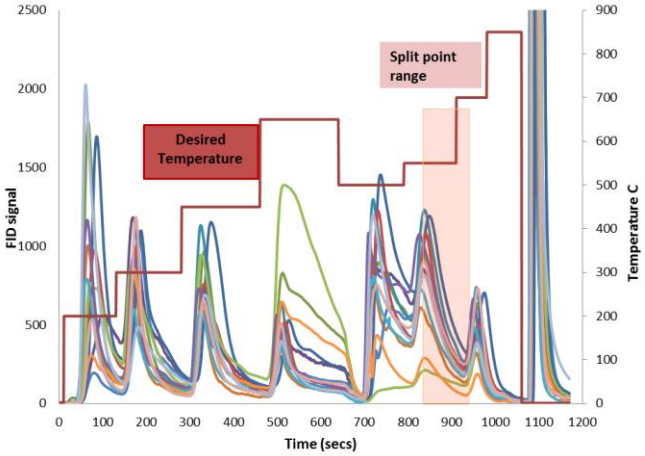

Figure 1. Thermograms of TOT ECOC analysis on PM loaded quartz filter, by EUSAAR2 for all participants.

the same filter in regard to the protocol applied. No differences were observed for total carbon (TC) where $TC_{NIOSH} = 0.99 \cdot TC_{EUSAAR2}$ (R^2=0.98) for loaded PM filters and $TC_{NIOSH} = 1.00 \cdot TC_{EUSAAR2}$ (R^2=0.98) for sucrose solutions was found.

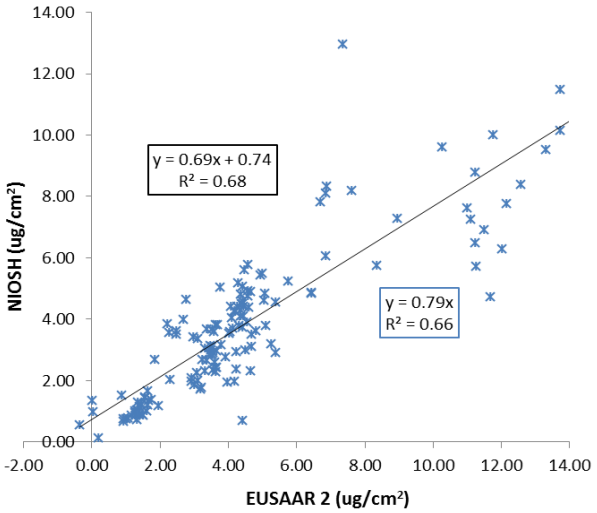

Figure 2. Comparison of EC concentrations by TOT EUSAAR2 and NIOSH on PM loaded quartz filters (N=150).

Birch, M.E. and Cary, R.C. (1996) *Aerosol Sci. Technol.* **25**, 221-241.

Cavalli, F., M. Viana, K. E. Yttri, J. Genberg and J.-P. Putaud (2010) *Atmos. Meas. Tech*. **3**, 79–89.