

The authors would like to thank Referee #2 for his/her comments and suggestions to improve the manuscript. We address all the comments one by one below.

Anonymous Referee #2

This paper aims to provide a literature review of the current state of knowledge of thermal-optical methods in the context of a reference method to be defined by CEN to analyze EC and OC in ambient air. This paper provides a quite exhaustive and valuable description of these thermal-optical methods addressing with many details a lot of issues related to charring correction, temperature protocols, optical correction, etc. In that sense, it fulfills its primary objective to gather in one paper all the studies related to this topic but hardly brings really new insights or useful guidance from the synthesis of this large amount of information. The paper is well written (sometimes too much descriptive). However, some sections are closer to a Standard Operating Procedure rather than a real literature review. Several major issues need to be addressed before considering it for publication. They are presented below.

Major comments:

- There is a clear need to reconsider the structure of the paper. There is not a clear and well justified scheme in this manuscript. At the end, it appears more like the superposition of several sections having poor interconnections. More specifically several sections are not directly related to the main topic of the paper (Thermal-optical analysis review) and should be either removed or eventually transferred in the supporting information. Namely section 3.1.1 (Laboratory blank filters), 3.1.2. (Field and trip blank filters), 3.2. (Sampling artifacts).

Response: We have restructured the manuscript as both reviewers recommended. Former sections 3.1.1, 3.1.2 and 3.2 have been moved to the supplement. The new structure is as follows:

Contents

- 1 Introduction
- 2 Thermal-optical analysis
 - 2.1.1 Thermal-optical analysis protocols
 - 2.1.2 Comparison of TOT and TOR
 - 2.1.3 Comparison of IMPROVE, NIOSH-like and EUSAAR_2 protocols
- 2.2 Inter-laboratory comparison studies
- 3 Critical factors causing uncertainties in thermal-optical analysis
 - 3.1 Temperature calibration
 - 3.2 Maximum temperature in the inert mode
 - 3.3 Charring and charring correction
 - 3.4 Dependence of OC/EC split on aerosol type
 - 3.4.1 Brown carbon
 - 3.5 Dependence of OC/EC split on sample oven soiling
- 4 Biases in thermal-optical analysis
 - 4.1 Interference from other aerosol components
 - 4.1.1 Carbonate carbon (CC)
 - 4.1.2 Metal oxides
 - 4.1.3 Inorganic salts
 - 4.2 Instrument parameters influencing the analysis :transit time
- 5 Reference materials for OC and EC determination by thermal-optical analysis
- 6 Conclusions

- There is nothing about the different techniques to check/calibrate thermal-optical methods (in terms of μgC) and almost nothing about the accuracy, the uncertainties associated with the few thermal-optical instruments (DRI, Sunset Lab) which cover the big majority of the studies reported here. A section could address this issue.

Response: We believe that dedicating a section about the calibration methods of the two analyzers would make the manuscript resemble to a technical document or standard operational procedure as this information is provided to TOA users by the manufacturers. The analytical characteristics of the most common thermal protocols including operational range limit of detection, accuracy and precision are given in Table 2 modified as follows

Table 1. Analytical characteristics of the most commonly used thermal-optical protocols.

Protocol	Analyzer (optical correction)	Aerosol type	Operational range, $\mu\text{gC cm}^{-2}$	Limit of detection, $\mu\text{gC cm}^{-2}$	Accuracy, %	Precision, $\mu\text{gC cm}^{-2}$
NIOSH5040, Birch and Cary, 1996; Peterson and Richards, 2002	Sunset Analyzer (TOT)	Diesel exhaust	0.7-70	0.15	± 16.7 (at $23 \mu\text{gC cm}^{-3}$)	± 0.13 for loadings of $0.67 \mu\text{gC cm}^{-2}$ ± 0.007 for loadings $6.67 - 48 \mu\text{gC cm}^{-2}$
IMPROVE_A, Chow et al., 1993	DRI Analyzer (TOR)	IMPROVE network	0.2-750	0.2	< 10 (TC accuracy)	± 0.5 for loadings $< 10 \mu\text{gC cm}^{-2}$ ± 0.03 for loadings $> 10 \mu\text{gC cm}^{-2}$
EUSAAR_2 Cavalli et al., 2010	Sunset Analyzer (TOT)	EMEP network	5-62	-	2-7 uncertainty for EC	-

However, as this issue was raised by the reviewer we added the following information in the thermal protocols section:

“At the moment, there is no standard reference material that can be used to calibrate these instruments for atmospheric EC and OC, so calibration is currently limited to that of TC in terms of $\mu\text{gC cm}^{-2}$ and to the response of the carbon detector. The principal calibration of the TOA analyzer is conducted by blank filter samples spiked with calibration solutions of pure organic compounds such as sucrose or oxalic acid or potassium hydrogen phthalate. Daily calibration checks (e.g: analysis of a control filter, known amounts of sucrose solution) are used to confirm that the detector response has not shifted substantially since the last calibration. Further information is given in the analytical instrument user’s manual. On a daily TOA analyzers incorporate an injection of calibration gas (5 % methane in helium) after each analytical run for internal calibration (to correct for any drift in the response of the carbon detector) (Kuhlbusch et al., 2009; CEN/TR 16243:2011 DRI Standard Operational procedure, http://www3.epa.gov/ttnamti1/files/ambient/pm25/spec/DRI_SOPforIMPROVEFINAL.pdf)

Specific comments:

- Introduction: Please describe in the introduction section how you have structured your review and justify why you have structured it like that. Please also recall in this section what is "EBC" and justify why thermal-optical analyses are important to determine EBC.

Response: The following has been added in the introduction section: "This review first provides a description of the thermal-optical analysis method followed by the existing thermal-optical analysis protocols and the comparison studies of the optical correction methods with the analysis protocols. The results of inter-laboratory comparison studies are also given in order to assess the reason of discrepancies (method dependent or not) between the participants. Furthermore, the critical factors causing uncertainties in thermal-optical analysis and the biases caused by the presence of other aerosol components and the instrument parameters are also discussed. Finally, the candidate reference materials for OC and EC determination by thermal-optical analysis are included."

Also the term EBC is now introduced as follows: "When the carbon mass is determined by the absorption coefficient it is recommended to use the term equivalent black carbon (EBC) instead of BC. The absorption coefficient is converted into EBC by comparing the online measurements with filter-based EC concentrations determined by thermal-optical analysis (Petzold et al., 2013; EEA 2013)."

Page 9652, line 25: "EC, which does not volatilize in an inert atmosphere at temperature below 700_C" Where you got this number? Not sure that biomass burning EC is resistant at 700_C under inert mode.

Response: This statement is from Chow et al. (2004). The phrase has been modified as follows: "Thermal methods make use of the thermal refractivity of EC, which does not appreciably volatilize in an inert atmosphere at temperatures below ~700 °C (Chow et al., 2004)."

- Page 9654, line 9: You should be more specific here. You are missing the step of carbonaceous vapors oxidized into CO₂ (and then converted into CH₄ with catalyst).

Response: We agree with the reviewer. The text has been modified to: "Carbonaceous vapours are oxidized to CO₂ (by passing through a MnO₂ catalyst at 912 °C) and then converted to CH₄ by passing the flow through a methanator (Ni-firebrick catalyst at ~550°C)".

- Page 9654, line 27: Sentence "When PC evolves...as the charred OC has been removed". As you clearly state later in the manuscript, there is a not a clear understanding of what is removed first under the oxidation step (EC or charred OC). For that reason, you cannot state here that charred OC is removed first.

Response: We agree with the reviewer, but this is one of the assumptions of charring correction. In fact, this is explained in the manuscript in section charring and charring correction: "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..." Hence, the text has been modified to: "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. The OC/EC split point is usually defined as the point when reflectance or transmittance increases to reach its original value, and it is assumed 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".

- Page 9655, line 10: Sentence “Since EC and PC have different optical properties...”. Not clear for me how with the spectral measurement of absorption you can better separate EC and PC. You should provide 1 or 2 sentences to better explain this point.

Response: As reflectance and transmittance are influenced by different type of PC (reflectance is dominated by PC on the filter surface, while the transmittance signal is dominated by the charring of organic vapours distributed throughout the filter) concurrent measurements of reflectance and transmittance at several wavelengths can provide information on the type of PC.

The sentence has been modified as follows: “Since reflectance is dominated by PC on the filter surface, while the transmittance signal is dominated by the charring of organic vapours distributed throughout the filter (Chow et al., 2004) this information may prove useful in the 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.”

- Page 9657, line 18: Sentence “Application of a too high maximum temperature...”. This sentence is very long. Also I don’t understand the point raised concerning CC. In all cases (low or high Tmax) CC will interfere with OC-EC measurements. So I do not understand why it is only an issue here for very low Tmax.

Response: Concerning the interference from CC, it is better if CC interferes with OC rather than with EC as CC concentrations are generally low with respect to OC but might be significant when compared to EC. This part has been modified as follows: “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, LAC that contains both PC and EC and also promote charring. On the other hand, a very low Tmax may result in an overestimation of the EC concentration due to the incomplete evolution of OC in the He mode. Furthermore CC would evolve in the He-O₂ mode and erroneously be determined as EC (Subramanian et al., 2006). As CC concentrations are generally low with respect to OC but might be significant when compared to EC it is important to ensure that CC evolves together with OC rather than with EC during the thermal-optical analysis (Karanasiou et al., 2011).”

- Section 2.2.3. Charring and charring correction. You are right to raise the issue of different values of attenuation cross section from PC and EC. But you should also mention that in the real-world we may also have a mixture of different sources of EC (for instance fossil fuel and biomass burning) with different attenuation cross section. This will also contribute to the uncertainties associated with the split point (charring correction) between OC and EC.

Response: We agree with the reviewer. The following has been added: “However, in the real world we may also have a mixture of different sources of EC (e.g: fossil fuel combustion and biomass burning) with different attenuation cross section increasing the uncertainty associated to the split point.”

Section 2.2.4. Dependence of OC/EC split on aerosol type. By comparison with wood burning samples, the authors state the traffic sites samples form little PC. One explanation given is the high diesel component (containing non pyrolyzing organic matter). There is a more straightforward reason that can be proposed to explain why fossil fuel samples produce less PC compared to wood burning samples: There is about 5 to 10 times less OC (relatively to EC) in fossil fuel samples compared to wood burning samples. End of this section, you are dealing with interference from other aerosol components (LAC, metal oxides). You should put this part under section 3.3 which is dedicated to this issue (interference).

Response: We agree with the reviewer. The sentence has been modified as follows: “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,

and the lower OC/EC in fossil fuel samples than in highly-influenced-wood-burning samples commonly found in some rural sites (Khan et al., 2012).”

In the end of the section we refer to samples containing high amounts of resuspended soil and road dust and how these samples can affect the split point (due to the premature evolution of LAC caused by metal oxides). Since the presence of these compounds depends on the aerosol type, we prefer to leave this part in this section to explain the reason of uncertainty in the case of road, soil dust influenced aerosol samples.

- Page 9660, line 18: Not sure that the 6 points (i to vi) are the only biases in thermal-optical analysis methods. You have previously reported in the manuscript many other biases (sections 2.1 and 2.2)

Response: In sections 2.1 and 2.2 we refer to critical factors causing uncertainty in thermal-optical analysis. As reviewer 1 recommended in this section we report the systematic uncertainties in thermal-optical analysis, as the true values of EC, OC are unknown. The paragraph has been modified as follows: “The term bias is used to describe the deviations between the measured values and the true, reference values. However in thermal-optical analysis the true value is unknown due to the lack of a reference material. So in this section we mostly refer to systematic uncertainties caused by (i) OC loading in blank filters(ii) catalytic oxidation interactions between OC, EC, and non-carbonaceous material in the sampled particles and iii) instrument parameters that influence the analysis. The biases caused by the OC loading in blank filters are discussed in the supplementary material since they are connected to manufacturing, transportation/storage, sampling and analysis procedures and not solely related to thermal-optical analysis.”

- Section 2.2.6. Instrument parameters influencing the analysis. You may focus this title a little more here and change it to something related to “transit time influence on OC/EC split”.

Response: The title has been changed to Instrument parameters influencing the analysis: transit time

- Section 3.3.4. Brown carbon. Sentence “BrC is prone to charring ...”. This sentence is not clear for me in particular “the more refractory part of BrC will be wrongly attributed to EC”. What do you mean exactly? Do you mean the more refractory part of charred BrC? Or not? Later in this section you state the BrC can generate more PC which, in the end, can lead to an overestimation of EC if charring is not properly accounted for. I don’t understand this part. We are talking in this paper about thermal-optical methods which do account for charring. Maybe the authors want to state that the more PC is generated the more uncertainties are associated with EC and OC determination and, since BrC is prone to charring, uncertainties may be higher in atmospheric samples containing significant amount of BrC?

Response: Yes, we mean the more refractory compounds of BrC. We agree with the reviewer’s remark, large amounts of PC increases the uncertainty in EC, OC determination. The sentence has been modified as follows: “Another effect of BrC is that compounds from this family can increase substantially the PC generated during the analysis. This increases the uncertainty of EC and OC determination especially in samples containing significant amounts of BrC.” The section of the paper has been further modified to include a recent paper dealing with the presence of BrC and TOA (Massabo et al., 2016). The new text is: “Recently Chen et al. (2015) and Massabo et al. (2016) have assessed the influence of BrC in TOA. 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. Chen et al., (2015) have shown the role of BrC in TOA by monitoring the transmittance and reflectance at multiple wavelengths, analyzing the time evolution of charring and comparing the different determined split points to allow a more accurate separation of the EC contained in the sample and the PC generated during the analysis (Chen et al., 2015). Massabo et al., (2016) have recently introduced a correction to TOA results to take into account the amount of BrC in the sample. This was done by means of a Multi Wavelength Absorbance Analyzer, MWAA that provides the absorbance values at 5 different wavelengths. The absorbance values from the MWAA were used to calculate the attenuation of the BrC present in the sample and afterwards the new starting point of the laser signal in TOA if BrC was not present. In this way the new split point that correctly attributed BrC to the OC fraction was calculated.”

- Page 9675, line 22. Sentence “These differences may be explained...”. I don’t think we can state that rural sites are more influenced by biomass burning than urban environments. Domestic heating should be higher above cities.

Response: We agree with the reviewer that residential heating is also important in urban areas. However, in rural sites the relative contribution of biomass burning is higher due to the lower impact of traffic emissions. Again in rural sites not only residential heating is considered a biomass burning source but also agricultural activities. The sentence in the text has been slightly modified as follows: “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: higher relative contribution by biomass burning processes than in urban areas).”

- Page 9678, line 26. Sentence “The agreement between laboratories : : :”. This is a correct statement for EC and OC; not for TC. The sentence just after “EC concentrations determined : : :”. Are you sure that this statement is aligned with the results presented by Schmid et al. (2001) ?

Response: We agree with the reviewer and the phrase has been modified as follows: “The agreement between EC concentrations reported by different laboratories improved when optical correction was applied with respect to results corresponding to only thermal methods (Birch, 1998; Schmid et al., 2001; EUSAAR, 2011).”

Regarding the next question, quoted by Schmid et al. (2001): “Two laboratories showed results for EC with and without using an optical feature for the correction of charring during pyrolysis, which is one of the major problems in the analysis of carbonaceous aerosols. It was found that the amount of EC resulting from the charring of OC during pyrolysis can be very high, which causes a strong overestimation of EC. Another laboratory obtained EC results after extracting the filters with a DMF/toluene mixture, which were very close to the average of the EC results of the TOT/TOR methods.” As we refer to optical correction of charring and not other methods as the filter extraction with organic solvents the sentence “EC concentrations determined with a method without optical correction were overestimated compared to IMPROVE_A and EUSAAR_2 results (EUSAAR, 2011)” is also in agreement with the results of Schmid et al. (2001).

Minor comments:

- In the title “:” could be added before “a literature review”

Response: Correct, “:” has been added.

- Page 9652, line 4: “inorganic carbon (IC), mostly present as carbonate carbon (CC)”. Since you state that IC is not exclusively CC, what are the other components of IC?

Response: In ambient air, inorganic carbon is present as carbonates and bicarbonates. Other forms of IC like carbides could be detected only in workplace air e.g. metal production and processing. The phrase has been modified as: "Atmospheric particulate carbon (total carbon, TC) may be broadly divided into three categories: organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC), present as carbonate and bicarbonate."

- **Page 9652 line 10: CC is also present in seawater (sea salts).**

Response: The phrase has been modified as follows: "CC is present in natural ground and building/demolition dust which can be resuspended and also in marine aerosol."

- **Page 9653, line 21: "in accordance to the new Air Quality Directive 2008/50/EC". Not really "new" anymore.**

Response: Correct, the word "new" has been deleted.

- **Page 9654, line 19: "the Sunset Carbon Aerosol Analysis Field instrument". This is not the correct name of this instrument. It should be more "semi-continuous OC-EC field analyzer commercialized by Sunset Laboratory Inc."**

Response: The name of the instrument has been changed to semi-continuous OC-EC field analyzer

- **Page 9654, line 23: ".. while the lab instruments can analyze samples from various sites". This a bit restrictive. For instance, it can also measure different aerosol sizes**

Response: Correct the following phrase has been added: "..while the lab instruments can analyze samples from various sites and different size fractions."

- **Page 9655, line 10: "Since EC and PC have different optical properties". "may" instead of "have".**

Response: "may" has been added

- **Page 9655, line 17: Please be consistent through the manuscript with some words like "analyzers" (written with z or s in the manuscript).**

Response: We have checked and changed these inconsistencies

- **Page 9656, line 5: "The main difference from NIOSH-like protocols is the lower temperature in the He phase of the analysis (580_C)". Do you mean the lower temperature of the last plateau in the He phase of the analysis?**

Response: Yes, the sentence has been modified as follows: "The main difference from NIOSH-like protocols is the lower temperature in the last temperature step in the He phase of the analysis (580 °C) and the analysis time"

- **Page 9659, line 8: "a carbon black sample". What does it mean exactly?**

Response: This sentence has been changed as reviewer 1 also pointed out and the term carbon black sample does not appear in the paper. The new phrase is: "The OC/EC split point for wood smoke source samples and samples dominated by biomass burning emissions is influenced by the temperature protocol since such samples exhibit significant charring (Khan et al., 2012; Schauer et al., 2003; Reisinger et al., 2008; Maenhaut et al., 2009; Soto-Garcia et al., 2011)."

- **Page 9659, line 1: "LAC". Why, from this point of the manuscript, you decide to speak about LAC whereas this term was not discussed before?**

Response: The term LAC is mentioned in the introduction as one of the terms used to describe BC, soot, EC.

- Page 9672, line 23. "A number of potential SRM candidates for thermal-optical, TOA have been introduced ..". I cannot understand this part of the sentence.

Response: The sentence has been modified to: "A number of potential SRM candidates for thermal-optical analysis, TOA have been proposed in recent years."

- Page 9675, line 4, "...adsorbed throughout the filter". I don't understand this part which seems to be disconnected for the rest of the sentence.

Response: Correct, it has been deleted from the sentence.

- Page 9679, line 12. Add "%" after "7".

Response: "%" has been added

- Page 9679, line 15. I had in my mind that Schmid et al. (2001) was not only dealing with thermal-optical methods but also with thermal methods. If so, discussion related to this paper should be removed from the manuscript as we are only dealing here with thermal-optical methods. Please check the other "old" references as well.

Response: From the studies that compare thermal with thermal-optical methods we present the results taking into account only the thermal-optical methods. For this reason from Schmid et al. (2001) we report relative standard deviations from 5 laboratories only and not from the 17 that participated in the robin round test.

- Page 9680, line 8. Add "%" behind numbers.

Response: Response: "%" has been added

- Page 9681, line 1. Sentence "An inter-laboratory ..". Again I do not understand why you have decided to discuss on intercomparison studies including thermal methods which methods are not addressed in the paper. If you wish to discuss these results (thermal vs thermal-optical), you may better justify in the manuscript why.

Response: As mentioned before we only present the results from the laboratories that used optical correction.

- Page 9684, line 1. Africa is not the only desert to produce dust aerosols.

Response: African dust has been changed to desert dust