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Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review

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Abstract

Thermal-optical analysis is currently under consideration by the European standardization body (CEN) as the reference method to quantitatively determine organic carbon (OC) and elemental carbon (EC) in ambient air. This paper presents an overview of the critical parameters related to the thermal-optical analysis including thermal protocols, critical factors and interferences of the methods examined, method inter-comparisons, inter-laboratory exercises, biases and artifacts, and reference materials. The most commonly used thermal protocols include NIOSH-like, IMPROVE_A and EUSAAR_2 protocols either with light transmittance or reflectance correction for charring. All thermal evolution protocols are comparable for total carbon (TC) concentrations but the results vary significantly concerning OC and especially EC concentrations. Thermal protocols with a rather low peak temperature in the inert mode like IMPROVE_A and EUSAAR_2 tend to classify more carbon as EC compared to NIOSH-like protocols, while charring correction based on transmittance usually leads to smaller EC values compared to reflectance. The difference between reflectance and transmittance correction tends to be larger than the difference between different thermal protocols. Nevertheless, thermal protocols seem to correlate better when reflectance is used as charring correction method. The difference between EC values as determined by the different protocols is not only dependent on the optical pyrolysis correction method, but also on the chemical properties of the samples due to different contributions from various sources. The overall conclusion from this literature review is that it is not possible to identify the “best” thermal-optical protocol based on literature data only, although differences attributed to the methods have been quantified when possible.

1 Introduction

Carbonaceous material accounts for a large and often dominant fraction of particulate matter, PM (Putaud et al., 2010, 2004; Fuzzi et al., 2006) that receives the attention of the climate, air pollution and health research communities (Lim et al., 2012; Shindell et al., 2012; Janssen et al., 2012). Particulate carbon (total carbon, TC) may be broadly divided into three categories: organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC), mostly present as carbonate carbon (CC). OC is either directly emitted into the atmosphere or formed by the condensation of compounds produced by the atmospheric photo-oxidation and polymerisation of organic species (Jimenez et al., 2009). In contrast, EC is exclusively of primary origin and emitted by the incomplete combustion of carbon-based fuels, principally wood used for residential heating and fossil fuels used in transportation, power generation, and industrial processes (Fuzzi et al., 2006). CC is present in natural ground and building/demolition dust which can be resuspended.

The terms EC, Black Carbon (BC), soot, and light absorbing carbon (LAC) have often been used loosely and interchangeably in the literature (Petzold et al., 2013). Soot, the product of incomplete combustion of any carbon containing fuels, is used by the Intergovernmental Panel on Climate Change to denote any light-absorbing, combustion-generated aerosols, whereas BC refers to the optical properties of soot defined as an ideally light-absorbing substance composed of carbon (Petzold et al., 2013; Baumgardner et al., 2012). Light-absorbing is not strictly specific to carbon, but BC features a much larger mass absorption cross-section than other aerosol constituents. In contrast, EC refers to chemical properties, i.e. to thermally-refractory carbon, including graphitic structures. The term EC is used when total carbon is gasified from the sample, and EC is differentiated from OC based on refractiveness properties (i.e. thermal methods) or optical measurements during the course of the thermal analysis (thermal-optical methods).

Thermal methods make use of the thermal refractivity of EC, which does not volatilize in an inert atmosphere at temperatures below ∼ 700 °C. EC can only be gasified by oxidation starting at temperatures above 340 °C (Petzold et al., 2013; Schmid et al., 2001). Therefore OC might be defined as the carbon fraction that evolves under a heating cycle in an inert atmosphere, and EC as the fraction which evolves during a subsequent

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heating step in an oxygen-containing gas mixture. However, some organic compounds can easily pyrolyze or “char” during the inert mode of the analysis. The char that is formed during the analysis process, if not properly accounted for, would be incorrectly reported as EC present in the original sample. Thermal-optical methods have been developed in which the continuous monitoring of the optical properties (reflectance or transmittance) of the filter sample during the analysis is used to correct for charring (Chow et al., 1993; Birch and Cary, 1996).

The European Union (EU) has issued a directive (2008/50/EC) which requires the monitoring of organic carbon and elemental carbon in $PM_{2.5}$ at selected rural background sites from mid-2010. The monitoring program of the Convention on long-range transport of air pollutants (EMEP) also includes the measurement of OC and EC in PM_{10}. The technical report from The European Committee for Standardization, CEN (CEN/TR 16243, 2011) recommends thermal-optical analysis to determine OC and EC concentrations in ambient air, but no European standard method exists yet. In this work, we provide an overview of scientific papers, protocols, guidelines, and reports related to thermal-optical methods for the determination of EC and OC. Many parameters are studied such as the critical factors and interferences of the methods examined, inter-comparison of the methods, biases and artifacts, reference materials and inter-laboratory exercises. The present literature review was conducted to serve as the scientific basis on the discussion over the performance and applicability of measurement methods of airborne EC and OC in $PM_{2.5}$ in accordance to the new Air Quality Directive 2008/50/EC.

2 Thermal-optical analysis

During the thermal analysis a fraction of the OC chars or pyrolyzes under the inert atmosphere phase (inert mode, He mode or He step) into a thermally stable form which, like the EC, can only be converted into vapor at higher temperature or in presence of O_2. This pyrolytic fraction, called pyrolytic carbon (PC), can be erroneously identified

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as EC. To overcome this interference, Huntzicker et al. (1982) developed a thermal-optical analysis method by incorporating an optical correction procedure in the thermal analysis. The light reflectance of the sample, which was continuously monitored by a He-Ne laser-based system, was used for charring correction.

A modified version of the Huntzicker et al. (1982) instrument designed by Chow et al. (1993) at the Desert Research Institute (DRI) is known as the DRI carbon analyzer. A temperature protocol named IMPROVE, was specifically developed to be applied to the Interagency Monitoring of PROtected Visual Environments network in the USA. Carbonaceous vapours are converted after volatilisation to CH_4 (see temperature steps in Table 1) and quantified with a flame ionization detector, FID. Similarly to the method of Huntzicker et al. (1982) the sample reflectance is monitored to correct for charring and the method is called the thermal-optical reflectance (TOR). A few years later, the Sunset laboratory instrument (Sunset Laboratories Inc.) was developed based on the same principle, but using transmittance monitoring to correct for charring (Birch and Cary, 1996). The thermal-optical transmittance (TOT) method was designed for the analysis of the carbonaceous fraction of particulate diesel exhaust based on the National Institute of Occupational Safety and Health method 5040 (NIOSH 5040) and the thermal protocol developed was called NIOSH (see Table 1). Additionally, the Sunset Carbon Aerosol Analysis Field Instrument was developed, which measures OC and EC in situ and in near-real time, based on the same analysis principle as in the Sunset laboratory instrument (Bae et al., 2004). However, the field instrument will not be further described in this review as it performs on-line measurements while the lab instruments can analyze samples from various sites.

The rationale of the optical correction method either with transmittance or with reflectance is based on the fact that EC does not volatilize up to very high temperatures but its release occurs only when oxygen is present. Charring is evidenced by the decrease of the filter sample reflectance or transmittance. When PC evolves, the sample reflectance or transmittance increases to reach its original value, as the charred OC has been removed. The OC/EC split point is usually defined in this manner. It is as-

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sumed that the carbonaceous material released after the split point is quantitatively nearly equal to the EC that was originally on the filter, based on assumptions related to the composition of the sample and the optical properties of PC.

It should be mentioned that traditionally the DRI analyzer uses reflectance (TOR) correction and the Sunset Laboratory instrument the transmission (TOT) correction, but both instruments have currently installed dual optics where simultaneous TOR and TOT corrections are possible. The latest instrumental development in thermal-optical analysis is the DRI 7 wavelength thermal-optical analyzer (Chen et al., 2015) using 7 different lasers for TOT/TOR corrections, resulting in 14 different wavelength dependent split points (TOT or TOR correction at each of the wavelengths). Since EC and PC have different optical properties this information may prove useful in characterization of PC during the analysis as it may allow a more accurate separation of the EC contained in the sample and the PC generated during the analysis. This should prove especially useful in the constraining of the separation between OC and EC in samples loaded with biomass smoke, containing water-soluble and light absorbing organic compounds.

2.1 Thermal-optical analysis protocols

Nowadays, both the Sunset and the DRI carbon analyzers are commercially available instruments and are capable to operate any thermal protocol. Table 1 summarizes several of the temperature protocols that have been applied to determine ambient OC and EC concentrations. Most protocols like the ACE-Asia, STN, CalTech, HKGL and MSC1 protocols (e.g., Schauer et al., 2003; Sin et al., 2002; Yang and Yung, 2002; Peterson and Richards, 2002) are NIOSH-like protocols, being modified versions of the Birch and Cary (1996) and Birch et al. (1998) protocols, with maximum temperatures in the He mode found in the range 820–900 °C and final temperatures in the He-O_2 mode set at 850–940 °C. NIOSH-like protocols are identified as NIOSH-840, NIOSH-850 or NIOSH-870 by the maximum temperature applied in the inert mode. Occasionally NIOSH-like protocols are also called “Quartz” (Querol et al., 2013; Quincey et al., 2009) or “Quartz.par” protocol (Yttri et al., 2009).

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The IMPROVE network currently uses IMPROVE_A, which is a modified version of the IMPROVE protocol to accommodate for an upgrade of the DRI analyzer. After the temperature calibration of the DRI analyser, the temperature steps of the IMPROVE protocol were increased by 20–40 °C (Chow et al., 2007). The main difference from NIOSH-like protocols is the lower temperature in the He phase of the analysis (580 °C) and the analysis time. The IMPROVE protocol advances from one temperature to the next one when a well-defined carbon peak has evolved, resulting in variable and generally longer analysis times.

Recently, in the framework of the EU-project EUSAAR (European Supersites for Atmospheric Aerosol Research, www.eusaar.net), the thermal-optical analysis protocol EUSAAR_2 was developed (using transmittance for charring correction) for European regional background sites (EMEP network) in order to improve the accuracy of the discrimination between OC and EC. The use of lower temperature steps in the He-mode and longer residence times aimed at the reduction of pyrolysis and at a more complete evolution of OC (Cavalli et al., 2010).

Table 2 provides the analytical specifications of the most commonly used temperature protocols (units are given in $\mu g\,C\,cm^{-2}$ of filter). The range for the NIOSH protocol is 0.7 to 70 $\mu g\,C\,cm^{-2}$ and the limit of detection (LOD) was calculated at 0.15 $\mu g\,C\,cm^{-2}$ (Birch and Cary, 1996; Peterson and Richards, 2002). The operational range for the IMPROVE_A protocols is 0.2–750 $\mu g\,C\,cm^{-2}$ and the LOD 0.2 $\mu g\,C\,cm^{-2}$ (Chow et al., 1993). The EUSAAR_2 protocol was designed and tested on samples collected during different seasons and at various sites in Europe, with filter loadings ranging from 5 to 62 $\mu g\,C\,cm^{-2}$. The residence times at each temperature step were selected such that the various carbon peaks are clearly separated and the uncertainty in the EC determination ranges from 2 to 7 % (Cavalli et al., 2010).

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2.2 Critical factors in thermal-optical analysis

2.2.1 Temperature calibration

Typically, the sample oven temperature is measured in thermal-optical instruments using a temperature sensor near, but not precisely at, the sample. However, temperature variability within the oven may result in different temperatures at the sample and the sensor (Phuah et al., 2009). Sample temperatures have been found to differ from sensor temperatures by 10 to 85 °C in both the DRI and Sunset analyzers by IMPROVE_A, NIOSH-like and EUSAAR_2 protocols (Chow et al., 2005b; Phuah et al., 2009; Pavlovic et al., 2014; Panteliadis et al., 2015). Chow et al. (2005b) demonstrated that temperature biases of 14 to 22 °C can influence the carbon fraction measurement in thermal-optical analysis. Therefore, the correlation between sample temperature and the sensor temperature should be calibrated so that the thermal protocol can truly reflect the sample temperature during the analysis.

2.2.2 Maximum temperature in the inert mode

Many researchers report that, in the thermal-optical method, the results depend upon the operational parameters, and in particular on the analysis temperature program including the temperature ramp step and the duration of the plateaus (Schauer et al., 2003; Chow et al., 2001, 2005a). Application of a too high maximum temperature in the inert mode, Tmax (the temperature of the last step in the inert mode) may cause the premature evolution of EC and light absorbing carbon that contains both PC and EC and also promote charring while a very low Tmax may result in an overestimation of the EC concentration due to the incomplete evolution of OC in the He mode and the evolution of CC in the He-O_2 mode (Subramanian et al., 2006). EC concentrations have been found to decrease linearly with the increase of the Tmax in the He mode (Subramanian et al., 2006; Zhi et al., 2009; Maenhaut et al., 2009; Kuhlbusch et al., 2009).

2.2.3 Charring and charring correction

Charring depends on many factors, including the amount and type of organic compounds, temperature steps in the analysis, the residence time at each temperature step, and the presence of certain inorganic constituents (Yu et al., 2002).

Yu et al. (2002) found that water-soluble organic compounds WSOC are responsible for a large fraction (13–66 %) of charring in thermal-optical analysis. The extent of the charring from WSOC was found to increase with the WSOC loading up to a certain value. Piazzalunga et al. (2011) demonstrated that the removal of WSOC from ambient samples reduces the differences observed between different thermal protocols and slightly improves their comparability. Charring is also influenced by the presence of inorganic constituents such as NH_4HSO_4 that can increase PC formation by a factor of 2 to 3 (Yu et al., 2002). Charring can be reduced when the residence time at each temperature step in the He atmosphere is sufficiently long to allow for maximum C evolution at each step (Cavalli et al., 2010).

Thermal-optical methods assume that: (1) PC caused by charring during the inert mode is more easily oxidized than EC, or (2) the specific attenuation cross section, σ of PC is similar to the specific attenuation cross section of the original EC on the filter. If either of these assumptions is correct, then the method will be quantitative for OC and EC. However, PC and EC and non light-absorbing carbon co-evolve during the oxidizing mode and, even prematurely, during the He-mode at high temperatures depending on the protocol used and they have been shown to have significantly different values of attenuation cross section (Cavalli et al., 2010 and references therein). The true EC concentrations can be either overestimated or underestimated depending on whether the fraction of PC that is burned after the EC/OC split point has a higher or a lower σ value than that of native EC. The σ value of PC is affected by the composition of its organic precursors, which vary greatly among aerosols collected from different locations and at different times. As a result, the magnitude of the uncertainty arising from the incorrect EC/OC split is expected to vary from one aerosol sample to another Yang and Yu (2002).

2.2.4 Dependence of OC/EC split on aerosol type

The relative amount of carbon allocated as OC and EC is sensitive to the type of aerosol collected (Chow et al., 2001; Schauer et al., 2003). The OC/EC split for wood smoke source samples, extracts of organic compounds from wood smoke and woodstove smoke is influenced by the temperature protocol; such samples exhibit significant charring while a carbon black sample has the same split between OC and EC regardless of the temperature protocol (Khan et al., 2012; Schauer et al., 2003; Reisinger et al., 2008; Maenhaut et al., 2009; Soto-Garcia et al., 2011). The explanation is found in the composition of wood and biomass burning emissions, which contain significant amounts of WSOC that appear highly amenable to charring. Moreover wood burning EC has been proven to be less refractory than fossil fuel burning EC (Zhang et al., 2012). In addition K and Na that are abundant in biomass burning emissions can alter the decomposition temperature of EC and provoke premature oxidation (Novakov and Corrigan, 1995). On the other hand, samples from traffic sites form little PC during thermal-optical analysis, possibly due to the high diesel component which contains non pyrolyzing organic matter, such as PAHs (Khan et al., 2012). Samples containing high amounts of resuspended soil and road dust can cause the premature evolution of LAC compounds in the inert mode due to increased oxidation at high temperatures by metal oxides present in soil and road dust (Khan et al., 2012). If this happens, the critical issue is to determine the type of LAC that evolves. If the LAC evolving in the He-mode at high temperature is pure PC, as suggested by Yu et al. (2002), this does not produce any bias in the OC and EC determination. However, Subramanian et al. (2006) and Cavalli et al. (2010) demonstrated that the LAC evolving in the He mode at high temperatures can be either EC or PC or a combination of them.

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2.2.5 Dependence of OC/EC split on sample oven soiling

The quartz oven hosting the sample during analysis is gradually soiled by oxidation and inorganic salts originating from filter matrices (when containing binders) and/or loaded samples. Chiappini et al. (2014) evidenced possible impact of the oven soiling on the EC/OC split point, especially for samples exhibiting high EC and PC amounts.

2.2.6 Instrument parameters influencing the analysis

The time necessary for the gaseous compounds desorbed to reach the FID unit from the filter is defined as transit time and is an instrument-specific parameter. As the transit time is taken into account to determine the split point, an incorrect transit time will result in a shift of the split point and thus incorrect concentration values for the OC and EC fractions. Maenhaut et al. (2004) and Panteliadis et al. (2015) have indicated that the FID response for the oxidized PC is somewhat delayed because of the laser-FID transit time resulting in the erroneous determination of the split point.

As discussed in the sections above, several factors directly influence the split point between EC and OC, but since no true split point could be defined so far, no direct judgments on how to balance the different factors can be made here.

3 Biases in thermal-optical analysis

Biases in thermal-optical analysis methods can come from the following: (i) non-uniform particle deposits on the filter, (ii) OC loading in blank filters, (iii) organic vapour filter adsorption, (iv) catalytic oxidation interactions between OC, EC, and non-carbonaceous material in the sampled particles, and (vi) light-absorbing organic matter that affects laser correction. As the filter homogeneity is a common source of possible interference for the determination of all ambient aerosol constituents it is not discussed specifically

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in this review. Inhomogeneities determined elsewhere were normally found in the range 3–5 % of variability (e.g.: John and Reischl, 1980; John and Wall, 1983).

3.1 OC loading in blank filters

Quartz fibre filters may adsorb volatile organic compounds very easily because of the high active surface resulting in the increase of blank levels for OC (Chai et al., 2012). Contamination of filters may also occur during transport and at the sampling site depending on the holder/container used for transport and during sampling. In order to estimate the carbon present in the blank filter or adsorbed on it, laboratory blank filters and field blank filters are used.

3.1.1 Laboratory blank filters

Quartz filters may be submitted to a thermal treatment (pre-firing) in the laboratory prior to sampling in order to remove volatile adsorbed carbon and therefore reduce their OC content. The EMEP draft protocol for EC/OC determination at EMEP sites (available at http://www.nilu.no/projects/ccc/manual/index.html) recommends pre-firing at 850 °C for 3 h. A similar protocol is followed by the US networks (STN, IMPROVE and SEARCH networks) where filters are pre-fired at 900 °C for 3 h under a slow stream of filtered air. The high temperatures used in pre-firing may increase the adsorption capacity of the filters. Thus, the CEN/TC 264 report (CEN/TR 16243, 2011) suggests pre-firing at lower temperatures (a minimum of 500 °C, for at least 1 h), whereas Arp et al. (2007) suggest more gentle procedures, such as pre-firing at temperatures $<$ 400 °C or possibly washing the filters with an organic solvent.

The adsorption capacity of organic gases is specific for each filter, varying between filters from the same brand, type, and even from the same lot number or box (Kirchstetter et al., 2001). Mean OC concentrations determined in blank quartz filters are in the range 0.06–2.4 µg cm^{-2} (Table 3).

Figure 1 shows the mean, median, and 25 and 75 percentiles of the OC blank concentrations determined for a total of 128 PALL Quartz filters (Pall Tissuquartz 2500-QAT, 150 mm) in the IDAEA-CSIC laboratory for the period 2012–2013 (IDAEA-CSIC unpublished results). These filters are commonly used for offline OC/EC determination after high-volume sampling. The filters were baked at 200 °C for 4 h and packaged in the same way as the filters used for sampling, but kept in the laboratory until the analysis. The average OC blank concentration was 0.80 ± 0.39 $\mu g\,cm^{-2}$. The results are compared to those obtained for the new Whatman ultra-pure Quartz filters (QM-H, 150 mm), 127 filters analyzed in 2014 without pre-firing, with slightly higher concentrations of OC (1.22 ± 1.11 $\mu g\,cm^{-2}$, Table 3).

Laboratory blank filters were analyzed by the Netherlands research project on Particulate Matter (ten Brink et al., 2009). For this study, Whatman QM- A quartz filters (47 mm) were used without pre-firing. The blank filters were analyzed as received from the factory, taken from batches that were opened shortly before analysis. The average value was 2.4 $\mu g\,cm^{-2}$ (Table 3). It was consistently observed that filters from the top of a stack contained high OC values (~ 6 $\mu g\,cm^{-2}$ on average). These values were even higher than those of the average field blank value. Further down the stack of filters, the values rapidly decreased down to ~ 0.4 $\mu g\,cm^{-2}$, on average, in the middle of the stack, and 1.2 $\mu g\,cm^{-2}$ at the bottom. The concentrations determined for the top filters should be considered as relatively high when compared with usual values in samples.

Chai et al. (2012) determined the concentrations of OC and EC for blank quartz filters (2500QAT-UP) before and after pre-firing at 600 °C for 2 h. The levels of EC were negligible for both baked and unbaked filters. The levels of OC were lower for the pre-fired filters (0.22 ± 0.11 $\mu g\,cm^{-2}$, on average) as compared with the non-pre-fired filters (0.38 ± 0.06 $\mu g\,cm^{-2}$, on average). The decrease of OC concentrations was considered not significant when compared with their usual sample loadings. As described in the section dealing with sampling artifacts, several authors report that pre-firing the filters may alter their sorption properties and enhance the occurrence of positive sampling artifacts.

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3.1.2 Field and trip blank filters

Trip blanks are used to assess artifacts associated with handling, transport and storage. Field blanks are additionally placed in the instrument during e.g. 1 week without forcing the passage of air through them, or passing air during a brief time period (from a few seconds to 1 min). Some studies assume that field blanks can be used as a proxy for the adsorption artifact during active sampling (Watson et al., 2007). However, filters may be subjected to a number of changes affecting the net absorption of gaseous carbon during sampling that are not reflected in the field blanks (Maimone et al., 2011), such as changes in ambient air concentrations of gaseous carbon, ambient temperature or pressure drop due to filter loading. EMEP recommends to analyse one field blank per week and to subtract its OC concentration from the sample OC concentrations when the positive and negative artifacts are not avoided or quantified (by means of a back-up quartz filter OC behind a quartz filter, QBQ; or behind a Teflon filter, QBT; denuder). Moreover, it has to be considered that part of the adsorbed gases may volatilize during sampling. Thus, Yttri et al. (2007) found that adsorbed carbon in the field blanks would partially evaporate, decreasing by as much as a factor of two, when passing a clean air flow through.

Field blank filters have been analyzed in a number of studies with different results. Yttri et al. (2007) found negligible EC concentrations and OC concentrations between 0.4 and 1.9 $\mu g\,C\,cm^{-2}$ in field blanks collected at EMEP European sites. Ten Brink et al. (2009) found 3.8 $\mu g\,C\,cm^{-2}$ adsorbed in Whatman quartz field blanks on average (although higher concentrations were recorded for a few field blanks), regardless of the type of environment (rural-traffic-urban). Maenhaut et al. (2006) found high blank OC concentrations, even exceeding some sample concentrations, and negligible EC concentrations in a set of field blank pre-fired Whatman quartz fiber filters. This adsorption was found to be seasonally dependent. Also in later studies, similar high OC field blank values were observed ($\sim 4\,\mu g\,cm^{-2}$), but the values did not depend on the site nor on the season (Maenhaut and Claeys, 2011, 2012).

The seasonality found for the field blanks (pre-fired Whatman quartz fiber filters) by Maenhaut et al. (2006) contrasts with a number of studies in the USA, which found that trip and field blanks have similar loadings that may vary significantly depending on sampler type but do not vary significantly by season, ambient temperature, or location (Solomon et al., 2000: no information about the brand; Flanagan et al., 2002: no information about the brand; Maimone et al., 2011: pallflex and whatman quartz fiber filters). The similarity between trip and field blanks and across seasons in the US studies suggests that the mounting process and short ambient exposure contribute little to the blank filter loadings. The differences in blank concentrations depending on the sampler can be attributed to the differences in the cassettes used for transport, which are sampler-specific, made up of different materials, and occasionally containing grease (Solomon et al., 2000; Flanagan el al., 2002; Maimone et al., 2011).

To minimize carbon adsorption, EMEP recommends storing pre-fired filters at −18 °C prior to being exposed and after exposure until they are analysed. Filters should be stored in petri dishes (e.g., Millipore/Whatman) or in pre-fired (< 500 °C for 3 h) aluminium foil (http://www.nilu.no/projects/ccc/manual/download/Protocol_EC_OC.doc). Other recommendations include the analysis of 2–3 blank filters from each box/batch and reject those boxes/batches with concentrations exceeding a specific value. Field blanks do not reflect the net artifact during sampling but they can be used to identify any problems related to transport and storage. The field blank values should not be subtracted from the sample OC concentrations as this may lead to overestimation or underestimation of the artifact-free particulate OC.

3.2 Sampling artifacts

Filters can take up volatile carbon and may lose collected semi-volatile compounds at the same time (Turpin et al., 2000). Under typical sampling conditions adsorption is the dominant artifact in the sampling of particulate OC, and longer sampling periods reduce the percentage of collected material that is adsorbed (Turpin and Huntzicker, 1994). In relative terms the positive artifact is generally most severe for samples with lowest OC loadings (Putaud and Cavalli, 2006). The adsorbed OC is distributed throughout the filter, as evidenced by visible darkening of the back side of the filter when it chars during heating in a non-oxidizing atmosphere (Chow et al., 2004). The methods available to minimise adsorption artifacts and to assess their magnitude are well described (ten Brink et al., 2004; Watson et al., 2007 and references therein) but are considered too elaborate for routine measurements in urban or regional background monitoring networks (ten Brink et al., 2009), even if configurations have been successfully tested (e.g.: within Aerosol, Clouds, and Trace Gases Research Infrastructure Network, ACTRIS, www.actris.eu).

The occurrence of positive and negative sampling artifacts depends on a number of factors:

- Sampling face velocity: The influence of OC sampling artifacts on quartz filters operated at 47 $\mathrm{cm\,s^{-1}}$ (case of the EU reference high-volume samplers operating at 30 $\mathrm{m^3\,h^{-1}}$ with 15 cm diameter filters) may be much lower than that for low-volume collectors, with usually lower face velocities (J.L. Besombes, personal communication). In the US, the Speciation Trends Network or Chemical Speciation Network (STN/CSN) carbon measurements aims to minimize artifacts by increasing the face velocity (e.g. from 23.7 to 107.2 $\mathrm{cm\,s^{-1}}$) via a higher flow rate (e.g. 22.8 lpm instead of 16.7 lpm) and a smaller deposit area (3.53 $\mathrm{cm^2}$ instead of 11.76 $\mathrm{cm^2}$). However, recommendations for a higher flow rate and a smaller deposit area ignore negative artifacts.

- Filter substrate: Filters manufactured by the same company but having different lot numbers exhibit variable adsorption capacity (Kirchstetter et al., 2001). Thus, a pair of front and back filter composed of filters from different lots may lead to significant under- or overestimation of particulate OC concentration. The use of the thinnest quartz fibre filters possible is recommended to minimise artifacts (Arp et al., 2007).

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- Sampling duration: The use of a back-up filter as a method to correct for the positive artifact (see explanation below) leads to under-correction if the sampling time is short (few hours) (Kirchstetter et al., 2001). The accuracy of the method improves with increased sampling time.
- Pre-firing of filters: Pre-firing the filters may increase their sorption capacity, and even make it irreproducible (Arp et al., 2007), therefore it is only recommended, provided it is not carried out at too high temperatures, if the blank filters contain too large amounts of OC (Arp et al., 2007; CEN/TR 16243, 2011).
- Aerosol type: The concentration of gases which can be adsorbed may be higher in urban than in non-urban environments (e.g., Watson et al., 2007). The oxidation of low-volatility hydrocarbons is a main channel for secondary aerosol formation. Fresh plumes may contain substantial amounts of semi-volatile organic compounds (SVOCs) in both gaseous and particle phases that come into equilibrium as the plumes age. In rural and remote atmospheres, many SVOCs will have evaporated or converted to more stable compounds. In this case, back-up filter OC may be similar to the OC field blank. Urban locations, on the contrary, experience more fresh emissions and with higher contributions from adsorbable vapors. These materials are more likely to be adsorbed when air is drawn through the filter than on the passive field blank (Watson et al., 2007). Eatough et al. (2003) evidenced that a substantial amount of back-up filter OC originates from positive artifacts when the contribution of biomass burning is important, in Utah (US).
- Ambient temperature: For studies at low or near-zero temperatures, the use of an upstream denuder to determine gaseous organic concentrations may lead to less artifacts than setups involving back-up filters and downstream sorbents (Arp et al., 2007). Due to the higher SVOC concentrations, higher positive artifacts are expected for sampling periods with high ambient temperature than for colder periods (Watson et al., 2007; Viana et al., 2006b).

Different approaches are used in research and in the networks to quantify and correct for the OC artifact, such as the use of back-up filters, parallel sampling trains, blank corrections, and denuders, among others. The amount of OC adsorbed onto a quartz filter can be determined by performing a double experiment with (a) a front quartz filter and a quartz back-up filter, and (b) a front Teflon filter and a quartz back-up filter. The determination of the OC concentrations in these filters allows for the calculation of the OC artifact (McDow and Huntzicker, 1990; Appel et al., 1983). Positive and negative sampling artifacts were quantified by numerous studies, for sites around the world, Table 4. The positive sampling artifacts ranged roughly between 10 and 50 % of OC, in the vast majority of studies. Conversely, negative artifacts were addressed by a very limited number of studies, which concluded that they may account for 5–6 or up to 50 % of the OC.

Sampling trains such as the one described by Cheng Y. et al. (2012) could be interesting for routine monitoring in networks, as the nitrate and OC can be measured by a single sampling channel if appropriate back-up sorbents are implemented. However, the accurate quantification of negative artifacts still remains a challenge. Chow et al. (2010) concluded that there is no simple way to correct for sampling artifacts using current measurements. In the US STN/CSN it is recommended to collect field blanks and back-up filters at the same frequency and passive deposit duration (e.g., once per month on an every-sixth-day sampling schedule; expose field blanks for a minimum of three days, Watson et al., 2007). Also Maimone et al. (2011) suggest, for relatively accurate, simple, and cost-effective artifact OC estimation in large networks, back-up filter sampling on at least 10 % of the sampling days at all sites with artifact correction on a sample-by-sample basis.

A number of authors suggest that further research is necessary on: sample duration for filter saturation of adsorbed gases; dependence of adsorbed gas saturation on particle composition, temperature, relative humidity, and sampling face velocity; evaporation rates of semi-volatile organic compounds during sampling; and source-specific tests (e.g., diesel, gasoline, and wood smoke) (Chow et al., 2010). More attention should be

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paid to semivolatile OC in the future, considering its secondary nature (Eatough et al., 2006; Modey et al., 2004), and its influence on regional haze (Long et al., 2005). The impact of OC negative sampling artifacts is still under-studied, especially in Europe, and remains a challenge.

3.3 Interference from other aerosol components

3.3.1 Carbonate carbon (CC)

The non-quantification of existing CC may significantly bias thermal OC and EC determination especially in certain areas (sites affected by construction works or resuspended road dust), and/or under specific meteorological conditions e.g., during desert dust intrusions. The decomposition temperature of carbonate may vary depending on a number of factors such as: the chemical composition of the carbonate compound (e.g., $CaCO_3$ vs. $CaMg(CO_3)_2$), the presence of other minerals (hematite), the crystal form (e.g. calcite vs. aragonite), the grain size and the temperature protocol used (Karanasiou et al., 2011). CC was reported to evolve during the maximum temperature step in He, i.e., between 700 and 850 °C (Karanasiou et al., 2011; Miyazaki et al., 2007; Birch and Cary, 1996) for a NIOSH-type protocol. Cavalli et al. (2010) demonstrated that natural calcite decomposes at 650 °C in the inert mode of the EUSAAR_2 protocol. When laboratory-grade calcium carbonate powder was analyzed by the IMPROVE protocol the evolved CO_2 was detected at the 550 °C set point (Chow et al., 2001). However, evolution temperatures may vary substantially depending on the mixture of CC with other materials; e.g., the presence of NaCl decreases the decomposition temperature of dolomite from 735 to 560 °C when pure dolomite was analysed by thermal analysis (Webb and Kruger, 1970).

The NIOSH 5040 method recommends fumigation of the aerosol samples with HCl prior to thermal-optical analysis to eliminate any interference of CC. However, fumigation with HCl causes losses of organic compounds like organic acids, induces intense charring phenomena and causes oven damage (Karanasiou et al., 2011; Cavalli et al., 2010). To calculate CC concentrations some researchers suggest manual integration of the sharp peak (if present) appearing in the last step of the inert mode of a NIOSH-like protocol (Miyazaki et al., 2007; Xu et al., 2004; Schauer et al., 2003; Birch and Cary, 1996; CEN/TR 16243, 2011). Jankowski et al. (2008) suggested a thermal treatment of aerosol loaded filters at 460 °C for 60 min in an O_2 atmosphere to remove OC and EC, and a subsequent determination of TC, which would be completely attributed to CC. Cavalli et al. (2010) also suggested a separate analysis for CC measurements, like the direct determination of the amount of CO_2 produced by acidifying the sample. Perrone et al. (2011) and Cuccia et al. (2011) used acid pretreatment and infrared spectroscopy measurements to identify CC presence in the sample and fitted a Gaussian function to the FID signal to determine CC, EC, and OC levels. Karanasiou et al. (2011) compared the HCl acidification method, the manual integration of the sharp peak appearing in the last step of the inert mode of a NIOSH-like protocol, and the acidification of the sample with phosphoric acid. The peak integration method provided higher CC concentrations than the acidification method (Karanasiou et al., 2011), and therefore the determination of CC with an independent method (e.g., by acidic decomposition of CO_3^{2-} and subsequent detection of CO_2) is recommended when other sample aliquots are available.

However, the overestimation of OC or EC due to CC interference might be negligible for fine particulate matter, since the contribution of CC in $PM_{2.5}$ is usually below 5 % of TC (Karanasiou et al., 2011; Querol et.al, 2004; Chow and Watson, 2002), but it could be significant if CC evolves with EC and for PM_{10} or coarse PM fractions.

3.3.2 Metal oxides

The presence of certain minerals in aerosol samples can complicate the optical correction for pyrolysis. Chow et al. (2001) and Fung et al. (2002) report that mineral oxides, like iron oxide might provide oxygen and oxidize some EC at high inert-mode temperatures. Mixtures of these minerals with carbonate such as calcite-hematite can decrease the decomposition temperature of pure calcite by 15 °C (Robles et al., 2011). For samples which contain large fractions of resuspended soil, demolition dust, desert dust or sites close to railways, trams and subways where a high content of Fe oxides is expected the split between OC and EC should be examined carefully (Chow et al., 2004; Querol et al., 2012).

3.3.3 Inorganic salts

The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants on the filters, or as part of the deposit material, has been shown to catalyze the removal of EC at lower temperatures (Lin and Friedlander, 1988). Such catalysis would affect the distribution of carbon peaks during the analysis.

In the study of Wang et al. (2010) metal salt particles generated in the laboratory, including alkali (NaCl, KCl, Na_2SO_4), alkaline-earth ($MgCl_2$, $CaCl_2$) and transition metal salts ($CuCl_2$, $FeCl_2$, $FeCl_3$, CuCl, $ZnCl_2$, $MnCl_2$, $CuSO_4$, $Fe_2\ (SO_4)_3$), were deposited on a layer of diesel particles to investigate their effect on EC and OC quantification with thermal-optical analysis using the NIOSH5040 protocol and the Sunset analyzer. The measurements showed that metal salts lowered the split time, reduced the oxidation temperature of EC and enhanced charring. The split point was more dependent on changes in EC oxidation temperature than it was on charring. The resulting EC/OC ratio was reduced by 0–80 % in the presence of most of the salts. Transition metals were more active than alkali and alkaline-earth metals; copper was the most active. Copper and iron chlorides were more active than sulfates. The melting point of metal salts was strongly correlated with the increase of OC charring, but not with the reduction of EC oxidation temperature. Hitzenberger et al. (2011) analysed mixtures of industrial carbon black (Elftex) and NaCl by thermal-optical analysis and concluded that Na lowers the combustion temperature of EC from 870 to approximately 800 °C. An older study by Novakov and Corrigan (1995) reported that high concentrations of the ions Na^+ and K^+ in biomass burning aerosol samples catalyze the combustion of EC material at lower temperatures.

Inorganic constituents that coexist with carbonaceous materials in ambient aerosol samples such as $(NH_4)_2SO_4$ and NH_4HSO_4 can enhance charring of insoluble OC (Yu et al., 2002). Moreover, the presence of oxygen in $(NH_4)_2SO_4$ could falsify the OC and EC concentrations (if charring correction is wrong) by releasing oxygen in the pure He mode and therefore allowing some of the EC to evolve in the inert mode (Hitzenberger et al., 2011).

3.3.4 Brown carbon

Light-absorbing organic matter in atmospheric aerosols of various origins, e.g., soil humic acids, humic-like substances (HULIS), tarry materials from combustion, bioaerosols, biomass burning aerosols often referred to as “Brown carbon”, BrC also interferes in thermal-optical analysis (Saleh et al., 2013; Andreae and Gelencser, 2006). The light absorption coefficient of these substances increases strongly from long to short wavelengths, resulting in their brown appearance. The presence of significant concentrations of BrC in atmospheric aerosol may cause substantial bias resulting in erroneous OC and EC concentration values. Indeed, BrC can affect the laser correction, causing changes in reflectance or transmittance as these compounds are removed.

The spectral absorption of BrC differs from that of EC. At the red wavelength of the HeNe laser used in thermal-optical instruments (DRI analyzer, Sunset analyzer), BrC absorbs much less than EC, so that the BrC fraction impacts the determination at this wavelength less than at potential lower wavelengths (Chen et al., 2015). BrC is prone to charring during the analysis and, as a result, the instrument will interpret the fraction of BrC combusted before the split point as OC, and the more refractory part of BrC will be wrongly attributed to EC, given the limitations of the charring optical correction. Monitoring the transmittance or reflectance at multiple wavelengths, analyzing the time evolution of charring and the comparison of different determined split time values may allow a more accurate separation of the EC contained in the sample and the PC generated during the analysis (Chen et al., 2015).

Reisinger et al. (2008) reported that the discrepancy in EC values between different thermal protocols is linked to the percentage of BrC in total LAC. Another effect of BrC

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is that compounds from this family can increase substantially PC generated during the analysis. This can erroneously be classified as EC and therefore lead to an overestimation of EC and underestimation of OC (Hitzenberger et al., 2011) if charring is not correctly accounted for. A NIOSH-like protocol with transmittance correction attributes more of the char and the BrC to OC than IMPROVE-TOR does, which may attribute these components more to EC (Soto-Garcia et al., 2011).

4 Reference materials for OC and EC determination by thermal-optical analysis

In May 2000, the Steering Committee for Black Carbon Reference Materials (http://www.geo.uzh.ch/en/units/physische-geographie-boden-biogeographie/services/black-carbon-reference-materials) defined reference materials for BC as those being: (1) generally available, (2) homogeneous, (3) stable over a long period of time, (4) inexpensive to obtain, and (5) representing natural samples. As discussed by Baumgardner et al. (2012) and Chai et al. (2012), at present there are no materials that have been shown to meet either these nor the ISO or NIST definitions for reference material (RM) or certified reference material (CRM), for soot properties. There are, however, numerous techniques for producing soot particles that might meet the requirements for a standard reference material (SRM). Some of these techniques use methods to continuously produce soot particles while other methods fabricate soot particles, put them in a liquid suspension and bottled them for application on filters or nebulization (Baumgardner et al., 2012). Many of these types of particles are not soot, because they are not produced from combustion; however, they have some characteristics of soot that can be used to test a sensor in an instrument.

A number of potential SRM candidates for thermal-optical analysis, TOA have been introduced in recent years (Iskandar et al., 2001; Lee et al., 2007; Master, 1991; Yang and Yu, 2002; Chen et al., 2004; Klouda et al., 2005); however, none have been accepted as a standard. For example, a filter-based NIST standard, reference material 8785, was developed with the intent of calibrating TOA methods. This RM was pro-

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duced by resuspending urban dust (NIST standard 1649a) and collecting the sample on quartz fibre filters (Klouda et al., 2005). The results for TC agreed quite well with the reference material, but the measured fraction of OC differed by more than 60 % (Klouda et al., 2005). Another material tested, in this case for soot, is diffusion flame soot (Kirchstetter and Novakov, 2007; Stipte et al., 2005) produced by burning methane in an inverted flow reactor (CAST soot generator, http://www.sootgenerator.com/). Another source of reference particles is the Palas GFG spark discharge aerosol generator (Roth et al., 2004). It produces a constant, reproducible particle size and concentration and has been widely used for studies of soot microstructure, composition, reactivity and oxidation, although it is not a combustion aerosol. It is used, in context with the comparison to an inert graphitic soot, to represent the full range of oxidative reactivity (Schmid et al., 2011). Also, NIST has issued the world's first RM for single-wall carbon nano-tube soot, and the performance of single-wall carbon nano-tube analysis by TOA techniques has already been tested (John et al., 2012).

A recent development (Popovicheva et al., 2011) is the creation of tailored soot whereby graphitized thermal soot is precisely coated with a known amount of organics, aimed at representing atmospheric EC and OC. With this approach, the EC/OC ratio was expected to be controlled such that TOA techniques would be evaluated. It should be noted, however, that one requirement for reference materials is that they are representative of the parameter they intend to provide a reference for, and in the case of OC and EC this implies that the EC and the OC/EC ratio of such a material should resemble the EC and the OC/EC ratio of ambient aerosol, as should its refractivity. These tailored materials do not yet meet this requirement because the EC in these materials evolves at a much higher temperature (> 800 °C) than ambient EC. Also the organic coatings tested so far do not resemble ambient aerosols (the coatings were initially selected to show minimum charring). Finally, Chai et al. (2012) describe a relatively simple approach for collection of a matched OC-EC filter set, based on aerosolization of an aqueous OC solution and EC suspension, to be used in inter-comparison and round robin tests.

One final limitation is the analytical procedure: any of the candidate RMs must be homogeneously deposited on clean filters with a well-known mass within the appropriate concentration range for each instrument to avoid saturation, to facilitate quantification of OC and EC and thus calibrate the separation between OC and EC. It is important that the method of application, i.e., how the RM is introduced to the measurement system, does not affect the response of the TOA to the SRM and that the method of application is a part of the SRM protocol. In addition, if the EC/OC fraction is to be determined, then this parameter must be fully characterized for the selected SRM and remain constant with time.

In sum, several materials have been tested in the past, although none have yet fulfilled the criteria to be considered eligible reference materials for soot or for OC and EC by TOA techniques.

5 Intercomparison of thermal-optical analysis methods

Various methods and laboratories usually agree well on the TC content, but large discrepancies have been found for the OC and EC concentrations (e.g.: Reisinger et al., 2008; Sciare et al., 2008; Maenhaut et al., 2009). These discrepancies are relatively more pronounced for EC due to its lower concentrations compared to OC. The differences observed among various methods are mostly reported as differences in EC concentrations and/or EC/TC ratios. As the thermal–optical methods mainly differ in the temperature protocol and charring correction approach we focus on NIOSH-like, IMPROVE_A and EUSAAR_2 protocols and on transmittance vs. reflectance based correction for charring.

5.1 Comparison of TOT and TOR

Many studies have investigated the effect of the optical correction on the OC and EC concentrations and they have all concluded that the EC values determined us-

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ing a thermal-optical transmittance (TOT) method are 30–70 % lower than those determined using a thermal-optical reflectance (TOR) method (Chow et al., 2001, 2004, 2009; Subramanian et al., 2006; Cheng et al., 2010, 2011; Soto-Garcia et al., 2011; Maenhaut et al., 2012; Chiappini et al., 2014) adsorbed througout the filter.

Table 5 provides the slope of the linear regression between EC concentrations determined using TOR and those using TOT when the same protocol is used.

Most studies found a slope of ~ 2 when they compared TOR EC with TOT EC using the IMPROVE (Chow et al., 2001; Subramanian et al., 2006) and IMPROVE_A (Cheng et al., 2010, 2011; Soto-Garcia et al., 2011) protocols. Chow et al. (2009) found a lower slope (1.2) with the IMPROVE protocol, and Wu et al. (2012) found larger differences (slope up to 3.4) using both IMPROVE_A and ACE-Asia protocols for urban samples in China.

Chow et al. (2004) compared the EC obtained from TOR and TOT with 2 temperature protocols, namely highT protocol with Tmax at 900 °C and LowT protocol with Tmax set at 550 °C. On average, TOT resulted in ~ 30 % lower EC than TOR for the LowT protocol and ~ 70 % lower EC for the HighT protocol. The same was also shown by comparing TOT EC and TOR EC using both EUSAAR_2 and NIOSH-900 protocols (Maenhaut et al., 2012). The difference between TOR EC and TOT EC was smaller for EUSAAR_2.

Chiappini et al. (2014) observed the largest differences between the TOT and TOR results for rural samples using the NIOSH-850 protocol (slope = 2.1). These differences may be explained by the aerosol chemical composition or its mixing state, which can be rather different between urban and rural sites as the latter ones could be much more influenced by light-absorbing organic material (e.g.: particles emitted by biomass burning processes).

The reason for the difference between TOT and TOR has been further investigated by examining charring of the filter backside and microscopic cross sections of a filter punch at different parts of the temperature cycle during the thermal analysis. It appeared that reflectance was dominated by charring of OC that co-existed with EC on the surface of the filter, while transmittance was dominated by the charring of organic vapours distributed throughout the filter. When oxygen was added to the analysis, the surface original EC and PC evolved before the charred OC that was distributed throughout the filter. Hence, transmittance achieved its initial value later than reflectance (Chow et al., 2004). Using a radiative transfer model, Chen et al. (2004) showed that this explanation is plausible, and that simultaneous reflectance and transmittance measurements can be used to estimate contributions to charring from the surface particulate OC and the charred vapours adsorbed throughout the filter.

5.2 Comparison of IMPROVE, NIOSH-like and EUSAAR_2 protocols

Table 6 summarizes the studies conducted on the comparison of thermal protocols and provides information on the test samples, analyzer used, optical correction method, protocols compared and the slope of the linear regression between the EC values obtained with two different protocols.

In the study of Chow et al. (2001) the NIOSH-850 EC was typically less than half of the IMPROVE EC. The difference was significantly higher for some specific source samples, such as cooking emission samples. By studying the increase of the light transmission and reflectance in the NIOSH protocol during the last temperature step in the He mode they concluded that the carbon fraction evolving at 850 °C in the He mode should be classified as EC rather than OC. When this portion of NIOSH OC was added to the NIOSH EC, the IMPROVE and NIOSH analyses were in good agreement.

Schauer et al. (2003) compared four thermal protocols that had the same temperature program in the oxidizing mode but different temperature steps and peak temperature in the inert mode. They tested the ACE-Asia, a NIOSH-like protocol with Tmax at 870 °C and the protocols He-750, He-650 and He-550 with Tmax equal to 750, 650, and 550 °C, respectively, with the latter being similar to the IMPROVE protocol. Light transmittance was used for charring correction. They concluded that He-550 EC is about 1.5 times higher than NIOSH-like EC for urban samples. The same slope (~ 1.5) was observed in the study of Subramanian et al. (2006) again for urban samples.

Many other studies report slopes in the range 1.2–2 when they compared a protocol with a low peak inert temperature (550–580 °C) like IMPROVE or IMPROVE_A with a NIOSH-like protocol with the peak inert temperature at 800–900 °C (Sciare et al., 2008; Reisinger et al., 2008; Chow et al., 2009; Maenhaut et al., 2009; Cheng et al., 2010, 2012, 2014; Piazzalunga et al., 2011; Zhi et al., 2011; Khan et al., 2012).

Only one study, Sharma et al. (2002) contradicts the general conclusion that IMPROVE EC is higher than the NIOSH EC. In that study, urban, suburban, rural and remote samples were tested and the NIOSH-like EC (TOT) was found to be slightly higher than the IMPROVE EC (TOR) (slope = 0.92).

The EUSAAR_2 protocol was more recently developed, with consequently fewer comparison studies. Maenhaut et al. (2012) compared EUSAAR_2 with a NIOSH-900 protocol (with the peak inert temperature set at 900 °C) against a batch of 70 PM_{10} samples collected at various sites in Belgium. A very good agreement was observed for TC (slope = 1.02, $R^2 = 0.99$). However, the slope between EUSAAR_2 EC and NIOSH EC when transmittance correction was used was 1.3 ($R^2 = 0.96$). When reflectance was used the slope was equal to 1.1 with $R^2 = 0.95$ (Maenhaut et al., 2012).

Cheng et al. (2014) concluded that the OC and EC results were more equivalent between IMPROVE_A and EUSAAR_2 than between IMPROVE_A and NIOSH-870. EC IMPROVE_ A vs. EC EUSAAR_2 had a slope of 0.9. Similarly a study conducted in Milan, Italy, showed that the slope of EC IMPROVE to EC EUSAAR_2 was about 1.1 while the slope between EC EUSAAR_2 and EC NIOSH-870 was 1.5 (Piazzalunga et al., 2011) consistent with the results of Schauer et al. (2003) when comparing a protocol with Tmax at 650 °C as in EUSAAR_2 and the ACE-Asia protocol.

The differences between thermal optical methods are higher when different optical correction methods are compared simultaneously; e.g., Chow et al. (2001, 2004), Soto-Garcia et al. (2011) and Cheng W. et al. (2012) observed that the IMPROVE EC (TOR) is higher than the NIOSH EC (TOT) (slope > 2.0). Wu et al. (2012) found that EC concentrations by the IMPROVE TOR method were on average 5.4 times higher than those by the ACE-Asia TOT protocol using the Sunset analyzer. The inconsistency in EC values by the two protocols was found to be more prominent in samples that produced more charring during the analysis, such as samples influenced by wood burning.

Nevertheless, no equivalence or correlation between the different thermal-optical protocols can be expected taking into account the variance in OC/EC composition and the influence of various salts, metals and metal oxides on the OC/EC split point. The general conclusion from the inter-comparison of thermal-optical protocols is that the identification of the “best” method is not possible so far. However it is evident that protocols with a rather low peak temperature in the inert mode like EUSAAR_2 and IMPROVE_A generally classify more carbon as EC compared to NIOSH-like protocols. OC and EC concentrations are more equivalent between IMPROVE_A and EUSAAR_2 than between IMPROVE_A and NIOSH protocols. This difference seems to be reduced when reflectance monitoring is used for charring correction. Moreover, the comparability of various methods also depends on the composition of the aerosol samples: samples highly influenced by biomass burning emissions display higher discrepancies when analyzed by different protocols.

6 Inter-laboratory comparison studies

Several inter-laboratory comparisons have been carried out over the years with the objective to evaluate the comparability of the results produced by the participants. Many studies include comparisons of laboratories using different methods, even with and without optical correction for charring, hence making difficult the identification of the variation due to the method and that due to the laboratories themselves. Different inter-comparison studies analyze and report the results in a different manner. As for the parameters reported, most of the studies report the TC, EC and OC filter loadings in $\mu g\,cm^{-2}$, others do so in equivalent ambient concentrations in $\mu g\,m^{-3}$, and others report the EC/TC ratio together with the TC loadings in $\mu g\,cm^{-2}$.

The agreement between laboratories was relatively poor when only thermal methods were used, and it improved when optical correction was applied (Birch, 1998; Schmid et al., 2001; EUSAAR, 2011). EC concentrations determined with a method without optical correction were overestimated compared to IMPROVE_A and EUSAAR_2 results (EUSAAR, 2011).

Table 7 shows the inter-laboratory studies using thermal-optical methods. Results are given as relative standard deviation of EC, OC and TC concentrations including, when available, the range of concentrations tested. When the relative standard deviation was not reported, and could not be calculated from the reported data, other statistics have been reported, such as the reproducibility. As for the intercomparison of thermal–optical methods, most of these studies have been conducted without any calibration of the temperature probe, which could partly be responsible for the discrepancies listed below.

Birch (1998) reported relative standard deviation for OC of 3 to 7, and 6 to 26 % for EC between 5 laboratories using a TOT method for a subset of 5 samples, and after excluding a sixth laboratory leading to a relative standard deviation for EC of 144 %. Schmid et al. (2001) reported relative standard deviation for TC from 6 to 7, and 26 to 48 % for EC concentrations for 5 laboratories.

An inter-laboratory comparison in which all the 3 participants used the NIOSH5040 method to analyze 50 samples showed relative standard deviations of 6, 12 and 10 % for TC, OC and EC, respectively (Birch et al., 1999; Birch, 2002).

Schauer et al. (2003) reported results from an inter-comparison of 8 different laboratories, all of them using a protocol similar to ACE-Asia, and used transmittance as a correction. The participants calibrated and operated their instruments following NIOSH guidelines. The ambient PM samples (including blanks) covered a wide range of concentrations, 0.4 to 25 $\mu g\,cm^{-2}$ of OC and 0.04 to 8.4 $\mu g\,cm^{-2}$ of EC. The relative standard deviation (excluding blanks) was 4 to 13 % for OC and 13 to 21 % for EC.

Chai et al. (2012) assessed the results of an inter-laboratory comparison with 7 participants using NIOSH-like protocols. The exact protocols were slightly different for different laboratories. Four sets of 10 to 12 filter samples were analyzed, which were considered to be equivalent and therefore reported together. Each laboratory analyzed between 2 and 12 punches of each set. The concentrations ranged between 8 to 14 µg cm^{-2} for EC, 10 to 17 µg cm^{-2} for OC, and 20 to 27 µg cm^{-2} for TC. The relative standard deviations were 7 to 9, 7 to 10, and 5 to 9 % for EC, OC, and TC, respectively.

Several inter-laboratory comparisons were carried out in the framework of the EUSAAR project. Different protocols were used by the participating laboratories: NIOSH, quartz, EUSAAR_1, EUSAAR_2, IMPROVE, and some customized protocols. The relative standard deviation for TC among the participating laboratories was 11 %, 17–20, 9 and 10 % for four different exercises (EUSAAR, 2007, 2008, 2010 and 2011). However, unacceptable differences were observed for samples with particularly low TC (< 5 µg cm^{-2}) (EUSAAR, 2007), or even for samples with high TC content (> 10 µg cm^{-2}) (EUSAAR, 2010). The variation for the EC concentrations was much higher (40 or 25 % including all laboratories and methods) (EUSAAR, 2007 and 2011), and it was protocol-dependent. The relative standard deviation was 29 % for laboratories using NIOSH or quartz protocols (EUSAAR, 2007) and 48 % for laboratories using the NIOSH protocol (EUSAAR, 2008), with differences up to a factor of 14 between two participants (EUSAAR, 2010), whereas it was reduced to 13 % for 2 laboratories using the EUSAAR_1 protocol (EUSAAR, 2007), and 30–36 % or 20 % for laboratories using the EUSAAR_2 protocol after removing the outliers (EUSAAR, 2008 and 2010). The differences among laboratories were found to be higher for the lowest loaded filters (EUSAAR, 2011).

An intercomparison study based on the reference material NIST 8785 with 12 laboratories using the EUSAAR_2 protocol found a relative standard deviation of the EC/TC ratio of 17 % (EUSAAR, 2009).

The differences in the EC/TC ratios were systematic and laboratory-dependent, i.e., each laboratory deviated from the average EC/TC ratio similarly for the different intercomparison exercises (EUSAAR, 2008, 2009 and 2010). The discrepancies may be related to the correction of the laser drift with temperature and/or to the inaccuracy of the temperature experienced by the filter with respect to the set temperature in the He-mode.

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An inter-laboratory comparison performed within the ACTRIS project with 18 participants applying thermal or thermal-optical methods (NIOSH-like or EUSAAR_2) to ambient PM samples reported reproducibility relative standard deviations from 13 to 27 % (ACTRIS, 2011) and 9 to 23 % when only laboratories using the EUSAAR_2 protocol were assessed. For the EC/TC ratio, the reproducibility relative standard deviations ranged from 12 to 33 %, including all the optical correction methods, and 10 to 29 % when only laboratories using the EUSAAR_2 protocol were assessed, after excluding one sample with EC/TC ratio below 0.05.

Two inter-laboratory comparison exercises were carried out between European Union National Reference Laboratories for air quality or delegated organizations, organized by JRC-IES European Reference Laboratory for Air Pollution (ERLAP). All the participants used the Sunset analyzer and used either NIOSH or EUSAAR_2 protocols. The first exercise (Emblico et al., 2012) involved 16 participants (two of them using the field version of the instrument). The laboratories using field versions of the analyzer gave results classified as outliers, in comparison with the rest of the values. Better reproducibility was found for TC (from 4 to 8 %) than for OC (5 to 12 %) and EC (10 to 25 %), and it was not shown to be protocol-dependent. The second exercise (Cavalli et al., 2012) involved 17 participants and reported reproducibility standard deviations for TC of 5 to 11 %. For the EC/TC ratio, the reproducibility standard deviations ranged from 8 to 35 % for the NIOSH-like protocol, and from 4 to 19 %, for the EUSAAR_2 protocol. The poorer reproducibility found for the NIOSH users could be partly caused by the number of variations of the NIOSH protocol used in this exercise in comparison to the single version of the EUSAAR_2 protocol.

Chiappini et al. (2014) report the results of an intercomparison study between 5 laboratories. Four laboratories used the Sunset analyser with transmittance correction (three of them employed the EUSAAR_2 protocol and one the NIOSH5040 protocol) while one laboratory used the DRI analyser with both transmittance and reflectance correction and the IMPROVE protocol. While there was good agreement on TC measurements (relative standard deviation < 5 %) the repeatability relative standard devi-

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ations ranged from 1 to 17 % for EC, and up to 9 % for OC. The differences observed between the laboratories for a given protocol were attributed to the lack of temperature offset calibration by the time of the analyses.

The department of Air Quality of Public Health Service Amsterdam organized a comparison exercise with 17 participating laboratories using an identical instrument set-up to analyze 5 filter samples and 2 sucrose solutions with both the EUSAAR_2 and the NIOSH-870 protocols. For the first time, a correction for temperature offsets was applied. Excluding 2 laboratories, the reproducibility relative standard deviations for TC were 15 % for EUSAAR_2 and 12 % for NIOSH-870; and for EC they were 20 % for EUSAAR_2 and 26 % for NIOSH-870. Poor performance or deviating results were shown not to be protocol-dependent. The analysis of sucrose solutions were used to identify wrong TC calibrations and deviating performance. The repeatability degree derived from analysis of known volume of sucrose solution depends on the analyst's performance, while it does not depend on the protocol used (Panteliadis et al., 2013 and 2015).

In sum, the inter-laboratory comparisons are better when all the laboratories use the same optical correction (either transmittance or reflectance) as opposed to mixed comparisons where different laboratories employ different corrections. The relative standard deviation for TC is lower than that for EC, OC or EC/TC regardless of the protocol used. The variations in the EC/TC ratios are often systematic and laboratory-dependent. The results from field instruments used off-line were difficult to assess, given that some studies showed a poor agreement between this type of instruments and the remainder of the participants, although some other studies showed a good agreement. The results of the intercomparisons did not improve over time, which implies the necessity of establishing a well-defined method to perform such measurements, including quality-control guidelines.

7 Conclusions

The thermal-optical analysis is currently considered by the European Committee standardization body (CEN) as the reference methodology to quantify atmospheric particulate EC and OC deposited on filters. The most commonly used thermal protocols include NIOSH-like, IMPROVE_ A and EUSAAR_2 protocols either with transmittance or reflectance correction. The review of the literature pointed out that it is not possible to identify the "best" thermal-optical method.

- All thermal evolution protocols are comparable for TC concentrations but the results vary significantly concerning OC and especially EC concentrations, due to the optical correction for charring which is not robust enough.
- Thermal protocols with a rather low peak temperature in the inert mode like IMPROVE_A and EUSAAR_2 generally tend to classify more carbon as EC compared to NIOSH-like protocols.
- The comparability of the various protocols also depends on the composition of aerosol samples. Samples highly influenced by biomass burning emissions display higher discrepancies in OC and EC determination when analyzed by different protocols.
- Comparing the optical correction methods, the difference between reflectance and transmittance tends to be larger than the difference between different thermal protocols. In addition, the comparability of thermal protocols seems to improve when reflectance is used as a charring correction method.
- OC and EC results are more comparable between IMPROVE_A and EUSAAR_2 than between IMPROVE_A and NIOSH.
- CC interference might be negligible for fine aerosol, but it can be significant for coarse OC or EC concentrations. For samples containing large fractions of resus-

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pended soil, demolition dust or African dust the interference from CC should be tested and the split between OC and EC should be examined carefully.

- The occurrence of brown carbon and other inorganic components such as oxides and salts in atmospheric aerosol samples may enhance charring and lead to erroneous determinations of OC and EC.
- Positive sampling artifact due to the adsorption of gaseous organics onto the filter is likely to be significant at remote sites, consequently affecting the OC/EC ratio. The positive artifact could be reduced by using samplers with high face velocity or implementing denuders while the use of back-up filters can provide reasonable measurement of this positive artifact. However the use of denuders and back-up filters to quantify possible artifacts are not seen as suitable and necessary for routine network monitoring.

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Table 1. Summary of thermal-optical protocols (updated from Watson et al., 2005).

Protocol	Carrier gas OC	Temperature steps OC, ˚C	Time, s for OC	Carrier gas EC	Temperature steps EC, ˚C	Time, s for EC	Correction	Detector	Reference
OGI	He	600	Varies	98 %He 2 %O$_2$	400, 450, 600	100, 120, > 200	Reflectance	FID/CH$_4$	Huntzicker et al. (1982)
IMPROVE	He	120, 250, 450, 550	150–580[a]	98 %He 2 %O$_2$	550, 700, 800	150–580[a]	Reflectance	FID/CH$_4$	Chow et al. (1993, 2001, 2004)
NIOSH5040	He	250, 500, 650, 850	60, 60, 60,90	98 %He 2 %O$_2$	650, 750, 860, 940	30, 30, 30, > 120	Transmittance	FID/CH$_4$	NIOSH, (1996); Birch (1998)
CalTech	He	310, 450, 575, 870	60, 60, 60, 90	90 %He 2 %O$_2$	550, 625, 700, 775, 850, 900	45, 45, 45, 45, 45, 120	Transmittance	FID/CH$_4$	Mader et al. (2001)
MSC1	He	250, 450, 550, 900	150, 150, 180, 90	90 %He 10 %O$_2$	550, 700, 800	240, 210, 150	Transmittance	FID/CH$_4$	Sharma et al. (2002)
STN or EPA/NIOSH	He	310, 475, 615, 900	60, 60, 60, 90	98 %He 2 %O$_2$	600, 675, 750, 825, 920	45, 45, 45, 45, 120	Transmittance	FID/CH$_4$	Peterson and Richards (2002)
HKGL	He	350, 550, 850	70, 70, 110	95 %He 5 %O$_2$	550, 600, 700, 750, 800, 850	10, 50, 40, 30, 30, 70	Transmittance	FID/CH$_4$	Sin et al. (2002); Chow et al. (2005a)
HKUST-3	He	250, 500, 650, 850	150, 150, 150, 150	99 %He 1 %O$_2$	650, 750, 850, 890	150, 150, 150, 150	Transmittance	FID/CH$_4$	Yang and Yu (2002); Yu et al. (2002)
RU/OGI	He	stepwise to 700	NA	90 %He 2 %O$_2$	stepwise to 700	NA	Transmittance	FID/CH$_4$	Lim et al. (2003)
ACE-Asia[b]	He	340, 500, 615, 870, oven off	60, 60, 60, 90, 45	98 %He 2 %O$_2$	550, 625, 700, 775, 850, 900	45, 45, 45, 45, 45, 120	Transmittance	FID/CH$_4$	Schauer et al. (2003)
IMPROVE-like	He	120, 250, 450, 550, oven off	60, 60, 60, 90, 45	98 %He 2 %O$_2$	550, 625, 700, 775, 850, 900	45, 45, 45, 45, 45, 120	Transmittance	FID/CH$_4$	Schauer et al. (2003)
IMPROVE_A	He	140, 280, 480, 580	150–580[a]	98 %He 2 %O$_2$	580, 740, 840	150–580[a]	Reflectance	FID/CH$_4$	Chow et al. (2007)
NIST-EPA	He	200, 400, 600, 785, 550	60, 60, 60, 150, 60	98 %He 2 %O$_2$	620, 690, 760, 830, 900	60, 60, 60, 45, 90	Transmittance	FID/CH$_4$	Conny (2007)
Quartz.par	He	220, 360, 525, 850	60, 60, 60, 90	98 %He 2 %O$_2$	550, 650, 720, 790, 820, 860, 890	30, 30, 30, 40, 30, 20, 40	Transmittance	FID/CH$_4$	Yttri et al. (2009)
Quartz	He	310, 475, 615, 870, oven off	70–80, 60, 60, 90–105, 45	98 %He 2 %O$_2$	525–550, 625, 700, 775–850, 870–890	45–60, 45–60, 45–60, 60, 90	Transmittance	FID/CH$_4$	Quincey et al. (2009); Querol et al. (2013)
EUSAAR_1	He	200, 300, 450, 650	120, 150, 180, 180	98 %He 2 %O$_2$	550, 850	240, 150	Transmittance	FID/CH$_4$	EUSAAR (2007)
EUSAAR_2	He	200, 300, 450, 650	120, 150, 180, 180	98 %He 2 %O$_2$	500, 550, 700, 850	120, 120, 70, 80	Transmittance	FID/CH$_4$	Cavalli et al. (2010)

[a] Advance from one temperature to the next one when a well-defined carbon peak has evolved.

[b] NIOSH-like protocol used for the laboratory intercomparison in the ACE-Asia project.

Table 2. Analytical characteristics of the most commonly used thermal-optical protocols.

Protocol	Aerosol type	Operational range, $\mu g\,C\,cm^{-2}$	Limit of detection, $\mu g\,C\,cm^{-2}$	Accuracy, %	Precision, $\mu g\,C\,cm^{-2}$
NIOSH5040	Diesel exhaust	0.7–70	0.15	±16.7 (at $23\,\mu g\,C\,cm^{-3}$)	±0.13 for loadings of $0.67\,\mu g\,C\,cm^{-2}$ ±0.007 for loadings $6.67–48\,\mu g\,C\,cm^{-2}$
IMPROVE_A	IMPROVE network	0.2–750	0.2	< 10 (TC accuracy)	±0.5 for loadings < $10\,\mu g\,C\,cm^{-2}$ ±0.03 for loadings > $10\,\mu g\,C\,cm^{-2}$
EUSAAR_2	EMEP network	5–62	–	2–7 uncertainty for EC	–

Table 3. Average concentration and standard deviation (SD) of OC (in µg cm^{-2}) in blank quartz filters. All filters are 47 mm diameter, except those marked with [a], which had a diameter of 150 mm.

N	OC				Pre-firing Filter	
	µg cm^{-2}	SD	T	Time	Brand and Type	Reference
73	0.062	0.064	900	3 h	Pall 2500 QAT UP	Flanagan et al. (2002)
72	0.148	0.095	900	3 h	Pall 2500 QAT UP	Flanagan et al. (2002)
55	0.126	0.106	900	3 h	Pall 2500 QAT UP	Flanagan et al. (2002)
73	0.130	0.095	900	3 h	Pall 2500 QAT UP	Flanagan et al. (2002)
78	0.121	0.096	900	3 h	Pall 2500 QAT UP	Flanagan et al. (2002)
–	0.15	0.15	900	3 h	Pall 2500 QAT UP	Chow et al. (2010)
–	0.1	0.15	900	3 h	Whatman QM-A	Chow et al. (2010)
8	0.1	0.09	650	4 h	Pall 2500 QAT UP	Olson and Norris (2005)
14	0.45		550	24 h	Pall 2500 QAT UP	Cheng et al. (2009a).
9	0.22	0.11	600	2 h	Pall 2500 QAT UP	Chai et al. (2012)
9	0.38	0.06	NO		Pall 2500 QAT UP	Chai et al. (2012)
	2.4		NO		Whatman QM-A	ten Brink et al. (2009)
128	0.797	0.395	200		Pall 2500 QAT UP[a]	IDAEA CSIC
127	1.22	1.11	NO		Whatman QM H[a]	IDAEA CSIC

Table 4. Summary of the results regarding the quantification of positive and negative sampling artifacts from the studies found in the course of this literature review.

Location	Negative artifact	Positive artifact	Comments	Reference
California	50 % of OC		Positive artifact underestimated by 3.7 % due to lack of gas-phase equilibrium	Appel et al. (1983)
Portland, Oregon (USA)		20–50 % of OC		McDow & Huntzicker (1990)
4 US sites (Portland, Glendora, Meadview, LookRock)		10–55 % of OC		Turpin et al. (2000)
ACE-Asia campaign		20–100 % of OC		Mader et al. (2003)
Tokyo (Japan)		30 % of TC		Matsumoto et al. (2003)
Vancouver (Canada)		18–37 % of OC	18 % during night, 37 % during day	Fan et al. (2004)
Budapest (Hungary)		10 ± 16 % of PM_{10}		Salma et al. (2004)
Pittsburg, Pennsylvania (USA)	< 10 % of OC with denuder	$0.5\,\mu g\,m^{-3}$ without denuder	Constant positive artifact regardless of the season	Subramanian et al. (2004)
Ghent (Belgium)		10–20 % of $PM_{2.5}$	Resulting from positive artifacts, both organic and inorganic	Viana et al. (2006a)
Barcelona (Spain)		11–16 % of OC	Sampling artifacts for OC were slightly higher in summer.	Viana et al. (2006b)
Barcelona (Spain)		3 % of $PM_{2.5}$		Viana et al. (2006b)
Budapest (Hungary)		28 % of WSOC		Salma et al. (2007)
Budapest (Hungary)		17 % of HULIS		Salma et al. (2007)
Budapest (Hungary)		17 % of OC		Salma et al. (2007)
Barcelona (Spain), Ghent (Belgium, Amsterdam (the Netherlands)		11–16 % of OC in Barcelona; 5–12 % of OC in Amsterdam; 5–7 % of OC in Ghent		Viana et al. (2007)
Barcelona (Spain), Ghent (Belgium, Amsterdam (the Netherlands)		1–3 % of $PM_{2.5}$	Impact on mean daily $PM_{2.5}$ mass concentrations	Viana et al. (2007)
IMPROVE, SEARCH and STN networks (USA)	50 % of OC	30–50 % of OC		Watson et al. (2007)

Table 4. Continued.

Location	Negative artifact	Positive artifact	Comments	Reference
IMPROVE, SEARCH and STN networks (USA)		21.7 % of $PM_{2.5}$		Watson et al. (2007)
Beijing (China)	6–50 % of OC			Cheng et al. (2009a)
Beijing (China)		10 % of OC	TOT-split-EC underestimated native EC by 21 and 28 %, for denuded and un-denuded samples, respectively.	Cheng et al. (2009b)
the Netherlands, national BOP programme		1 $\mu g\,m^{-3}$	The artifact was constant and thus independent of season and site.	ten Brink et al. (2009)
Milano (Italy)		23–39 % of OC	39 % in summer, 23 % in winter	Vecchi et al. (2009)
US networks IMPROVE, SEARCH and STN		5–30 % of OC		Chow et al. (2010)
Dar es Salaam (Tanzania)		1 to 9 %of $PM_{2.5}$ mass		Mkoma et al. (2010)
Dar es Salaam (Tanzania)		5–8 % of OC in $PM_{2.5}$	Little difference between dry and wet seasons	Mkoma et al. (2010)
Dar es Salaam (Tanzania)		6–7 % of OC in PM_{10}	Little difference between dry and wet seasons	Mkoma et al. (2010)
Ghent (Belgium)		6–19 % of OC in $PM_{2.}$	Without denuder	Mikuška et al. (2012)
Ghent (Belgium)	−4–7 % of OC in $PM_{2.}$		With denuder	Mikuška et al. (2012)
Europe (forested sites)		13–18 % of OC in $PM_{2.}$	Without denuder	Mikuška et al. (2012)
Europe (forested sites)	2–5 % of OC in $PM_{2.}$		With denuder	Mikuška et al. (2012)
EUSAAR sites (regional background)		14–70 % of TC	Without denuder	EUSAAR (2011)
EUSAAR sites (regional background)		1–21 % of TC	With denuder	EUSAAR (2011)
Ispra (Italy)	5.4±2.1 % of OC			EUSAAR (2011)
STN/IMPROVE, PAQS and RIOPA studies		15–34 % of OC	PAQS sites	Maimone et al. (2011)
STN/IMPROVE, PAQS and RIOPA studies		31–43 % of OC	RIOPA sites	Maimone et al. (2011)
Beijing (China)		15 % of OC		Cheng Y. et al. (2012)
Xueshan Tunnel (Taiwan)		48 % of $PM_{0.1}$		Zhu et al. (2012)

Table 5. Comparison of TOT and TOR. The slope of the linear regression between EC concentrations determined using TOR vs. those using TOR is given.

Site	Analyzer	IMPROVE_A (Tmax)	NIOSH (Tmax)	EUSAAR_2	slope TOR TOT	Reference
9 $PM_{2.5}$ non-urban samples, IMPROVE Network	DRI	IMPROVE (550 °C)	NIOSH (850 °C)		1.0–2.0 (IMPROVE) 1.0–3.5 (NIOSH)	Chow et al. (2001)
13 $PM_{2.5}$ urban samples, Mexico	DRI	IMPROVE (550 °C)	NIOSH (850 °C)		1.2–1.9 (IMPROVE) 1 (NIOSH)*	Chow et al. (2001)
30 $PM_{2.5}$ samples Fresno California, USA	DRI	LowT (550 °C)	HighT (800 °C)		1.4 (LowT) 2.5 (HighT)	Chow et al. (2004)
10 $PM_{2.5}$ Pittsburgh, USA	Sunset	He4–550 (550 °C)	He4–700 (700 °C)		1.9 (He4–550) 2.2 (He4–700)	Subramanian et al. (2006)
$PM_{2.5}$ Fresno California, USA	DRI	IMPROVE_A (580 °C)			1.2	Chow et al. (2009)
$PM_{2.5}$, Beijing, China	DRI	IMPROVE_A (580 °C)			1.8 (denuded samples) 1.9 (undenuded samples)	Cheng et al. (2010)
10 $PM_{2.5}$ Amazon Basin, Brasil	DRI	IMPROVE_A (580 °C)			2.0	Soto-Garcia et al. (2011)
$PM_{2.5}$, Beijing, China	DRI	IMPROVE_A (580 °C)			0.9–2.2	Cheng et al. (2011)
70 PM_{10} samples from Flanders, Belgium	Sunset		NIOSH (900 °C)	EUSAAR_2	1.5 (EUSAAR_2) 1.7 (NIOSH)	Maenhaut et al. (2012)
$PM_{2.5}$ urban samples China	Sunset	IMPROVE_A (580 °C)	ACE-Asia (870 °C)		3.4(IMPROVE_A) 3.1 (ACE-Asia)	Wu et al. (2012)
$PM_{2.5}$ urban samples China	DRI	IMPROVE_A (580 °C)	ACE-Asia (870 °C)		2.6(IMPROVE_A) 3.4 (ACE-Asia)	Wu et al. (2012)
245 PM_{10} urban samples France 128 PM_{10} and $PM_{2.5}$ urban and rural samples Belgium, 325 $PM_{2.5}$ rural samples, Ispra Italy	Sunset		NIOSH (850 °C)	EUSAAR_2	1.3 (EUSAAR_2) all samples 1.4 (EUSAAR_2) urban samples 1.8 (EUSAAR_2) rural samples 1.3 (NIOSH) all samples 1.2 (NIOSH) urban samples 2.1 (NIOSH) rural samples	Chiappini et al. (2014)

* The difference between NIOSH EC-TOR and EC-TOT was often zero because reflectance and transmittance returned to their initial values prior to the addition of oxygen for many of the samples during the 850 °C step of the analysis.

Table 6. Comparison of thermal-optical protocols. The slope of the regression of EC between two different protocols is given.

Site	Analyzer	Optical Correction	IMPROVE_A	NIOSH	EUSAAR_2	Slope EC	Reference
41 $PM_{2.5}$ IMPROVE, USA 19 source samples	DRI	Transmittance, Reflectance	IMPROVE (550 °C)	NIOSH (850 °C)		2.5 (IMPROVE TOR/NIOSH TOT)	Chow et al. (2001)
$PM_{2.5}$ Toronto, Canada	DRI, Sunset	Transmittance, Reflectance	IMPROVE (550 °C)	MSC1 (900 °C)		0.9 (IMPROVE TOR/MSC1 TOT)	Sharma et al. (2002)
$PM_{2.5}$ Bakersfield, St. Louis, USA and source samples	Sunset	Transmittance	He4-550	ACE-Asia (870 °C) He4-750	He4-650	1.5 (He4-550/ACE-Asia) 1.2 (He4-550/He4-750) 1.5 (He4-650/ACE-Asia) 2.2^a, 1.1^b, 1.0^c (He4-650/ACE-Asia)	Schauer et al. (2003)
30 $PM_{2.5}$ samples Fresno California, USA	DRI	Transmittance, Reflectance	LowT (550 °C)	HighT (800 °C)		1.0 (LowT TOR/HighT TOR) 2.2 (LowT TOT/HighT TOT) 3.5 (LowT TOR/HighT TOT)	Chow et al. (2004)
$PM_{2.5}$ samples Hong Kong, China	DRI, Sunset	Transmittance, Reflectance	IMPROVE_A (580 °C)	HKGL (850 °C) STN (900 °C)		1.3 (IMPROVE TOR/STN TOR) 1.4 (IMPROVE TOR/HKGL TOT) 0.8 (STN TOT/HKGL TOT)	Chow et al. (2005a)
$PM_{2.5}$ Pittsburgh, USA	Sunset	Transmittance, Reflectance	He4-550 (550 °C)	He4-700 (700 °C) He4-870 (870 °C)		1.5 (He4-550/He4-870) 1.5 (He4-550/He4-700) 1.3 (He4-700/He4-870)	Subramanian et al. (2006)
Crete, Greece	Sunset	Transmittance	IMPROVE (550 °C)	NIOSH (870 °C)		1.2 (He4-550/He4-870)	Sciare et al. (2008)
PM_{10} Vienna, Austria	Sunset	Transmittance	TOT-A3 (Improve -like (550 °C)	NIOSH (870 °C)		1.7 (TOT-A3/NIOSH TOT)	Reisinger et al. (2008)
TSP southern Austria	Sunset	Transmittance	TOT-A3 (Improve -like (550 °C))	NIOSH (900 °C)	EUSAAR_2	1.5 (TOT-A3/NIOSH TOT) 1.2 (EUSAAR_2/NIOSH TOT)	Maenhaut et al. (2009)
$PM_{2.5}$ Ghent, Belgium	Sunset	Transmittance	TOT-A3 (Improve -like (550 °C))	NIOSH (900 °C)	EUSAAR_2	1.7 (TOT-A3/NIOSH TOT) 1.7 (EUSAAR_2/NIOSH TOT)	Maenhaut et al. (2009)
$PM_{2.5}$ Amazon basin (dry season), Brazil	Sunset	Transmittance	TOT-A3 (Improve -like (550 °C))	NIOSH (900 °C)	EUSAAR_2	2.9 (TOT-A3/NIOSH TOT) 2.7 (EUSAAR_2/NIOSH TOT)	Maenhaut et al. (2009)
TSP Beijing, China	Sunset	Transmittance	TOT-A3 (Improve -like (550 °C))	NIOSH (900 °C)	EUSAAR_2	2.0 (TOT-A3/NIOSH TOT) 1.7 (EUSAAR_2/NIOSH TOT)	Maenhaut et al. (2009)
$PM_{2.5}$ Fresno California, USA	DRI/ Sunset	Transmittance, Reflectance	IMPROVE_A (580 °C)	STN (900 °C)		1.3 (IMPROVE_A TOR/STN TOT)	Chow et al. (2009)

Table 6. Continued.

Site	Analyzer	Optical Correction	IMPROVE_A	NIOSH	EUSAAR_2	Slope EC	Reference
$PM_{2.5}$, Beijing, China	DRI	Transmittance, Reflectance	IMPROVE_A (580 °C)	He4-800 (800 °C)		1.9, 2.0^{d} (IMPROVE_A/He4-800)	Cheng et al. (2010)
26 PM_{10} urban background, Milan, Italy	Sunset	Transmittance	IMPROVE_A (580 °C)	NIOSH (870 °C)	EUSAAR_2	1.5, 1.2^{e} (EUSAAR_2 TOT/NIOSH TOT) 1.6, 1.4^{e} (IMPROVE_A TOT/NIOSH TOT) 1.1, 1.1^{e} (IMPROVE_A TOT/EUSAAR_2 TOT)	Piazzalunga et al. (2011)
$PM_{2.5}$ Amazon Basin, Brasil	DRI, Sunset	Transmittance, Reflectance	IMPROVE_A (580 °C)	NIOSH		> 3 (IMPROVE_A/NIOSH)	Soto-Garcia et al. (2011)
urban and source samples from multiple sites, China	DRI, Sunset	Transmittance, Reflectance	IMPROVE_A (580 °C)	NIOSH (850 °C)		2 (IMPROVE_A TOR/NIOSH TOT)	Zhi et al. (2011)
$PM_{2.5}$ Beijing, China	DRI	Transmittance	IMPROVE_A (580 °C)	IMCAS (850 °C)	EU similar to EUSAAR_2 (650 °C)	2.0 (IMPROVE_A/IMCAS) 1.2 (IMPROVE_A/EUSAAR_2)	Cheng W. et al. (2012)
PM_{10} samples from 7 sites in Flanders, Belgium	Sunset	Transmittance, Reflectance		NIOSH (900 °C)	EUSAAR_2	1.3 (EUSAAR_2 TOT/NIOSH TOT)	Maenhaut et al. (2012)
$PM_{2.5}$ rural samples North Carolina USA, TSP Nairobi, Kenya diesel exhaust, cookstove samples	Sunset	Transmittance, Reflectance	IMPROVE (580 °C)	NIST-EPA (785 °C) NIOSH (870 °C)		1.3,^{f} 2.9^{g}, 1.5^{h}, 1.5^{i} (IMPROVE TOR/NIOSH TOT)	Khan et al. (2012)
$PM_{2.5}$ multiple sites, China	DRI, Sunset	Transmittance, Reflectance	IMPROVE_A (580 °C)	ACE-Asia (870 °C)		1.8,^{j} 1.7^{k} (IMPROVE TOR/ACE-Asia TOR) 1.6^{f}, 1.6^{h} (IMPROVE TOT/ACE-Asia TOT) 5.4^{j}, 4.3^{k} (IMPROVE TOR/ACE-Asia TOT)	Wu et al. (2012)
$PM_{2.5}$ Beijing, China	DRI, Sunset	Transmittance	IMPROVE_A (580 °C)	NIOSH (870 °C)	EUSAAR_2	1.3 (IMPROVE_A/NIOSH) 0.9 (IMPROVE_A/EUSAAR_2)	Cheng et al. (2014)

[a] Wood smoke samples.
[b] Coal fly ash samples.
[c] Carbon black samples.
[d] Calculated when denuders were used.
[e] Calculated after removal of water-soluble organic compounds, WSOC.
[f] TSP urban samples.
[g] $PM_{2.5}$ rural samples.
[h] Diesel exhaust samples.
[i] Cookstove samples.
[j] Calculated using the Sunset analyzer.
[k] Calculated using the DRI analyzer.
TOT: thermal-optical transmission.
TOR: thermal-optical reflectance.

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Table 7. Inter-laboratory comparisons using thermal-optical methods for the determination of EC, OC and TC concentrations. Number of laboratories participating, number of samples analyzed, protocols used, range of concentrations and relative standard deviation (RSD) for each carbonaceous fraction.

Study	n labs	n samples	Protocols	Range EC µg cm^{-2}	Range OC µg cm^{-2}	Range TC µg cm^{-2}	Range EC/TC	RSD EC (%)	RSD OC (%)	RSD TC (%)	RSD EC/TC (%)
Birch (1998)	5	5	NIOSH5040	0.3–16.1	10.4–139.8			6–26[a]	3–7		
Schmid et al. (2001)	5	3	TLT TOT TOR	21–518		32–150		26–48		6–7	
Birch (2002) Birch et al. (1999)	3	50	NIOSH5040					10	12	6	
Schauer et al. (2003)	8	11	ACE-ASIA modified	0.04–8.4	0.4–25	–		13–21[d]	4–13[e]	–	
EUSAAR (2007)	12[f] 10[g]	8[f] 7[g]	NIOSH quartz EUSAAR_1 IMPROVE others	2–9	3–60	3–75		40[h] 13[i] 29[j]	15	11	
EUSAAR (2008)	13[fk], 9[fl], 11[gk], 8[gl]	6	NIOSH EUSAAR_2	0.3–3		5–45	0.03–0.14			17[k] 20[l]	30[km] 36[lm] 48[n]
EUSAAR (2009)	12[k]	NIST8785	EUSAAR_2				0.45				17
EUSAAR (2010)	13[fk], 4[fo], 11[gk], 4[go]	8	quartz EUSAAR_2 EUSAAR_1 VDI 2465 others	0.9–4		10–52	0.05–0.15			9[p]	20[q]
EUSAAR (2011)	3	27 5 blks 4 NIST8785	EnvCan IMPROVE_A EUSAAR_2	< DL-1.5 µg m^{-3}		0.5–7 µg m^{-3}		25[b]		10[c]	

Table 7. Contiuned.

Study	n labs	n samples	Protocols	Range EC $\mu g\,cm^{-2}$	Range OC $\mu g\,cm^{-2}$	Range TC $\mu g\,cm^{-2}$	Range EC/TC	RSD EC (%)	RSD OC (%)	RSD TC (%)	RSD EC/TC (%)
ACTRIS (2011)	18	6	EUSAAR_2 quartz NIOSH			8.1–36.4	0.01–0.11			13–27[c]	12–33[c]
Chai et al. (2012)	7	4	NIOSH5040	8–14	10–17	20–27		7–9	7–10	5–9	
Emblico et al. (2012) (AQUILA, 1st interc.)	16, 6[m], 11[n]	14	EUSAAR_2 NIOSH (transmittance)	4–14[m] 3–9[n] (excl. blk)	1.4–65	1.5–76		10–25[m] 10–24[n]	5–11[mr] 4–9[nr]	4–7[s]	
Cavalli et al. (2012) (AQUILA, 2nd interc.)	17, 10[m], 7[n]	10	EUSAAR_2 NIOSH (transmittance, reflectance)			5–39	0.02–0.56[m] 0.05–0.45[n]			5–11[c]	4–19[cmt] 8–35[cnt]
Chiappini et al. (2014)	5	3, (N1, N2, N3)	NIOSH5040 EUSAAR_2 (transmittance, reflectance)	4.73–23.02	11.98–52.67	17.41–72.04	0.25–0.49	N1:6.8 N2:19.2 N3:10	9.6 9.1 4.8	6.9 4.6 3.2	9.7 20.3 10.1
Panteliadis et al. (2013) and 2015	17	5	EUSAAR_2 NIOSH-870	1–14		8–80		20[cm] 26[cn]		15[cm] 12[cn]	

[a] For samples with avg above 0.3 $\mu g\,cm^{-2}$ of EC.
[b] Random error.
[c] Reproducibility.
[d] For samples with avg above 0.15 $\mu g\,cm^{-2}$ of EC.
[e] For samples with avg above 1.0 $\mu g\,cm^{-2}$ of OC.
[f] For the TC results.
[g] For the EC, OC and EC/TC results.
[h] For the thermal-optical methods only.
[i] For the two labs using EUSAAR_1 only.
[j] For the labs using NIOSH or quartz only.
[k] EUSAAR partners only.
[l] EUSAAR associates only.
[m] EUSAAR_2 only.
[n] NIOSH-like only.
[o] EMEP laboratories only.
[p] 10 EUSAAR partners among 13, and 14 participants among 17.
[q] 6 EUSAAR partners among 11, 9 participants among 15, and 9 participants among 12 using EUSAAR_2.
[r] For samples with avg above 1.4 $\mu g\,cm^{-2}$ of OC.
[s] For samples with avg above 1.5 $\mu g\,cm^{-2}$ of TC.
[t] For samples with EC/TC avg above 0.10.
TLT: thermal method with linear T.
TOT: thermal-optical transmission.
TOR: thermal-optical reflectance.

Table A1. List of Acronyms and abbreviations.

BC	Black carbon
BrC	Brown carbon
CC	Carbonate carbon
CEN	European Committee for Standardization
DRI	Desert Research Institute
EC	Elemental carbon
EMEP	Convention on long-range transport of air pollutants
EUSAAR	European supersites for atmospheric aerosol research
FID	Flame ionization detector
IC	Inorganic carbon
IMPROVE	Interagency monitoring of protected visual environments
LAC	Light absorbing carbon
NIOSH	National institute of occupational safety and health
OC	Organic carbon
PC	Pyrolitic carbon
RSD	Relative standard deviation
SD	Standard deviation
SVOCs	Semi-volatile organic compounds
TC	Total carbon
Tmax	Maximum temperature in the inert mode
TOA	Thermal-optical analysis
TOR	Thermal-optical reflectance
TOT	Thermal-optical transmittance
TSP	Total suspended particles
WSOC	Water-soluble organic compounds
TOT EC	EC determined by TOT methood
TOR EC	EC determined by TOR method
VMM	Flemish Environment Agency

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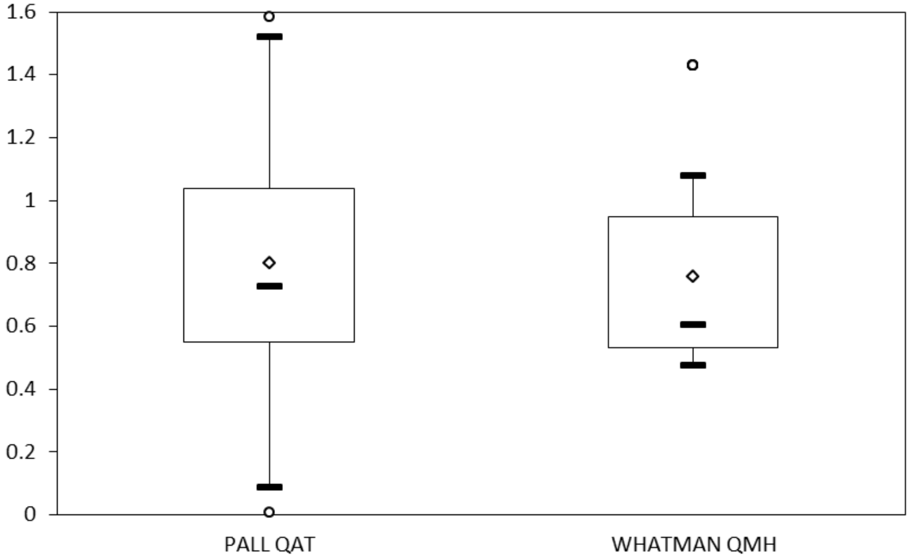

Figure 1. Mean, median, and 25 and 75 percentiles of the OC blank concentration (µg cm^{-2}) determined for Pall Tissuquartz filters 2500-QAT, 150 mm (QAT, $n = 128$) and ultra-pure Quartz filters, 150 mm (QM-H, $n = 127$) determined in the IDAEA-CSIC laboratory in the period 2012–2014 (CSIC, unpublished results).