Atmos. Meas. Tech. Discuss., 7, 8697–8742, 2014
www.atmos-meas-tech-discuss.net/7/8697/2014/
doi:10.5194/amtd-7-8697-2014
© Author(s) 2014. CC Attribution 3.0 License.

Atmospheric Measurement Techniques Discussions

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

ECOC comparison exercise with identical thermal protocols after temperature offsets correction – instrument diagnostics by in-depth evaluation of operational parameters

P. Panteliadis[1], T. Hafkenscheid[2], B. Cary[3], E. Diapouli[4], A. Fischer[5], O. Favez[6], P. Quincey[7], M. Viana[8], R. Hitzenberger[9], R. Vecchi[10], T. Maggos[11], J. Sciare[12], J. L. Jaffrezo[13], A. John[14], J. Schwarz[15], M. Giannoni[16], J. Novak[17], A. Karanasiou[8], P. Fermo[18], and W. Maenhaut[19]

[1]Municipal Health Service (GGD) Amsterdam, Department of Air Quality, Amsterdam, the Netherlands
[2]National Institute for Public Health and the Environment, Bilthoven, the Netherlands
[3]Sunset Laboratory Inc, Tigard, Oregon, USA
[4]National Center for Scientific Research "Demokritos", Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, Athens, Greece

AMTD
7, 8697–8742, 2014

[5]EMPA – Swiss Federal Laboratories for Materials Science and Technology, Duebendorf, Switzerland
[6]INERIS, Verneuil-en-Halatte, France
[7]National Physical Laboratory, Teddington, UK
[8]Institute for Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain
[9]Aerosolphysics and Environmental Physics, Faculty of Physics, Vienna, Austria
[10]Department of Physics, Università degli Studi di Milano, Milano, Italy
[11]Demokritos, National Center for Scientific Research, Environmental Research Laboratory, Athens, Greece
[12]Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CEA-CNRS-UVSQ, Gif/Yvette, France
[13]Univ. Grenoble Alpes, CNRS, LGGE, 38000 Grenoble, France
[14]Institute for Energy and Environmental Technology e.V. Air Quality & Sustainable Nanotechnology Division, Duisburg, Germany
[15]Institute of Chemical Process Fundamentals AS CR, Prague, Czech Republic
[16]Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Firenze, Florence, Italy
[17]Czech Hydrometeorological Institute, Prague, Czech Republic
[18]Department of Chemistry, Università degli Studi di Milano, Milano, Italy
[19]Department of Analytical Chemistry, Ghent University, Gent, 9000, Belgium

Received: 6 June 2014 – Accepted: 3 August 2014 – Published: 26 August 2014

Correspondence to: P. Panteliadis (ppanteliadis@ggd.amsterdam.nl)

Published by Copernicus Publications on behalf of the European Geosciences Union.

AMTD
7, 8697–8742, 2014

Abstract

A comparison exercise on thermal-optical elemental carbon/organic carbon (ECOC) analyzers was carried out among 17 European laboratories. Contrary to previous comparison exercises, the 17 participants made use of an identical instrument set-up, after correcting for temperature offsets with the application of a recently developed temperature calibration kit (Sunset Laboratory Inc, OR, US). Five filter samples and two sucrose solutions were analyzed with both the EUSAAR2 and NIOSH870 thermal protocols. z Scores were calculated for total carbon (TC) and nine outliers and three stragglers were identified. Three outliers and eight stragglers were found for EC. Overall, the participants provided results within the warning levels with the exception of two laboratories that showed poor performance, the causes of which were identified and corrected through the course of the comparison exercise. The TC repeatability and reproducibility relative standard deviations were 11.4 and 14.6 % for EUSAAR2 and 9.2 and 11.7 % for NIOSH870; the standard deviations for EC were 15.3 and 19.5 % for EUSAAR2 and 19.9 and 25.5 % for NIOSH870. TC was in good agreement between the two protocols, $TC_{NIOSH870} = 0.98 \cdot TC_{EUSAAR2}$ ($R^2 = 1.00$, normalized means). Transmittance (TOT) calculated EC for NIOSH870 was found to be 20 % lower than for EUSAAR2, $EC_{NIOSH870} = 0.80 \cdot EC_{EUSAAR2}$ ($R^2 = 0.96$, normalized means). The thermograms and laser signal values were compared and similar peak patterns were observed per sample and protocol for most participants. Notable deviations of plotted values indicated absence or inaccurate application of the temperature calibration procedure and/or pre-oxidation during the inert phase of the analysis. Low or no pyrolytic organic carbon (POC), as reported by a few participants, is suggested as an indicator of pre-oxidation. A sample-specific pre-oxidation effect was observed for filter G, for all participants and both thermal protocols, indicating the presence of oxygen donors on the suspended particulate matter. POC (TOT) levels were lower for NIOSH870 than for EUSAAR2, which is related to the heating profile differences of the two thermal protocols.

AMTD
7, 8697–8742, 2014

1 Introduction

Carbon in suspended atmospheric particulate matter usually falls into one of three wide categories, elemental carbon (EC), organic carbon (OC) and carbonate carbon (CC). Recently, more attention has been drawn to EC, due to its adverse health (Highwood and Kinnersley, 2006; Adar and Kaufman, 2007; Janssen et al., 2011, 2012) and climate effects (Jacobson, 2001; IPCC, 2007; Ramanathan and Carmichael, 2008). Several studies suggest EC as a valid indicator for traffic originated air pollution and include its analysis during monitoring campaigns (Lena et al., 2002; Schauer, 2003; Qadir et al., 2013; Panteliadis et al., 2014). A number of EC measurement techniques exist (Watson et al., 2005; Hitzenberger et al., 2006) with the thermal-optical transmittance (TOT) or reflectance (TOR) being broadly used in Europe and the USA. Several thermal protocols, which apply to TOT or TOR analyzers, have been developed with NIOSH5040 (Birch and Cary, 1996), IMPROVE A (Chow et al., 2007) and EUSAAR2 (Cavalli et al., 2010) being the most commonly applied.

Even though quality assurance and quality control (QA&QC) procedures are of importance for ECOC measurements (Chow et al., 2011), no standard has yet been establised in Europe, as for other compounds. Following the EU Directive 2008/50/EC in ambient air and cleaner air for Europe, a technical report has been drafted (CEN TR 16243, 2011) and further work is currently carried out towards method standardization within CEN-TC 264 (European Committee for Standardisation) Working Group 35. Besides the implementation of the technical report in the standard operation procedures of laboratories, comparison exercises are an additional step towards QA&QC optimization.

The department of Air Quality of Public Health Service Amsterdam has been organizing laboratory comparison exercises for the past few years on thermal-optical ECOC analyzers (Panteliadis, 2009a, 2011). To our knowledge, previous laboratory comparisons performed in Europe up to 2012 considered results derived from different protocols applied per participant, usually NIOSH-like or EUSAAR2, on filter samples,

AMTD
7, 8697–8742, 2014

limiting comparability of the performance of each laboratory. Numerous studies have demonstrated that ECOC analysis of ambient samples is sensitive to the temperature protocol selected (Sciare et al., 2003; Schauer et al., 2003; Chow et al., 2004; Cavalli et al., 2010; Zhi et al., 2011; Piazzalunga et al., 2011; Cheng et al., 2011, 2012). As a result, the temperature protocol selection may bias the conclusions obtained from comparisons between thermal-optical and optical (black carbon) analysis (Schmid et al., 2001; Schauer et al., 2003; ten Brink et al., 2004). Differences also occur with regard to the optical method used for the charring carbon correction, transmittance or reflectance, with the latter usually resulting in greater EC concentrations (Chow et al., 2004; Panteliadis, 2009b; Maenhaut et al., 2011).

The scope of the 2012 comparison exercise was to evaluate results based on an identical instrument set-up for all participants. By definition the same thermal protocol should then apply. Yet, the debate over the NIOSH-like and the EUSAAR2 thermal protocols is still ongoing in Europe and the selection of a single temperature protocol would have been complex and limiting. The comparison exercises performed so far have let the participants decide on the protocol applied (Panteliadis, 2009a, 2011; Emblico et al., 2012; Cavalli et al., 2012). As an alternative, we decided the use of both NIOSH870 and EUSAAR2 by each participant, providing additional information that could point out possible differences between the two protocols.

Each thermal protocol facilitates several temperature steps and instrument-specific deviations of the desired temperature may alter the sample treatment and bias the analysis result. These deviations may originate from differences in type, age or installation of the heating coils used in each instrument. Since the introduction of a temperature calibration kit by the analyzer's manufacturer (Sunset Laboratory Inc, OR, US) in early 2012, it became possible to overcome these deviations. All participants performed the calibration procedure and compensated for the temperature offsets before the comparison exercise analysis.

A common practice for total carbon (TC) calibrations and routine checks is the use of standard sucrose solutions. Such sucrose solutions were included in the current

AMTD
7, 8697–8742, 2014

exercise in order to provide an insight on the degree of repeatability of these procedures as well as to evaluate the practicability of adding a known volume of sucrose on the filter to be analysed. Unfortunately, the standard sucrose solutions can only provide information on the calibration of TC while a reference material for EC is still lacking (Baumgardner et al., 2012). Finally, on top of the ordinary statistical analysis, which is usually performed in such comparison exercises, a more in-depth approach was selected by the inspection of instrument specific parameters and characteristics like the laser and the flame ionization detector (FID) signal as well as the peak distribution and calibration peak area.

2 Methods

2.1 Sample preparation and distribution

A total of five 24 h PM-loaded samples were collected for the needs of the current ECOC laboratory exercise. The selection of filters was performed in order to cover a common range of characteristics that occur in samples used for ECOC analysis. It is realised, though, that the limited number of filters selected is not fully representative of the wide variety of ambient samples which can be influenced by a number of parameters such as particle composition, pollution sources, seasonal and spatial variation.

The urban background sample from Amsterdam, the Netherlands, was collected with a PM_{10} high volume sampler (HVS) (ESM Andersen Instruments GmbH, Germany) on a Whatman QMA rectangular filter, 20.3 cm × 25.4 cm. The same filter type was used for the urban background sample from Athens, Greece, collected with a PM_3 GS2312 BL HVS (Tisch Environmental, Ohio, US). Two $PM_{2.5}$ suburban samples were collected in Duebendorf, Switzerland, with the use of a DHA80 (Digitel Elektronik AG, Switzerland) on 150 mm diameter Pallflex Tissuquartz filters, on two subsequent dates. The same type of sampler and filter was used for the urban sample collected in Berne, Switzerland. The amount of transmitted laser light compared to a blank was reported

AMTD
7, 8697–8742, 2014

by the organizing laboratory. An overview of the filters characteristics and sampling details is presented in Table 1.

Upon receipt at GGD Amsterdam, all filters were stored at a temperature below 5 °C till the distribution date. Four rectangular punches of 1 cm × 1.5 cm were cut out from each filter and stored in separate closed Petri slide dishes, which were sent to each participant together with 30 mL vials of two standard sucrose solutions S1 and S2 with nominal OC concentrations of 10.00 and 33.58 µg 10 µL^{-1}, respectively. For the two participants, who use a field instrument, four circular punches of 2 cm^2 were prepared instead.

The homogeneity of PM loaded HVS filters, similar to those of this exercise has been already tested by GGD Amsterdam, for the exact same samplers and filter media and resulted in relative standard deviations of 10.6 % for EC, 6.4 % for OC and 5.3 % for TC for 150 mm Pallflex Tissuquartz HVS filters and 9.9 % for EC, 8.7 % for OC and 6.3 % for TC for Whatman QMA HVS filters (Supplement, Table S1). These values, however, represent only an indication of the expected within sample standard deviation for filter samples used in the current comparison exercise.

2.2 ECOC analysis

The EC, OC and TC concentrations in the PM samples and sucrose solutions were determined by all participants with the use either of a lab ECOC aerosol analyzer or a semi-continuous ECOC field analyzer, all manufactured by Sunset Laboratory Inc. (Tigard, OR, US).

In detail, during analysis OC desorbs from the quartz fibre filter through progressive heating under a pure He stream, while a fraction of OC chars and forms pyrolyzed organic carbon (POC). The sample is then heated in temperature steps under a mixture of 98 % He – 2 % O_2 (HeOx phase) and POC and EC are desorbed. In order to correct for the pyrolysis effect, the analyzer utilizes laser light reflectance and/or transmittance. The split point, which separates OC and EC and compensates for POC, is determined when the laser signal reaches its initial value. OC, EC and POC are

AMTD
7, 8697–8742, 2014

catalytically converted initially to CO_2 and finally to CH_4, which is quantified with the use of an FID. The time necessary for the gaseous compounds desorbed to reach the FID unit from the filter media is defined as transit time and it is an instrument-specific parameter. A fixed volume of calibration gas (5 % CH_4 in Helium) is injected in the instrument at the end of each analysis and the responding FID signal forms the calibration peak. The area of the calibration peak together with a calibration constant are used for the calculation of the sample concentration. The calibration constant depends on the calibration gas fixed volume analysed per run, which is set by the manufacturer and is an instrument-specific parameter.

The operating conditions of the analyzer may vary in regard to the thermal protocol used during analysis. The two protocols that are mainly used in Europe, NIOSH870 and EUSAAR2, were applied by all participants for the individual analysis of the sample punches provided. Before analysis, most participants calibrated their instruments for temperature offsets per step, with the use of a recently developed calibration kit. The temperature calibration procedure had to be applied for each thermal protocol separately, since they vary in the number of steps and their temperature and duration. The differences between EUSAAR2 and NIOSH870 together with the observed offset ranges are illustrated in Table 2.

Two participants performed the temperature calibration only for the EUSAAR2 protocol while one did not apply it at all. Two more participants used the temperature offsets as defined for the GGD instrument. The temperature calibration procedure was not applicable for the field analyzers. A wide range of temperature offsets was observed as well among participants (−93 to 100 °C) as between the temperature steps of the same analyzer (up to 86 °C). An overview of the thermal protocols, optical method and temperature offsets applied by each participant can be found in Table 3. The heating profile of each analyzer after the temperature offset correction was also recorded for both protocols (Supplement, Figs. S1 and S2).

AMTD
7, 8697–8742, 2014

Two of the four punches received by each participant were analysed with NIOSH870 and the remaining two with EUSAAR2, whereas triplicate analyses with both protocols were applied for the two sucrose solutions.

2.3 Statistical analysis

2.3.1 Laboratory performance

The robust means for the filter samples, derived from the means of replicate measurements, were calculated following ISO 13528:2005, Annex C. Due to lack of a certified reference material, the consensus value from participants approach was selected in order to determine the robust mean for each sample. The z scores were calculated for TC and EC, for EUSAAR2 and NIOSH870, from the robust means in order to evaluate the capacity of each laboratory to comply with the selected fit-for-purpose standard deviation:

$$z = (x - X)/\sigma$$

where:

x : the result of the participant (average of duplicate analyses)

X : the robust mean

σ : the fit-for-purpose standard deviation

Due to lack of certified reference methods for ECOC measurements the fit-for-purpose standard deviations were arbitrarily selected, defining the desired level of compliance based on empirical knowledge, 8.3 % for TC and 25 % for EC. The 8.3 % for TC roughly corresponds to a range of ±25 % into which all results should fall. z Scores between the warning signals, −2 and +2, were considered as indication of satisfactory performance while z -scores between the warning and the action signals, −3 and +3, were considered questionable. All z scores outside the action signals range were considered as indication of unsatisfactory performance.

AMTD
7, 8697–8742, 2014

2.3.2 Method performance

The laboratory performance was initially evaluated graphically, by sucrose solutions plots and Mandel's *h* and *k* statistics for TC and EC results pooled for both EUSAAR2 and NIOSH870. The Mandel's *h* statistic indicates the between-laboratory consistency while Mandel's *k* the within-laboratory consistency. Laboratory results reported above the critical value at 1 % significance level are identified as possible outliers, between the critical values of 1 and 5 % significance level as stragglers (ISO 5725-2:1994). Grubbs' and Cochran's statistical outlier tests were also applied and outliers were removed from the dataset for the calculations of the corrected standardized means, repeatability and reproducibility relative standard deviations (ISO 5725-2:1994).

3 Results

3.1 Data evaluation

All results, as reported by the participating laboratories, namely TC, EC, OC and EC/TC for both TOT and TOR are given in the Supplement, Tables S2–S8. The reported TC concentrations ranged on average per filter from 10.09 to 79.02 $\mu g\,cm^{-2}$, while for EC from 0.91 to 11.52 $\mu g\,cm^{-2}$ (TOT) and 1.83 to 17.47 $\mu g\,cm^{-2}$ (TOR) depending on the thermal protocol used.

3.2 Laboratory performance

An initial overview of possible deviating performances can be identified in Fig. 1, which presents graphically the reported results of all participants for the two sucrose solutions.

The *z* scores for the EC and TC results of the filter samples, calculated separately for EUSAAR2 and NIOSH870, are shown in Figs. S3–S6, Supplement. For TC, seven outliers and three stragglers were identified for EUSAAR2 and 12 outliers for NIOSH870,

AMTD
7, 8697–8742, 2014

all of which reported by three participants. For EC, one outlier and four stragglers were identified for EUSAAR2 while two outliers and four stragglers for NIOSH870. All outliers and stragglers were reported by three participants, out of which two were the same as for the TC z scores.

3.3 Method performance

Figure S7, Supplement, presents the Mandel's k statistic for the sucrose solutions, with the use of EUSAAR2 and NIOSH870 TC pooled results. Five outliers were identified, two for laboratory 10, two for 12 and 1 for 16. The outliers of laboratories 10 and 12 were confirmed by Cochran's test while the one of laboratory 16 was identified as a straggler. The Mandel's h statistic values for the sucrose solutions can be found in Fig. S8, Supplement. Two outliers were found for laboratory 11, confirmed also by Grubb's test.

Figure S9, Supplement, presents the Mandel's k statistic values for the loaded filters, EUSAAR2 and NIOSH870 pooled TC results. Seven outliers were identified, three for laboratory 12, two for 16, and one for each of 10 and 11. Two stragglers were also identified, one for laboratory 13, and one for 16. Two out of the three outliers of laboratory 12, both for 16 and the one for 10 were confirmed by Cochran's test while the one for laboratory 11 was identified as a straggler.

The Mandel's h statistic values for the loaded filters, EUSAAR2 and NIOSH870 pooled TC results, can be found in Fig. S10, Supplement. Five outliers were identified, all for laboratory 11, four of which were indicated as stragglers by Grubb's test. Four stragglers were observed, all for laboratory 10, one of which confirmed by Grubb's test.

Similarly to Fig. S9, Fig. S11 presents the Mandel's k statistic values for pooled EC (TOT) results of the loaded filters. Three outliers and two straggles were identified; one outlier for each of laboratories 3, 4 and 16 and one straggler for 15 and 16. The three outliers were also confirmed by the Grubb's test. Figure S12, Supplement, presents the Mandel's h statistic values for the filters pooled EC (TOT) results. Four outliers and

AMTD
7, 8697–8742, 2014

three stragglers were identified in total. Laboratories 10 and 11 reported two outliers and one straggler each while one straggler was reported by laboratory 3 and one by 8. The Grubb's test confirmed all outliers and stragglers for laboratories 10 and 11 but not the stragglers for 3 and 8.

The normalized mean values and the repeatability and reproducibility relative standard deviations for the filter samples were calculated initially for the full data set and then after discarding the verified outliers. Table S9, Supplement, shows the values separated per protocol for TC while Table S10, Supplement, shows the same for EC. For the corrected results, the repeatability relative standard deviation for TC was 11.4 % for EUSAAR2 and 9.2 % for NIOSH870. The reproducibility standard deviation was 14.6 % for EUSAAR2 and 11.7 % for NIOSH870. For EC, the repeatability standard deviation was 15.3 % for EUSAAR2 and 20.1 % for NIOSH870. The reproducibility standard deviation was 19.5 % for EUSAAR2 and 25.5 % for NIOSH870. All standard deviations were higher for EC than TC. All standard deviation values were higher for EUSAAR2 for TC, while the opposite holds for EC.

The robust means and standard deviations per filter pooled for both protocols can be found in detail in Table S11, Supplement. Repeatability standard deviations ranged from 8.5 to 11.7 % and reproducibility standard deviations from 10.7 to 14.6 %.

No significant differences were observed between EUSAAR2 and NIOSH870 for TC where $TC_{NIOSH870} = 0.97 \cdot TC_{EUSAAR2}$ ($R^2 = 0.96$) for loaded PM filters and $TC_{NIOSH870} = 1.00 \cdot TC_{EUSAAR2}$ ($R^2 = 0.98$) for sucrose solutions raw data (Supplement, Fig. S13). When raw data of EC for the loaded filters were compared, EUSAAR2 was found to report higher values, $EC_{NIOSH870} = 0.73 \cdot EC_{EUSAAR2}$ ($R^2 = 0.72$) for TOT. For TOR, EUSAAR2 and NIOSH870 were closer to each other, $EC_{NIOSH870} = 0.85 \cdot EC_{EUSAAR2}$ ($R^2 = 0.69$) (Supplement, Fig. S14). For both protocols the use of TOR resulted in notably higher EC concentrations than TOT, 64 % ($R^2 = 0.52$) for EUSAAR2 and 113 % ($R^2 = 0.44$) for NIOSH870 ($N = 89$). All zero NIOSH870 EC concentrations shown in the graphs were reported by a single participant due to laser failure. Note that not all

AMTD
7, 8697–8742, 2014

participants reported data for both TOT and TOR, as a result of instrument configuration.

When the normalized means were used for the same plots $TC_{NIOSH870} = 0.98 \cdot TC_{EUSAAR2}$ ($R^2 = 1.00$) for loaded PM filters and $EC_{NIOSH870} = 0.80 \cdot EC_{EUSAAR2}$ ($R^2 = 0.96$) for TOT and $EC_{NIOSH870} = 1.15 \cdot EC_{EUSAAR2}$ ($R^2 = 0.95$) for TOR were found (Supplement, Fig. S15).

3.4 Comparison of EUSAAR2 and NIOSH870

Table 4 shows the ranges of split points as reported by the participants for each filter sample, protocol and optical method used. In all cases the split points in EUSAAR2 occur 300 to 400 s later than the ones obtained for NIOSH870, due to the extended overall duration of EUSAAR2. The split point defined by TOR appears to occur earlier than by TOT. In most cases the overall split point range among participants for the same filter is ~ 100 s, except for sample A, where it extends up to 200 s, and sample G, up to 300 s. Both A and G samples were collected on the same filter media, Whatman QMA, while B, D and U on Pallflex, Tissuquartz, which may relate to the observed deviation. Note that Whatman QMA is thicker, 450 µm, than Pallflex Tissuquartz, 432 µm, as reported by their manufacturers.

The relative standard deviations of the calibration area of each instrument together with the calibration constant, the transit time and the atmospheric pressure are presented in Table 5. The calibration area relative standard deviations ranged from 1.4 to 24.6 % and the calibration constant from 17.1 to 28.7. Fluctuations of the atmospheric pressure of the laboratory may be of influence to the gas flows and consequently to the calibration area. The fluctuations in atmospheric pressure, as measured by each instrument, were in most cases within a range of 10 mm Hg. Nevertheless, five instruments reported values significantly lower than the expected value, between 374 and 427 mm Hg, indicating either a possible deficiency or absence of the pressure sensor, which results for the instrument to return an offset value.

AMTD
7, 8697–8742, 2014

The transit time ranged from 6 to 15 s. When it is erroneously determined it may result in a shift of the split point and thus erroneous concentration values of the OC and EC fractions. A check procedure of the transit time is available by the analyzer's manufacturer but its application was not included in the prerequisites of the current comparison exercise.

NIOSH870 analysed samples A and B showed a similar peak distribution for all participants with a high first peak, low second, third and fourth and a high fifth when POC and EC evolve. In both cases the split point range covered almost the whole fifth peak and no EC was measured after the 600 s (Figs. 2 and 3). The EUSAAR2 thermograms for samples A and B showed more variation in the peak distribution than the NIOSH870 thermograms, but in principal started with a high first peak, going down gradually on the second, third and fourth. Then a high fifth peak can be observed when the POC and EC desorb followed by a gradual decrease in the sixth and seventh peak. EC seems to desorb up to the very end of the analysis. The split point range in TOT covers a wider area for filter A than for filter B (Figs. 4 and 5).

For the sucrose solutions, with an exception of a couple of participants, there is good agreement in the peak distribution, which is better for NIOSH870 than EUSAAR2 (Figs. 6 and 7). For NIOSH870, most of the OC is evolved in the first peak, followed by low second, third and fourth peaks and a slightly higher fifth for the POC. Almost no carbon is measured after 600 s. For EUSAAR2, most of the participants reported a high second peak and lower third, fourth, and fifth. The POC evolves in a wide area from 700 s till the end of the analysis in some cases. Four participants report a medium to low first peak, while for the rest of the participants it is not present. This first peak may be indication of contamination due to handling during the sucrose analysis procedure. Such a contamination indication is not visible with the use of NIOSH870 due to the override with the already high first peak.

Figures 8 and 9 show the concentrations per temperature step and protocol for samples A and B. In most cases POC and EC are lower for NIOSH870 compared to EUSAAR2. Some participants reported limited or no POC for sample A, suggesting that

AMTD
7, 8697–8742, 2014

oxygen may have been entering the system in the inert phase. This becomes less visible for sample B, where concentrations are higher. For sucrose, most participants report the greatest fraction of OC at the first temperature step (OC1) for NIOSH870 and the second (OC2) for EUSAAR2 (Fig. 10). Similarly to filter A, some participants reported limited or no POC for the sucrose solutions, possibly due to pre-oxidation occurring with their analyzer.

Figures 11–16 show the laser transmission signal plots per participant through the analysis of samples A, D and G for both EUSAAR2 and NIOSH870. A high frequency noise to the laser signal can be observed in all cases for laboratory 5, and non-systematic deviating behavior for laboratories 4 and 11. Laboratory 12 shows a low frequency noise for all samples. A laser signal ramping up earlier than the HeO_x phase, indicating pre-oxidation, is seen occasionally for several laboratories but mostly for 1, 3, and 4. The same ramping effect in the He phase, as seen by almost all participants for filter G, indicates that most of the pre-oxidation for this sample is not instrument specific but it is rather sample related. A possible explanation may be the presence of metals and/or metal oxides at the sample in question (Wang et al., 2010). The laser transmission signal for a blank filter, as derived from the values at the end of each analysis, covers a wide range among the participants, from ~ 1000 to ~ 20 000. The respective figures for the laser reflectance signal plots can be found in the Supplement, Figs. S16 to S21. Yet, no similar observations can be drawn.

A limited number of participants reported data from instrument blank analysis. Supplement Figs. S22 and S23 show the laser signal, TOT and TOR, for EUSAAR2 and NIOSH870 for the blank filters. The laser signal is stable throughout each analysis with an exception of laboratory 3, showing no dependency on the temperature.

4 Discussion and conclusions

An ECOC comparison exercise was organized by GGD Amsterdam among 17 laboratories. The participants had to perform temperature calibrations and adjust for offsets

AMTD
7, 8697–8742, 2014

prior to analysis. The offsets ranged from −90 to +100 °C, varying for each temperature step and instrument. Duplicate punches of 5 filter samples were analysed with both the EUSAAR2 and the NIOSH870 thermal protocols by all participants in order to evaluate the laboratory performance without inserting protocol related biases.

Based on *z* scores for TC, two laboratories showed poor performance, reporting results with a significant positive systematic error; seven outliers and two stragglers for laboratory 10 and ten outliers for laboratory 11 (Figs. S3 and S4). In the course of this work the causes of the observed deviations were identified and corrected. Laboratory 16, which uses the semi-automated field analyzer, reported two outliers and one straggler, while the rest of participants were within the warning signal levels. Similar observations can be drawn for the EC *z* scores, with laboratory 10 reporting one outlier and three stragglers, laboratory 11 one outlier and four stragglers, and laboratory 3 one outlier and one straggler. It should be noted that different fit-for-purpose deviations were selected as levels of satisfactory performance for TC (8.3 %), which is thermally defined, and EC (25 %) which is both thermally and optically defined.

As seen in Fig. 1, the analyses of sucrose solutions in comparison exercises can serve as an indicator of an erroneously conducted TC calibration and deviating performance. Furthermore, it is clear that the repeatability, derived from the analysis of a known volume of sucrose solution is dependent on the laboratory performance and independent of the thermal protocol used. When performed properly, analysis of standard sucrose solutions can provide a reliable TC calibration procedure. In principle, only three participants showed difficulties in the within laboratory consistency and only one in the between laboratory consistency (Figs. S7 and S8).

No clear differences could be noticed between the *z* scores for EUSAAR2 and NIOSH870, suggesting that poor laboratory performance or deviating results are not protocol specific. The TC repeatability and reproducibility relative standard deviations, 11.4 % and 14.6 % for EUSAAR2 and 9.2 % and 11.7 % for NIOSH870, respectively, are at satisfactory levels, taking into account the homogeneity of similar PM sampled HVS filters that ranges from 6 to 10 %. It can be observed that all standard deviations

AMTD
7, 8697–8742, 2014

are lower for NIOSH870, which may be explained by the fact that all TC seems to evolve relatively early during analysis while a larger fraction is present in further steps for EUSAAR2. It is then possible that for EUSAAR2 a small fraction of TC may not evolve through analysis for some samples, usually the highly loaded ones, resulting in greater standard deviations. Nevertheless, the findings of the current exercise suggest that after the temperature calibration, almost identical concentrations of TC are measured by both protocols, $TC_{NIOSH870} = 0.98 \cdot TC_{EUSAAR2}$ ($R^2 = 1.00$) for normalized means.

The EC repeatability and reproducibility relative standard deviations, 15.3 % and 19.5 % for EUSAAR2 and 19.9 % and 25.5 % for NIOSH870, respectively, are greater than the TC ones, indicating the additional uncertainties inserted by the optical determination of EC, supported also by the wide split point ranges that extended even more than 200 s for the same sample among different participants. The standard deviations are higher for NIOSH870 probably due to the fact that the split point is located on steep areas of high FID peaks and deviations of a few seconds may result in relatively great alterations of the EC amount reported. For EUSAAR2, the split point usually falls into less steep areas of lower FID peaks. Further, the wide range of the laser transmission signal value for a blank filter, from ~ 1000 to ~ 20 000, may also affect the capacity of specific instruments to determine accurately the split point. Pre-oxidation causing early desorption of POC and EC can also potentially alter the split point's position.

Based on normalized means, TOT EC reported by NIOSH870 is 20 % lower than by EUSAAR2, $EC_{NIOSH870,TOT} = 0.80 \cdot EC_{EUSAAR2,TOT}$ ($R^2 = 0.96$). Similar results were found in a comparison performed by GGD Amsterdam, prior to temperature calibration, with $EC_{NIOSH870,TOT} = 0.83 \cdot EC_{EUSAAR2,TOT}$ ($R^2 = 0.94$) (Supplement, Fig. S24). The above suggests that the temperature offsets correction resulted in no particular improvement in the agreement between thermal protocols. However, the selection of a thermal protocol has an influence on EC analysis and should be stated whenever results are reported to secure clarity and comparability.

AMTD
7, 8697–8742, 2014

An additional parameter of influence to the EC results is the optical method used. As expected, TOR results were higher than TOT for EC, 64 % higher for EUSAAR2 (R^2 = 0.52) and 113 % higher for NIOSH870 (R^2 = 0.44). Nevertheless, the above values are based on raw data obtained by a limited number of participants that reported both TOR and TOT results, 10 out of a total of 17. Similarly to TOT, the EC data also varied when applying TOR. More specifically, TOR EC measured with NIOSH870 resulted in higher values by 15 % compared to EUSAAR2, $EC_{NIOSH870,TOR} = 1.15 \cdot EC_{EUSAAR2,TOR}$ (R^2 = 0.95).

The stability of the calibration area throughout sequential analysis could serve as an additional indicator of robustness of the instrument since observed deviations are usually caused by gas flows fluctuations, leaks or oven failures. A typical relative standard deviation (% rsd) of the calibration areas reported throughout an analysis day would usually fall below 5 %. Nevertheless, in some cases it was reported much higher, mostly due to the fact that analysis was performed on different analysis days (Table 5). In that occasion, flows where shut down at the end of one day and re-adjusted the following. It should be noted that gas flows are not strictly defined but have to lie within a suggested range that is set manually by the user. The calibration area can be also affected when the calibration gas cylinder is replaced. While the nominal concentration of CH_4 in Helium is 5 %, deviations are possible. A verification of the concentration of the calibration gas is advised with the use of external standards, e.g., sucrose solution, every time a cylinder is replaced.

When the thermograms were graphically compared among participants, patterns in peak distribution were identified per sample and protocol used. Peaks evolving systematically earlier or later may indicate an error in the determination of the transit time of the instrument (Figs. 2–7). Variations in peak distribution may be an outcome of absent or inaccurate application of the temperature calibration procedure or even indication of possible contamination. Pre-oxidation is another potential cause, which can be verified by the POC concentrations. Low or no POC reported during analysis may be an indication of oxygen entering the main oven during analysis at the Helium phase (Figs. 8–10).

AMTD
7, 8697–8742, 2014

Pre-oxidation can be identified more easily for sucrose solution analysis, when no or low peaks evolve at the oxygen phase and no or low POC is measured (Figs. 6, 7, and 10). A possible cause of pre-oxidation may be traces of oxygen present in the Helium stream which can be sorted out with the use of an in-line oxygen trap.

Leaks, loose connections and oxygen in the helium stream are potential causes of pre-oxidation that may result in a constant presence of oxygen flow in the instrument during the inert phase of analysis and consequently to instrument-specific systematic deviations. Nevertheless, the same effect may result from sample and/or filter specific properties such as the presence of metals, metal oxides, oxygen donors or other substances that can catalytically affect the pyrolytical processes taking place in the oven. An example of this behavior is seen when the laser transmittance signal values for filter G are observed, where all participants show signs of pre-oxidation, which is not the case for the rest of the filters analysed (Figs. 15 and 16). Through the current study no indication that the pre-oxidation effect is thermal protocol specific was identified. While such comparison exercises can point out instrument specific pre-oxidation behavior, individual users should also perform routinely diagnostics of a potential problem through thorough examination of the laser signal behavior during analysis of sucrose solutions. The laser signal can serve as a pre-oxidation indicator when it is observed to systematically ramp up in the He phase, caused by the early desorption of POC from the filter.

When the laser transmittance signal was compared among the participants a wide range in the intensity for a blank filter was noted, varying from ~1000 to ~20 000. However, no systematic differences were observed on the definition of the split point when comparing weak signals with stronger ones. High or low frequency noise in the laser signal was identified for a few participants which may cause a shift in the split point definition.

NIOSH870 has a heating profile in the Helium phase that ramps up to 870 °C in 360 s, which appears short and aggressive when compared to EUSAAR2 that ramps up to 650 °C in 640 s (Table 2). Consequently, it would be expected that the POC (TOT) levels

AMTD
7, 8697–8742, 2014

would be higher for NIOSH870 after the temperature offsets correction, as observed by Phuah et al. (2009) and Pavlovic et al. (2014). Nevertheless, when POC is compared between the two thermal protocols, NIOSH870 reports in principle lower concentrations than EUSAAR2, even for sucrose solutions (Figs. 8–10). A possible explanation may be that lower temperature steps in the inert phase result in more OC exposed in the highest temperature step of the inert phase and thus more POC (Phuah et al., 2009; Pavlovic et al., 2014). Alternatively, when comparing the TOT laser signal between the two thermal protocols, there is no clear difference on the lowest, darkest point, which is related to POC. This may suggest that not all OC is evolved or transformed to POC during the inert phase of EUSAAR2 and therefore is erroneously measured as POC and EC in the oxygen phase.

EC TOT levels were found lower for NIOSH870 than for EUSAAR2, justified by the heating profile differences between them. Considering the fact that almost all analyzers of this exercise had to correct to higher temperatures during calibration, it may be expected that lower EC values are reported after the temperature offsets correction than before, for the same analyzer and sample. The magnitude of this effect is instrument-specific and can be evaluated by each user independently.

In conclusion, ECOC measurements have drawn the interest of research institutes and air quality monitoring networks due to the relevance of EC to human health as well as to climate change. Nevertheless, no standardized protocol exists and researchers may also report biased results, influenced by operational parameters. The issues highlighted by the current comparison exercise findings are two-fold. On the one hand, comparison exercises that focus on laboratory performance should be implemented in laboratories' QA&QC procedures in order to reduce the likelihood of systematic errors and/or inaccuracies during ECOC analysis. On the other hand, additional operational parameters and protocols have to be considered and agreed to be reported by users, similarly to the temperature offsets correction and the use of identical thermal protocols applied in the current study. A list of such parameters would also include the initial laser value, POC concentration, calibration area stability, FID and laser signal plots.

AMTD
7, 8697–8742, 2014

Actions of that kind can improve consistency of reported EC and TC results, as well as comparability to surrogates of EC, such as black carbon and black smoke.

The Supplement related to this article is available online at doi:10.5194/amtd-7-8697-2014-supplement.

Acknowledgements. The authors would like to thank all laboratories participating in the current comparison exercise for their kind collaboration. They are particularly thankful to the providers of the HVS samples, Christoph Hüglin (EMPA, Switzerland), Kostas Eleftheriadis (Demokritos, Greece) and the department the Air Quality Monitoring Network of Amsterdam. Finally, they would like to thank Sunset Laboratory for providing the temperature calibration kits and helping with their application.

References

Adar, S. D. and Kaufman, J. D.: Cardiovascular disease and air pollutants: evaluating and improving epidemiological data implicating traffic exposure, Inhal. Toxicol., 19, 135–149, 2007.

Baumgardner, D., Popovicheva, O., Allan, J., Bernardoni, V., Cao, J., Cavalli, F., Cozic, J., Diapouli, E., Eleftheriadis, K., Genberg, P. J., Gonzalez, C., Gysel, M., John, A., Kirchstetter, T. W., Kuhlbusch, T. A. J., Laborde, M., Lack, D., Müller, T., Niessner, R., Petzold, A., Piazzalunga, A., Putaud, J. P., Schwarz, J., Sheridan, P., Subramanian, R., Swietlicki, E., Valli, G., Vecchi, R., and Viana, M.: Soot reference materials for instrument calibration and intercomparisons: a workshop summary with recommendations, Atmos. Meas. Tech., 5, 1869–1887, doi:10.5194/amt-5-1869-2012, 2012.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Tech., 25, 221–241, 1996.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.

AMTD
7, 8697–8742, 2014

Cavalli, F., Douglas, K., and Borowiak, A.: Results of the 2nd Comparison Exercise for EU National Quality Reference Laboratories (AQUILA) for TC, OC and EC Measurements, Joint Research Center, Ispra, 2012.

CEN: TR 16243 "Guide for the measurement of Elemental Carbon (EC) and Organic Carbon (OC) deposit on filters", European Committee for Standardization, Brussels, 2011.

Cheng, Y., Duan, F. K., He, K. B., Zheng, M., Du, Z. Y., Ma, Y. L., and Tan, J. H.: Intercomparison of thermal-optical methods for the determination of organic and elemental carbon: influences of aerosol composition and implications, Environ. Sci. Technol., 45, 10117–10123, 2011.

Cheng, Y., Duan, F. K., He, K. B., Du, Z. Y., Zheng, M., and Ma, Y., L.: Intercomparison of thermal-optical method with different temperature protocols: implications from source samples and solvent extraction, Atmos. Environ., 61, 453–462, 2012.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414–4422, 2004.

Chow, J. C., Watson, J. G., Chen, L.-W. A., Paredes-Miranda, G., Chang, M.-C. O., Trimble, D., Fung, K. K., Zhang, H., and Zhen Yu, J.: Refining temperature measures in thermal/optical carbon analysis, Atmos. Chem. Phys., 5, 2961–2972, doi:10.5194/acp-5-2961-2005, 2005.

Chow, J. C., Watson, J. G., Chen, L. W. A., Chang, M. C. O., Robinson, N. F., Trimble, D. L., and Kohl, S. D.: The Improve – a temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, J. Air Waste Manage., 57, 1014–1023, 2007.

Chow, J. G., Watson, J. G., Robles, J., Wang, X. L., Cheng, L. W. A., Trimble, D. L., Kohl, S. D., Tropp, R. J., and Fung, K. K.: Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon, Anal. Bioanal. Chem., 401, 3141–3152, 2011.

Emblico, L., Cavalli, F., Hafkenscheid, T., and Borowiak, A.: Results of the First E/OC Comparison Exercise for EU National Air Quality Reference Laboratories (AQUILA), Joint Research Center, Ispra, 2012.

Highwood, E. J. and Kinnersley, R. P.: When smoke gets in our eyes: the multiple impacts of atmospheric black carbon on climate, air quality and health, Environ. Int., 32, 560–566, 2006.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L., and Puxbaum, H.: Intercomparison of thermal and optical measurement methods for elemen-

AMTD
7, 8697–8742, 2014

tal carbon and black carbon at an urban location, Environ. Sci. Technol., 40, 6377–6383, 2006.

IPCC: Climate Change 2007: Impacts, Adaptation and Vulnerability, Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Parry, M. L., Canziani, O. F., Palutikof, J. P., van der Linden, P. J., and Hanson, C. E., Cambridge University Press, Cambridge, UK, 976 pp., 2007.

ISO 5725–2: Accuracy (Trueness and Precision) of Measurement Methods and Results – Part 2: Basic Method For the Determination of Repeatability and Reproducibility of a Standard Measurement Method, ISO, Geneva, 1994.

ISO 13528: Statistical Methods For Use in Proficiency Testing by Inter-Laboratory Comparisons, ISO, Geneva, 2005.

Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, Nature, 409, 695–697, 2001.

Janssen, N., Hoek, G., Simic-Lawson, M., Fischer, P., van Bree, L., ten Brink, H. Keuken, M., Atkinson, R., Anderson, H. R., Brunekreef, B., and Cassee, F. R.: Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM_{10} and $PM_{2.5}$, Environ. Health Persp., 119, 1691–1699, 2011.

Janssen, N., Gerlofs-Nijland, M., Lanki, T., Salonen, R., Cassee, F., Hoek, G., Fischer, P., Brunekreef, B., and Krzyzanowski, M.: Health Effects of Black Carbon, WHO, Regional Office for Europe, Copenhagen, Denmark, 2012.

Lena, S. T., Carter, M., Holguin-Veras, J., and Kinney, P. L.: Elemental carbon and $PM_{2.5}$ levels in an urban community heavily impected by truck traffic, Environ. Health Persp., 110, 1009–1015, 2002.

Maenhaut, W., Claeys, M., Vercauteren, J., and Roekens, E.: Comparison of reflectance and transmission in EC/OC measurements of filter samples from Flanders, Belgium, in: Abstract Book of the 10th International Conference on Carbonaceous Particles in the Atmosphere (ICCPA), 26–29 June 2011, Vienna, Austria, Abstract F-6, 2011.

Panteliadis, P.: "EC/OC Interlaboratory Comparison Measurements, 2009 Report", GGD/LO 09-117, Public Health Service Amsterdam, Department of Air Quality, 2009a.

Panteliadis, P.: EC-OC Measurements: Comparison of Reflectance and Transmittance Techniques, GGD/LO 09-1135, Public Health Service Amsterdam, Department of Air Quality, 2009b.

AMTD
7, 8697–8742, 2014

Panteliadis, P.: "EC/OC Interlaboratory Comparison, 2010 Report", GGD/LO 11-1112, Public Health Service Amsterdam, Department of Air Quality, 2011.
Panteliadis, P., Strak, M., Hoek, G., Weijers, E., van der Zee, S., and Dijkema, M.: Implementation of a low emission zone and evaluation of effects on air quality by long-term monitoring, Atmos. Environ., 86, 113–119, 2014.
Pavlovic, J., Kinsey, J. S., and Hays, M. D.: The influence of temperature calibration on the OC-EC results from a dual optics thermal carbon analyzer, Atmos. Meas. Tech. Discuss., 7, 3321–3348, doi:10.5194/amtd-7-3321-2014, 2014.
Phuah, C. H., Peterson, M. R., Richards, M. R., Turner, J. H., and Dillner, A. M.: A temperature calibration procedure for the Sunset Laboratory carbon aerosol analysis lab instrument, Aerosol Sci. Tech., 43, 1013–1021, 2009.
Piazzalunga, A., Bernardoni, V., Fermo, P., Valli, G., and Vecchi, R.: Technical Note: On the effect of water-soluble compounds removal on EC quantification by TOT analysis in urban aerosol samples, Atmos. Chem. Phys., 11, 10193–10203, doi:10.5194/acp-11-10193-2011, 2011.
Qadir, R. M., Abbaszade, G., Schnelle-Kreis, J., Chow, J. C., and Zimmermann, R.: Concentrations and source contributions of particulate organic matter before and after implementation of a low emission zone in Munich, Germany, Environ. Pollut., 175, 158–167, 2013.
Ramanathan, V. and Carmichael, G.: Global and regional climate changes due to black carbon, Nat. Geosci., 1, 221–227, 2008.
Schauer, J.: Evaluation of elemental carbon as a marker for diesel particulate matter, J. Expo. Sci. Env. Epid., 13, 443–453, 2003.
Schauer, J., Mader, B., Deminter, J., Heidemann, G., Bae, M., Seinfeld, H., Flagan, R. C., Cary, R. A., Smith, D., Huebert, B. J., Bertram, T., Howell, S., Kline, J. T., Quinn, P., Bates, T., Turpin, B., Lim, H. J., Yu, J. Z., Yang, H., and Keywood, M.: ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon, Environ. Sci. Technol., 37, 993–1001, 2003.
Schmid, H., Laskus, L., Abraham, H. J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H. M., Giesen, K. P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J. P., Toom-Sauntry, D., and Puxbaum, H.: Results of the "carbon conference" international aerosol carbon round robin test stage I, Atmos. Environ., 35, 2111–2121, 2001.

AMTD
7, 8697–8742, 2014

Sciare, J., Cachier, H., Oikonomou, K., Ausset, P., Sarda-Estève, R., and Mihalopoulos, N.: Characterization of carbonaceous aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach, Atmos. Chem. Phys., 3, 1743–1757, doi:10.5194/acp-3-1743-2003, 2003.

ten Brink, H., Maenhaut, W., Hitzenberger, R., Gnauk, T., Spindler, G., Even, A., Chi, X., Bauer, H., Puxbaum, H., Putaud, J.-P., Tursic, J., and Berner, A.: INTERCOMP2000: the comparability of methods in use in Europe for measuring the carbon content of aerosol, Atmos. Environ., 38, 6507–6519, 2004.

Wang, Y., Chung, A., and Paulson, S. E.: The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis, Atmos. Chem. Phys., 10, 11447–11457, doi:10.5194/acp-10-11447-2010, 2010.

Watson, J. G., Chow, J. C., and Chen, L. W. A.: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, Aerosol Air Qual. Res., 5, 65–102, 2005.

Zhi, G. R., Chen, Y. J., Sun, J. Y., Chen, L. G., Tian, W. J., Duan, J. C., Zhang, G., Chai, F. H., Sheng, G. Y., and Fu, J. M.: Harmonizing aerosol carbon measurements between two conventional thermal/optical analysis methods, Environ. Sci. Technol., 7, 2902–2908, 2011.

AMTD
7, 8697–8742, 2014

Table 1. Loaded filters description and sampling details.

Filter code	Location	Site description	PM fraction ($\mu g\,m^{-3}$)	Filter type	Date	Volume (m^3)	Sampling time (h)	Instrument	% Transmitted laser intensity compared to blank
A	Athens	Urban background	3.0 (NA)[b]	Whatman QMA 20.3 cm × 25.4 cm	1 Mar 2012	1411	24	Andersen GS2312 BL HVS	38
B	Berne	Urban	2.5 (72.8)	Pallflex Tissuquartz 150 mm	9 Feb 2012	720	24	Digitel DHA80	14
D	Duebendorf	Suburban	2.5 (7.8)	Pallflex Tissuquartz 150 mm	15 Feb 2012	720	24	Digitel DHA80	51
G	Amsterdam	Urban background	10 (24.4)	Whatman QMA 20.3 cm × 25.4 cm	13 Dec 2005[a]	1625	24	Andersen/GMW 1200 HVS	32
U	Duebendorf	Suburban	2.5 (37.0)	Pallflex Tissuquartz 150 mm	14 Feb 2012	720	24	Digitel DHA80	23

[a] Stored below 5 °C till the distribution date.
[b] Not available.

AMTD
7, 8697–8742, 2014

Table 2. Details of the 2 thermal protocols applied by the participants and observed temperature offsets range per step.

	NIOSH870			EUSAAR2		
Carrier gas	Seconds	°C	Range *T* offsets (°C)	Seconds	°C	Range *T* offsets (°C)
Purge time	10	–	–	10	–	–
Helium	80	310	(−58–46)	120	200	(−71–100)
Helium	80	475	(−51–63)	150	300	(−67–54)
Helium	80	615	(−50–70)	180	450	(−60–47)
Helium	110	870	(−68–81)	180	650	(−58–51)
OC analysis time	360			640		
Helium (Oven cool)	45	550	(−93–65)	30	–	–
Oxygen in Helium (2 %)	45	550	(−93–65)	120	500	(−68–49)
Oxygen in Helium (2 %)	45	625	(−75–67)	120	550	(−59–40)
Oxygen in Helium (2 %)	45	700	(−65–70)	70	700	(−68–51)
Oxygen in Helium (2 %)	45	775	(−70–72)	80	850	(−85–64)
Oxygen in Helium (2 %)	45	850	(−76–73)	–	–	–
Oxygen in Helium (2 %)	110	870	(−80–63)	–	–	–
EC analysis time	380			390		
Calibration	120			110		
Total analysis time	14 min and 20 s			19 min and 30 s		

AMTD
7, 8697–8742, 2014

Table 3. Thermal protocols used for replicate analysis, optical method applied and temperature offsets range per laboratory.

Laboratory	Protocols – Replicates	Optical method	*T* offsets range (°C)
1	NIOSH870 – EUSAAR2	TOT – TOR	(−58–−10)
2	NIOSH870 – EUSAAR2	TOT – TOR	(−65–−6)
3	NIOSH930 – EUSAAR2	TOT – TOR	(−87–21)
4	NIOSH870 – EUSAAR2	TOT	(−86–−50)
5	NIOSH-like – EUSAAR2	TOT – TOR	(−55–−5)
6	NIOSH870 – EUSAAR2	TOT – TOR	(−93–−7)
7	NIOSH870 – EUSAAR2[a]	TOT – TOR	(−60–−24)
8	NIOSH870 – EUSAAR2	TOT – TOR	(30–81)
9	NIOSH870 – EUSAAR2	TOT	(−73–−31)
10	NIOSH870 – EUSAAR2	TOT – TOR	(−12–3)[b]
11	NIOSH870 – EUSAAR2	TOT	(−64–−16)[c]
12	NIOSH870 – EUSAAR2	TOT	(−59–−26)
13	NIOSH870 – EUSAAR2	TOT – TOR	(33–100)[b]
14	NIOSH870 – EUSAAR2	TOT – TOR	(−58–−10)[c]
15	NIOSH870 – EUSAAR2	TOT	Not performed
16	NIOSH870 – EUSAAR2	TOT	Not Applicable[e]
17	NIOSH870 – EUSAAR2[d]	TOT	Not Applicable[e]

[a] Limited number of filters analyzed in EUSAAR2.
[b] Applied only for EUSAAR2 protocol.
[c] No calibration performed, GGD offsets applied instead.
[d] Limited sample set analyzed.
[e] Field analyzer.

AMTD
7, 8697–8742, 2014

Table 4. Split point ranges as reported by all participants, per sample, protocol and optical method.

Sample	Protocol	Split point range (seconds)	
		Transmittance	Reflectance
A	EUSAAR2	(745–941)	(772–862)
	NIOSH870	(434–531)	(344–518)
B	EUSAAR2	(826–932)	(772–886)
	NIOSH870	(427–518)	(414–499)
D	EUSAAR2	(875–997)	(840–982)[a]
	NIOSH870	(490–593)[b]	(467–569)
G	EUSAAR2	(582–859)	(736–888)
	NIOSH870	(302–524)	(324–521)
U	EUSAAR2	(808–977)	(809–898)[c]
	NIOSH870	(471–561)	(347–534)

One participant reported clearly outlying split points.
[a] 1073 s.
[b] 819 s.
[c] 991 s.

AMTD
7, 8697–8742, 2014

Table 5. Relative standard deviations (% rsd) of calibration area for all analyses per participant. Instrument specific characteristics, calibration constant, transit time and atmospheric pressure.

Laboratory	% rsd calibration area	Calibration constant	Transit time (s)	Atmospheric Pressure (mm Hg)
1	1.9	23.4	11	(729.3–744.1)
2	2.0	19.9	11	(426.1–426.9)
3	14.9	24.7	8	(751.4–763.6)
4	1.4	17.1	7	(741.4–747.7)
5	2.8	24.6	13	(748.3–750.9)
6	3.0	24.6	12	(725.8–739.6)
7	2.3	20.9	15	(761.7–775.0)
8	1.4	25.5	7	(384.3–384.4)
9	14.4	23.4	6	(742.2–746.5)
10	14.6	20.1	12	(375.4–375.7)
11	4.6	28.7	12	(774.6–785.0)
12	24.6	18.6	11	(374.6–374.9)
13	8.9	22.0	14	(382.0–382.6)
14	10.2	22.3	13	(723.5–726.3)
15	3.8	22.5	7	(719.7–731.4)

AMTD
7, 8697–8742, 2014

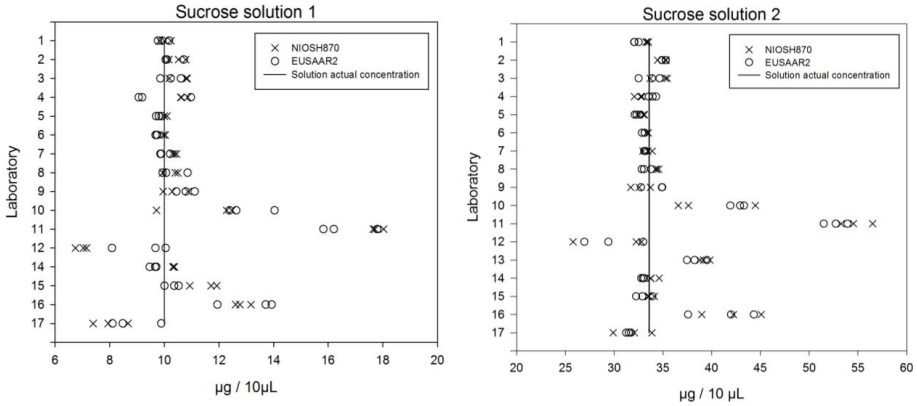

Figure 1. Triplicate sucrose solution analysis (S1 and S2) per protocol and participant. S1 and S2 concentrations of 10.00 and 33.58 µg 10 µL^{-1}, respectively.

AMTD
7, 8697–8742, 2014

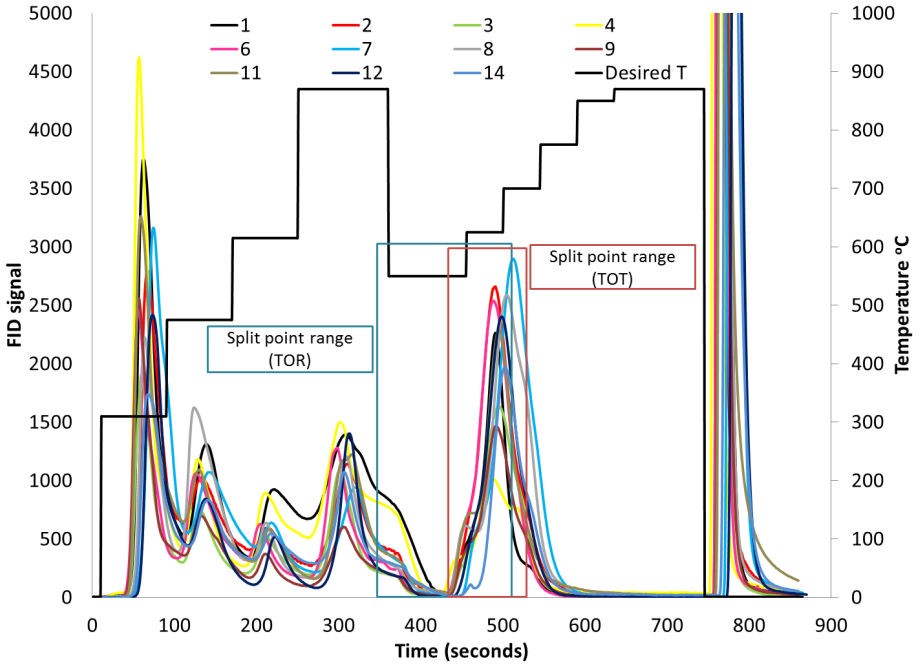

Figure 2. Thermograms of ECOC analysis on PM loaded quartz fibre filter (A sample), by NIOSH870 for all participants.

AMTD
7, 8697–8742, 2014

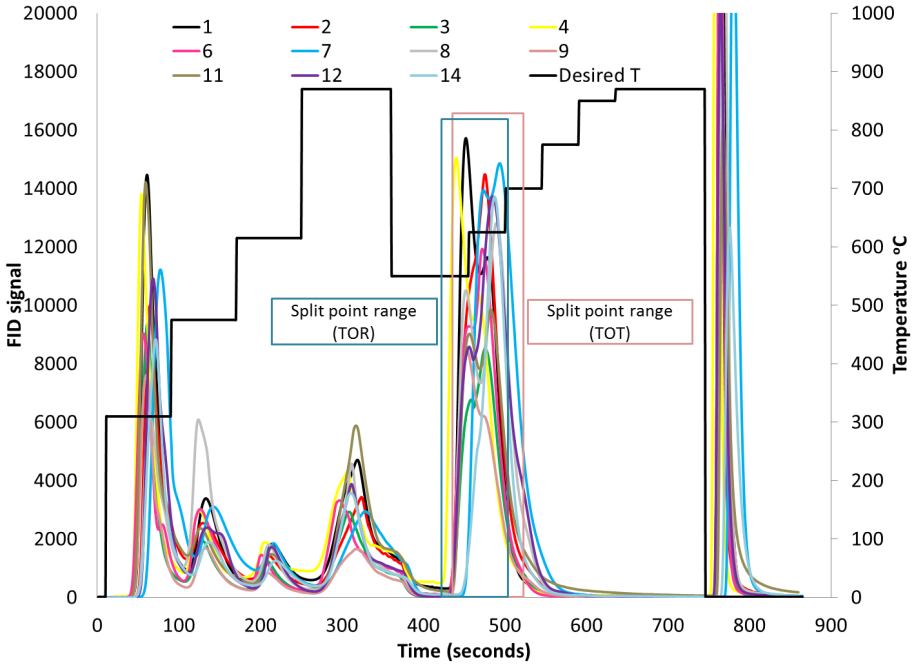

Figure 3. Thermograms of ECOC analysis on PM loaded quartz fibre filter (B sample), by NIOSH870 for all participants.

AMTD
7, 8697–8742, 2014

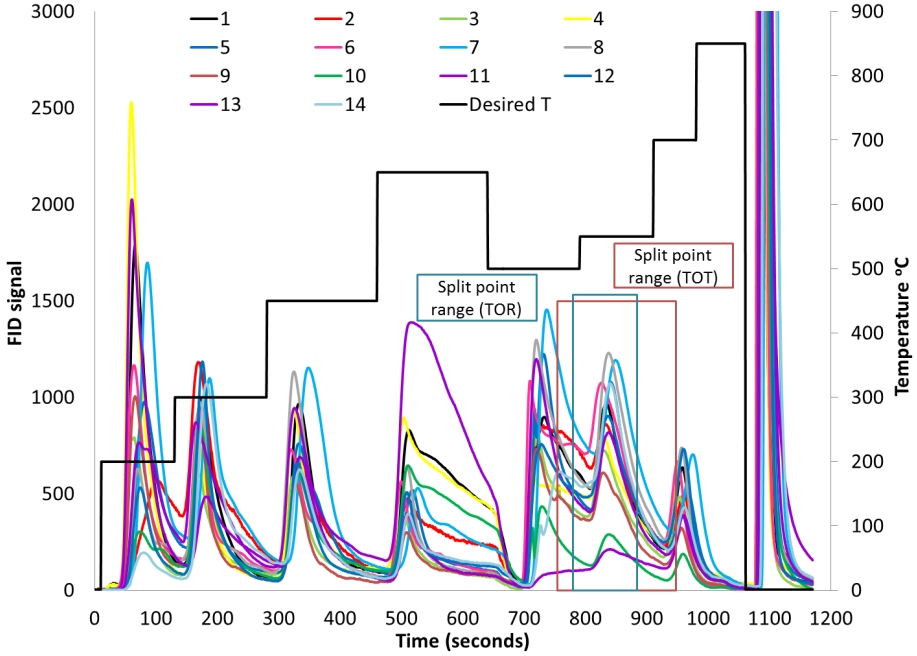

Figure 4. Thermograms of ECOC analysis on PM loaded quartz fibre filter (A sample), by EUSAAR2 for all participants.

AMTD
7, 8697–8742, 2014

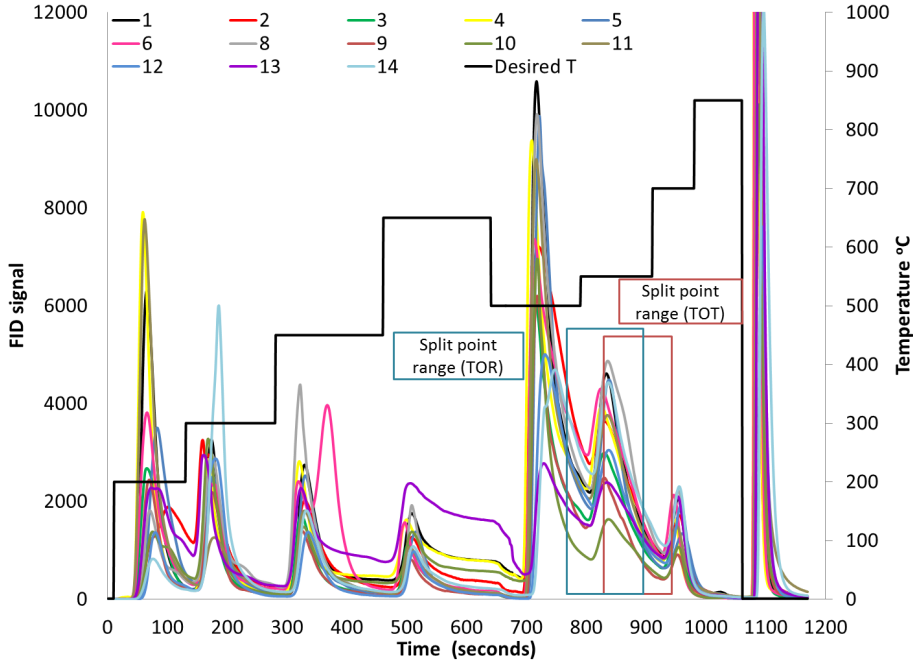

Figure 5. Thermograms of ECOC analysis on PM loaded quartz fibre filter (B sample), by EUSAAR2 for all participants.

AMTD
7, 8697–8742, 2014

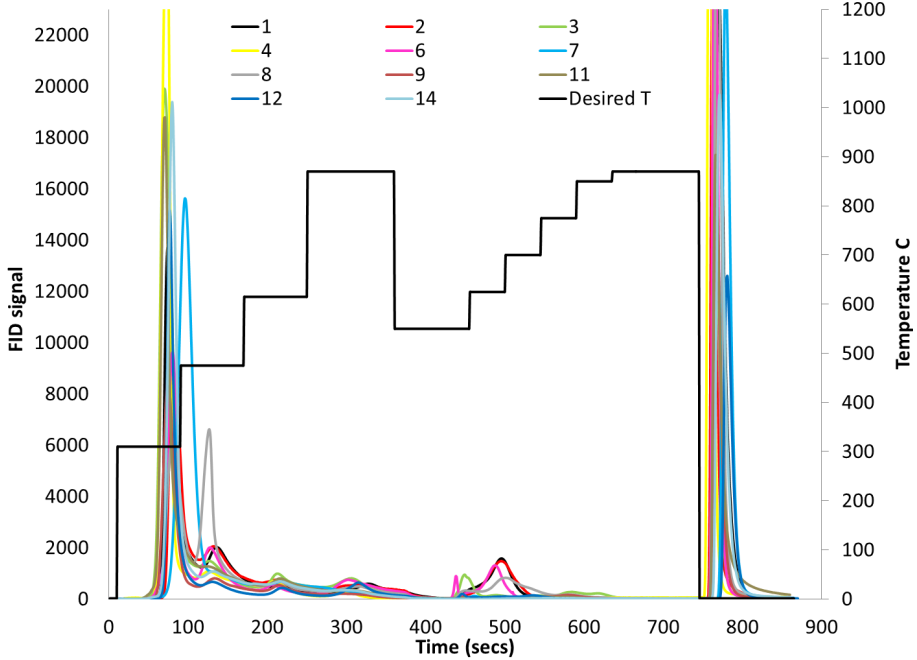

Figure 6. Thermograms of ECOC analysis on standard sucrose solution (S2), by NIOSH870 for all participants.

AMTD
7, 8697–8742, 2014

CC BY

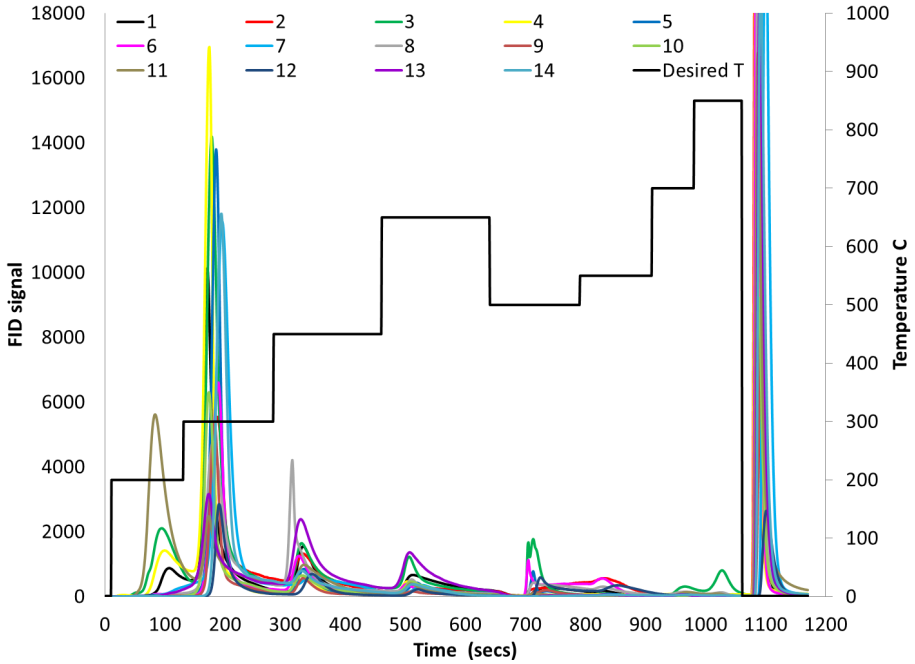

Figure 7. Thermograms of ECOC analysis on standard sucrose solution (S2), by EUSAAR2 for all participants.

AMTD
7, 8697–8742, 2014

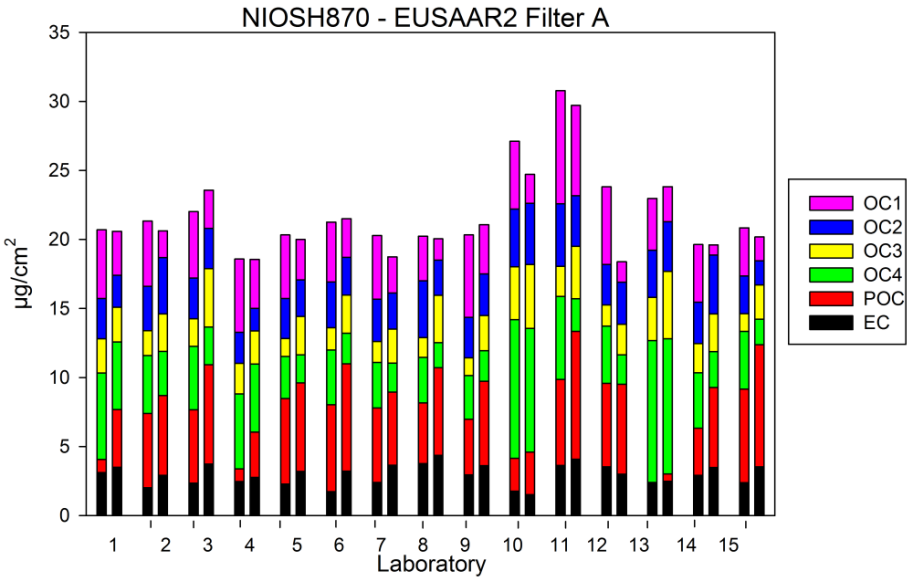

Figure 8. OC, POC and EC (TOT) concentrations ($\mu g\,cm^{-2}$) per temperature step and protocol for PM loaded quartz fibre filter (Sample A).

AMTD
7, 8697–8742, 2014

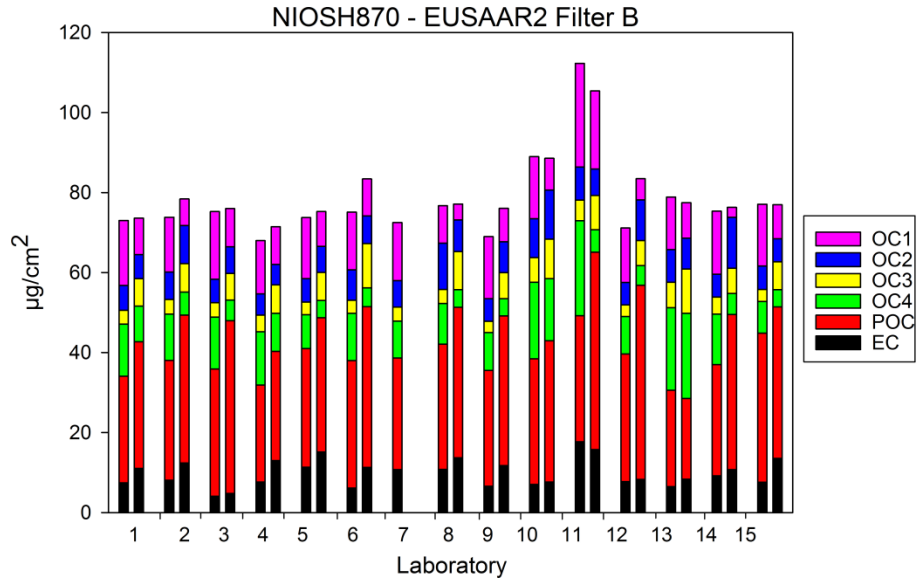

Figure 9. OC, POC and EC (TOT) concentrations ($\mu g\,cm^{-2}$) per temperature step and protocol for PM loaded quartz fibre filter (Sample B).

AMTD
7, 8697–8742, 2014

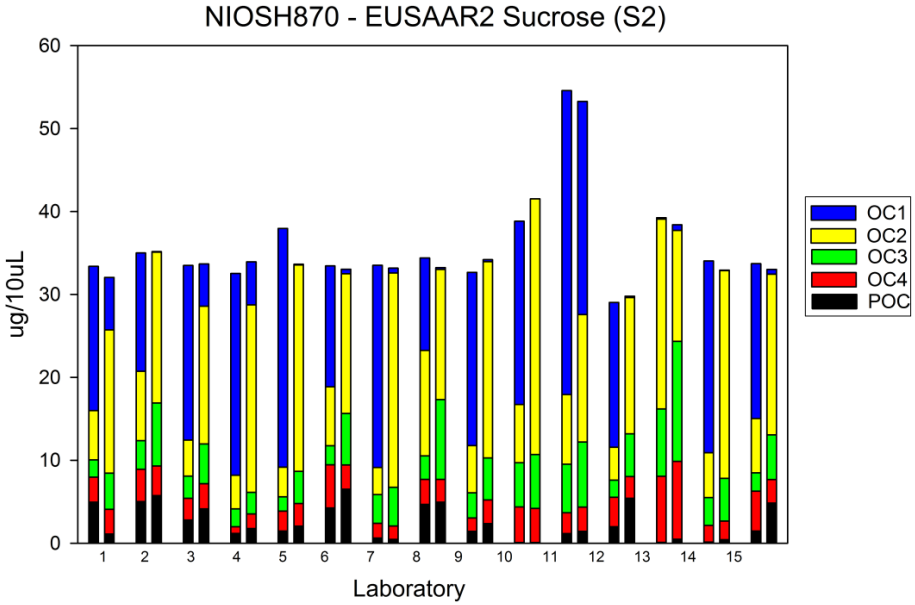

Figure 10. OC, POC and EC (TOT) concentrations (µg 10 µL^{-1}) per temperature step and protocol for sucrose solution (S2).

AMTD
7, 8697–8742, 2014

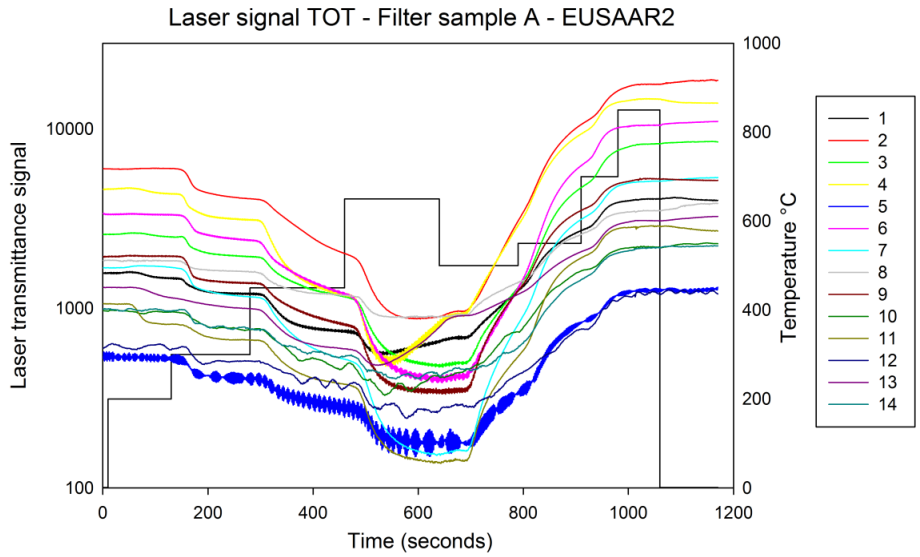

Figure 11. Laser transmittance signal during filter sample A analysis with the use of EUSAAR2 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014

CC BY

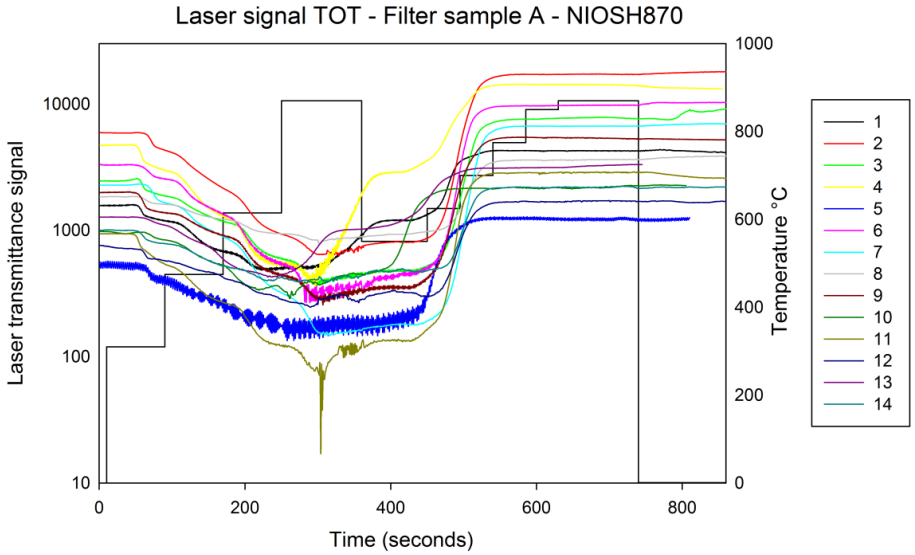

Figure 12. Laser transmittance signal during filter sample A analysis with the use of NIOSH870 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014

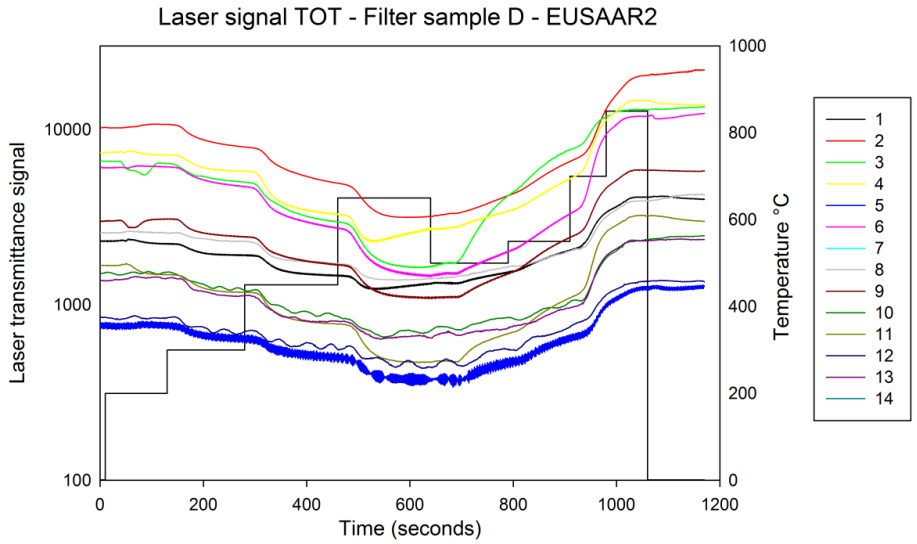

Figure 13. Laser transmittance signal during filter sample D analysis with the use of EUSAAR2 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014

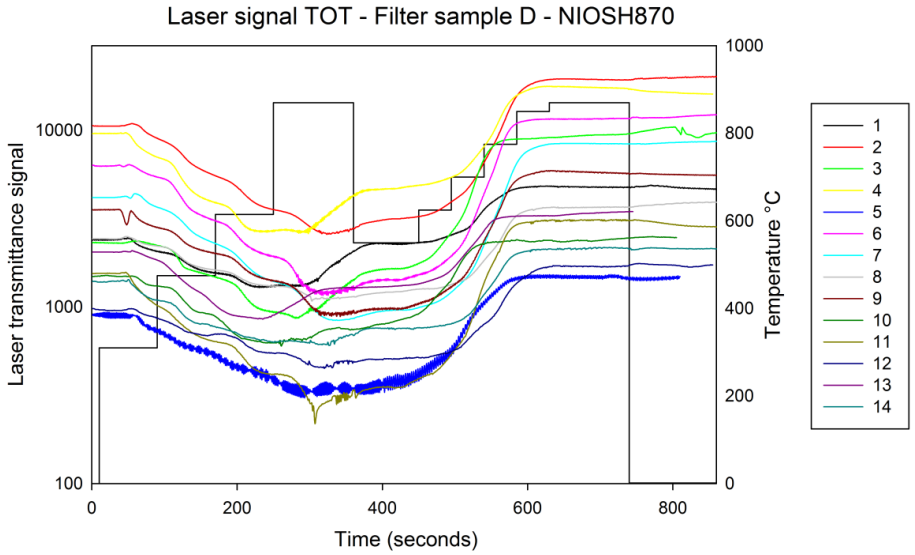

Figure 14. Laser transmittance signal during filter sample D analysis with the use of NIOSH870 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014

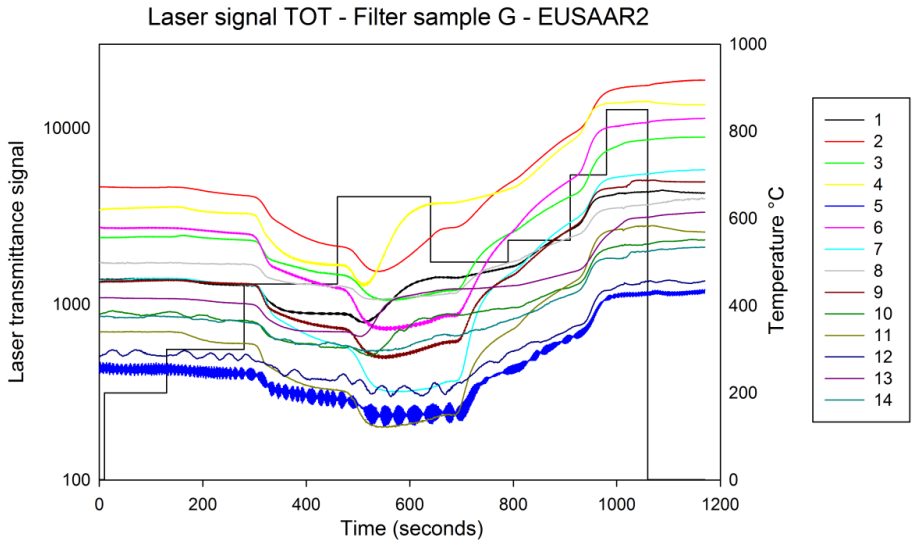

Figure 15. Laser transmittance signal during filter sample G analysis with the use of EUSAAR2 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014

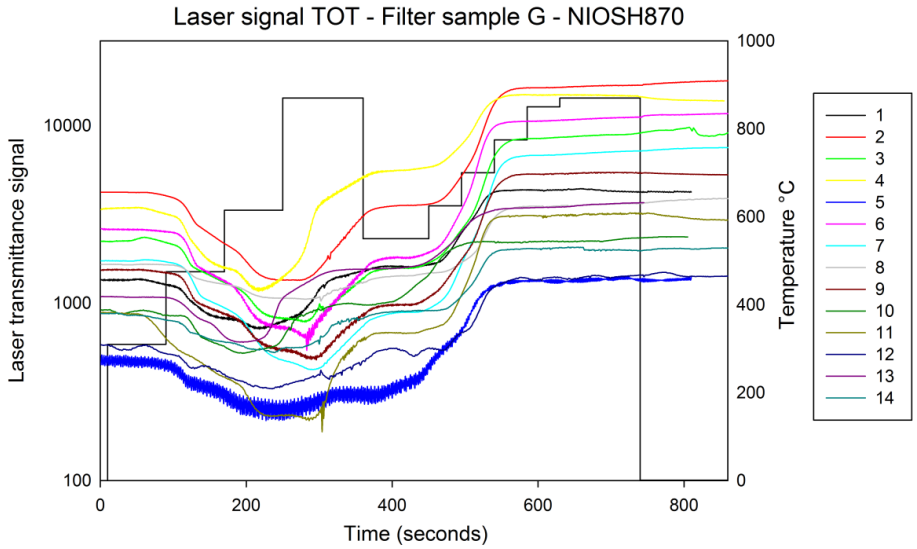

Figure 16. Laser transmittance signal during filter sample G analysis with the use of NIOSH870 thermal protocol for all laboratories.

AMTD
7, 8697–8742, 2014