

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

By A. Karanasiou et al.,

Review for amt-2015-217

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### **General comments:**

To link black carbon from emission sources to climate forcing, the determination of atmospheric black carbon (BC) mass concentration is needed. Thermal-optical / or thermal methods are still widely used for this purpose, measuring BC mass contents in the samples from source regions to rural and to remote areas for both intensive campaigns and long-term observations.

Unfortunately, as the nature of carbonaceous aerosols, their changes in optical (e.g., absorption and scattering) and chemical properties (e.g., thermal refractory) are in continuous mode (instead of discrete mode), therefore, the determination of organic carbon (OC) and elemental carbon (EC) is method/protocol dependent. By individual method, a specific part of OC and EC are detected on the continuous spectrum. In this manuscript, the authors have tried to present a comprehensive review for OC and EC analysis (with a focus only on thermal-optical methods), including thermal protocols, critical parameters related to the analysis, the biases/ interferences and references. Although the task is a challenge, the authors did a reasonably good job.

However, the contents are not effectively organized, the logic flow is not well presented and some important mechanisms are not discussed. To improve the quality of the manuscript, the authors should address the following concerns and comments for final publication in AMT.

- 1) In general, it seems too much description/assembling information instead of discussions of mechanisms causing the variations, the knowledge gaps and suggestions for future work. It is suggested to condense the manuscript via removing some unnecessary contents (e.g., removing “Sampling artifacts” from the section 3 to focus on the issues of analysis since all the comparison results are not related to the sampling but the analytical protocols using the same filters).

- 2) To my point of view, charring correction /minimization is the most important aspect related to the discrepancies between different thermal-optical methods. To have a consistency in charring correction or to minimize the extent of charring (assuming a constant FID sensitivity in a run), **temperature** and **retention time** (i.e., time elapsed at each temperature step), particularly in inert modes, are key factors.

*Recent comparison studies show that using the same protocols at different laboratories, the temperature offsets could be significant ranging from -90 °C to + 100 °C (Panteliadis et al., 2015). It is certain that such large temperature offsets could influences OC and EC determinations. Although it is thought that the higher temperature in an inert mode, the more charring (PC) would be formed, it is also observed that the increase of transmittance signal was observed at the inert mode of  $T_{max}(>800\text{ °C})$  without evidence of trace oxygen involving (p757 in Yu et al., 2002, Figure 8 in Huang et al., 2006), and that the signatures of transmittance/ or reflectance could return to the initial values at 850 °C prior to the addition of oxygen (Chow et al., 2001), cited by the authors in Table 5 of this manuscript. Those observations indicate that not only the temperature but also the*

*residence time at the inert mode (e.g., the time at each step in IMPROVE protocol could be as long as 580s) is important to affect the amount of charring (PC). As stated in Yu et al., 2002 (p760), the extent of charring formation is dependent on the temperature program parameters and the prolonging the residence time at each temperature step reduces charring formation.*

*It is also known that water soluble OC (WSOC) / or oxygenated OC contributes the most to the charring (Yu et al., 2002; Chan et al., 2010). It is possible to form CO or other trace gases from oxygenated OC through gasification process at such high temperatures ( $T_{Max} > 700\text{ }^{\circ}\text{C}$ ) in the inert mode. This may be one of the possible reasons to explain the long residence time, the less charring formation observed by Yu et al., 2002 (i.e., the possibility of pre-oxidation at  $850\text{ }^{\circ}\text{C}$  in the inert mode has been ruled out in these cases). **Unfortunately, temperature calibration and the relationship between  $T_{Max}$  / or the time elapsed at  $T_{Max}$  and the amount of charring have not been well discussed in the manuscript.***

- 3). Using universally accepted references may be a solution to improve uncertainties in OC & EC analysis via optimizing the protocols to minimize charred PC. However, it is challenging having accepted references due to the definition of EC (which is related to BC definition as discussed in Petzold et al., 2013). It is known that the ambient EC and OC are mixtures from various emission sources with different proportions (e.g., fossil fuel combustions, biomass burning, biogenic emissions and photochemical oxidations in the atmosphere). Although it is impossible to have references representing all kinds of ambient EC and OC aerosols (with a range of mixing ratios from various sources), it is possible having references for representatives of individual OC and EC components. Using those typical OC and EC references, at least, it can be done to optimize /assess the effectiveness of a method for EC and OC determinations.
- 4). To improve the logical flow, a suggested structure of the manuscript is included below. For a purpose of comparison, the original structure is also assembled here (highlighted in gray).

The original structure of the paper:

Abstract

## 1. Introduction

## 2. Thermal-optical analysis

### 2.1 Thermal-optical analysis protocols

### 2.2 Critical factors in thermal-optical analysis

#### 2.2.1 Temperature calibration

#### 2.2.2 Maximum temperature in the inert mode

#### 2.2.3 Charring and charring correction (*residence time in inert modes should be an important factor*)

#### 2.2.4 Dependence of OC/EC split on aerosol type (*which is source dependence. It depends on how much oxygenated OC in the samples* )

#### 2.2.5 Dependence of OC/EC split on sample oven soiling (*this should be related to the change in laser sensitivity*)

2.2.6 Instrument parameters influencing the analysis (*this should be included in section 3: biases in thermal-optical analysis*)

### **3. Biases in thermal-optical analysis**

#### 3.1 OC loading in blank filters

3.1.1 Laboratory blank filters (*likely only affecting OC concentrations*)

3.1.2 Field and trip blank filters (*likely only affecting OC concentrations*)

#### 3.2 Sampling artifacts (*this should be removed from the paper since it is beyond the scope*)

#### 3.3 Interference from other aerosol components

3.3.1 Carbonate carbon (CC)

3.3.2 Metal oxides

3.3.3 Inorganic salts

3.3.4 Brown carbon

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

### **5. Inter-comparison of thermal-optical analysis methods**

5.1 Comparison of TOT and TOR\_ (*for charring correction*)

5.2 Comparison of IMPROVE, NIOSH-like and EUSAAE\_2 protocols

### **6. Inter-laboratory comparison studies (*this should be part of section 5*)**

### **7. Conclusion**

*The sections 5 and 6 should be moved in front of the papers, showing the differences in protocols and comparison results before discussing the possible critical factors, the biases/interferences. Having proper references (i.e., representatives of individual OC and EC components) is a possible solution to reduce the uncertainties in OC and EC measurements. Thus, Reference materials should be the last followed by "Conclusion".*

Therefore, the suggested structure :

#### **Abstract**

#### **1. Introduction**

#### **2. Thermal-optical analysis**

##### 2.1 Thermal-optical analysis protocols

2.1.1 Comparison of TOT and TOR\_ (*for charring correction*)

2.1.2 Comparison of IMPROVE, NIOSH – like and EUSAAE\_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 (*residence time should be discussed here*)

3.4 Dependence of OC/EC split on aerosol type (*source dependence. It all depends on how much oxygenated OC in the samples*)

3.5 Dependence of OC/EC split on sample oven soiling (*this should be related to the change in laser sensitivity...*)

#### **4. Biases in thermal-optical analysis**

##### 4.1 OC loading in blank filters

4.1.1 Laboratory blank filters (*likely only affecting OC concentrations*)

4.1.2 Field and trip blank filters (*likely only affecting OC concentrations*)

##### 4.2 Interference from other aerosol components

4.2.1 Carbonate carbon (CC)

- 4.2.2 Metal oxides
- 4.2.3 Inorganic salts
- 4.2.4 Brown carbon
- 4.3 Instrument parameters (e.g., FID sensitivity and the transit time: the time elapsed from carbon fraction left from the filter to its arrival at the FID)
- 5. Reference materials for OC and EC determination by thermal-optical analysis**
- 6. Conclusion**

### **Specific comments:**

p9651, L15-16: authors said “ the difference between reflectance and transmittance correction tends to be larger than the difference between different thermal protocols”. It was also noticed that in Table 5 (p9706) for comparison between TOT and TOR, the slope of TOR to TOT is 1 for NIOSH (850°C), which is not larger than these between IMPROVE and NIOSH (Chow et al., 2001), *indicating that the above statement is not valid in this case when the time at  $T_{max}$  (850 °C) is long enough (using the DRI instrument), the signals of either reflectance or transmittance would return to the initial value before the addition of oxygen, the charring was minimized and the slope of TOR to TOT would equal to **one**.*

p9651, L25-26: it is suggested to include "e.g.," before the cited references since there are many more references not included.

p9652, L1-2: it is suggested to include "e.g.," before the cited references since there are many more references not included. You may apply this to other citations too...

p9652, L21-22: the expression, i.e., “ The term EC is used when total carbon is gasified from the sample...” is not clear and please rephrase it.

p9653, L24: the “chars and pyrolyzes” should be replaced with “ is charred and pyrolyzed”.

p9654, L18-23: the main difference between the lab and the field instruments is the detector. The detector of the field instrument is NDIR instead of FID as in the lab one. This should be mentioned here.

p9656, L12: please replace the “accuracy” with “uncertainty” since the accuracy is the difference between the determination and the true value (you don’t know the true value regarding EC and OC contents).

p9657, L1: replace the title with “Critical factors causing uncertainties in Thermal-optical analysis”.

p9658, L10-12: the sentence of “Charring is also influenced by the presence of inorganic constituents such as  $\text{NH}_4\text{HSO}_4$  that can increase PC formation by a factor of 2 to 3 (Yu et al., 2002).” is not always correct. According to Yu et al., (2002), although the amount of charring of starch and cellulose was increased in the presence of  $\text{NH}_4\text{HSO}_4$ , the amount of charring from levoglucosan, however, drops by 15% in the presence of  $\text{NH}_4\text{HSO}_4$  (p760 in Yu et al., 2002).

p9659, L5-10: the expression is not clear, please rephrase it.

p9659, L18-21: As mentioned before, an increase in transmittance was observed at 850°C in inert mode, regardless of the presence of absence of the trace oxygen (e.g., Yu et al., 2002, Huang et al., 2006), indicating that premature-oxidation of light absorption carbon (LAC) is not the only reason for the increase of transmittance at  $T_{max}$  ( $> 800^\circ\text{C}$ ) in inert mode. The possibility

of other mechanisms (e.g., gasification of charring (PC) at high temperatures) should be mentioned.

p9660, L1-5: this section should be discussed in relation to laser sensitivity changes due to oven soiling (which is a process). This particularly impacts on trend determinations of long-term measurements.

p9660, L6-16: the factors mentioned in this section (i.e., instrument parameters) belong to the section of “Biases in thermal-optical analysis”, as mentioned in General Comments. Agreed with the authors, true OC/EC could be not defined (due to not having proper references).

p9660, L17: The “biases” should be defined. To me, they should be deviations between the measured values and the true values. Without knowing true values, it is hard to talk about biases. It may be better to replace “biases” with “systematic uncertainties”.

p9660, L17-22: the “non-uniform particles deposits on the filters” should belong to random events (i.e., outliers which contribute to sampling heterogeneity) instead of systematic uncertainties; categories (ii) and (iii) should be combined into one category as “OC blanks” which could be caused by manufacturing, transportation/storage, sampling and analysis procedures.

p9664, L20-21: I don’t agree on this statement, i.e., “the field blank values should not be subtracted from the sample OC concentrations...”. It is suggested to correct the field blank for all measured concentrations using the averages with the same manufacturing lot number (the outliers should be excluded), particularly for the long-term observation.

p9664, L23: please remove the section as mentioned in General Comments since it beyond the scope of the manuscript (the sampling artifacts do not belong to the factors of thermal-optical analysis).

p9669, L18-21: it could be also important if the sampling sites are close to coast of oceans (due to sea-spray aerosols).

p9671, L5: It is known (Zhao et al., 2015) that there are some relationship between WSOC/ or oxygenated OC /or pyrolysis OC and brown carbon (BrC). Different terminologies may talk about the same thing, e.g., the former is about chemical properties and the latter is about the optical property of the same thing. It is likely that BrC could be WSOC or oxygenated OC and they could be charred into PC. Part of BrC could also be EC. Therefore, it is a little confusing to consider BrC as interference to OC and EC. BrC should be the optical characteristic of WSOC or oxygenated OC or relatively low temperature EC (e.g., from biomass burning sources). Please re-consider how to accommodate the content of “BrC” in the manuscript.

p9672, L14-15: what are the ISO or NIST definitions for references material?

p9673, L18-20: the expression is not clear. Please rephrase.

p9673, 20-22: I disagree on this statement”... 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.”. It is known that the EC and OC/EC ratio in ambient aerosols is a range of variations, it is impossible to have references to represent the entire range. However, it should be to have a set of references representing main end members as found in ambient aerosols (e.g., fossil fuel combustions and biomass burning and etc).

p9673, 23-24: According to Bond et al., 2013, black carbon is a distinct type of carbonaceous material. Its properties include strong absorption of visible light and refractory with a vaporization temperature near 4000K (much higher than 800°C). At least, one category of EC

(e.g., forming from fossil fuel combustion or flaming) in ambient aerosols should have this kind of refractory if not all EC (e.g. the type of EC from biomass burning). Thus, the materials with EC evolving at high temperature (>800°C) should not be excluded as a candidate of references. This kind of EC should be reasonably detected by all thermal-optical / thermal methods.

p9674, L4-7: the expression is not well understood. Please rephrase it.

p9674, L8: what does it mean for the “this parameter”? Do you mean the protocol, including temperature steps and the corresponding residence time ranges?

p9676, L1-4: According to the description, it sounds that the charring identified by transmittance is better representative of the entire filter than those identified by reflectance (only for the surface charring...). Due to lack of proper references, it is impossible to know the true value.

p9678, L6-7: I agree on this general conclusion, i.e., “that the identification of the “best” method is not possible so far.”, because there no proper references have been used for establishing the true values as benchmarks. Therefore, establishing proper references and carrying out regular inter-comparison exercises (including different networks from different continents) are priorities in the carbonaceous aerosol measurement (i.e., OC/EC) field to maximize the scientific value of the current OC and EC datasets.

p9678, L26-27: The statement (i.e., “ the agreement between laboratories was relatively poor when only thermal methods were used...” ) is very ambiguous! In the reported results by Schmid et al., (2001) there are total 17 methods involved in the comparison. The authors only picked up five labs, including only one lab using thermal method without detailed description of the protocol. In fact, the relative standard deviation (RSD) of TC measurements when excluding the lab (using thermal method) is worse than that including the lab. Please clarify the expression.

p9680, L11-12, L19-20: It is realized that the RSD of the results in 2007 is 40% is higher than that in 2011 (i.e., 25%). The former is obtained by only using thermal-optical methods, whereas the latter is obtained by both thermal-optical and thermal methods. Please confirm.

p9681, L1-7: The sentences are not clear, please rephrase them. It seems no statistically significant improvement from 13-27% to 9-23% (of total mass of ambient PM or TC?) or from 12-33% to 10-29% for EC/TC.

p9681, L9-11: The expression is not very clear to me (should the “between” be replaced with the “within”?). Please re-phrase it.

p9681, L24 to p9682, L3: It seems that the RSD results for TC (< 5%), EC (< 20 %) and OC (10%) are within accepted ranges and interesting to see that the RSD results are method-independent.

p9682, L20-23: The expressions are not clear to me. Please re-phrase them.

p9683, L22-23: The results by Chiappini et al. (2014) seems not strongly supporting this point.

p9684, L3-5: Brown carbon is a part of charred OC (PC). BrC should not be considered as an interference of OC and EC determination (see comments on p9671).

p9684, L6-12: If “sampling artifacts” is removed from the manuscript as suggested in General Comments, this paragraph should be removed.

p9688, L18-28: Are those five references, i.e. EUSAAR 2007, 2008, 2009, 2010, 2011 publically accessible?

p9702, Please list the original data sources in Table 2.

p9704. If “sampling artifacts” is removed from the manuscript as suggested in General Comments, Table 4 should be removed.

p9706, In the note under the table, it is stated that “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.”, indicating that once the residence time is long enough at the high temperatures as used here, the differences between EC-TOR and EC-TOT can be minimized (see point#2 in General Comments).  
p9709, in Table 7,

- Is the reference, i.e., Cavalli et al. (2012) publically available?
- Please spell out/ list all the acronym names used (e.g., TLT, and EnvCan) and briefly describe the protocols;
- Please provide all the RSD values for EC, OC and TC, if it is any possible (e.g., the cases by Schmid et al 2001; EUSAAR 2008, 2009, 2010, 2011 and the rest of the table). As long as there are OC and EC or EC/TC measurements, the corresponding RSD values should be available.
- What is the difference in definition between the superscripts “b (random error)” and “c (reproducibility)” for EUSAAR (2011)? It seems that EC, OC and TC have been measured for all samples.

p9711, in Table A1, please add “TLT” and “EnvCan” in the table.

#### References related to the review:

- Bond, T.C., S. J. Doherty, D. W. Fahey, P. M. Forster, T. Berntsen, B. J. DeAngelo, M. G. Flanner, S. Ghan, B. Kärcher, D. Koch, S. Kinne, Y. Kondo, P. K. Quinn, M. C. Sarofim, M. G. Schultz, M. Schulz, C. Venkataraman, H. Zhang, S. Zhang, N. Bellouin, S. K. Guttikunda, P. K. Hopke, M. Z. Jacobson, J. W. Kaiser, Z. Klimont, U. Lohmann, J. P. Schwarz, D. Shindell, T. Storelvmo, S. G. Warren, and C. S. Zender.: Bounding the role of black carbon in the climate system: A scientific assessment, *Journal of Geophysical Research: Atmospheres*, Vol. 118, 5380–5552, doi:10.1002/jgrd.50171, 2013.
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- Chiappini, L., Verlhac, S., Aujay, R., Maenhaut, W., Putaud, J. P., Sciare, J., Ja\_rezo, J. L., Liousse, C., Galy-Lacaux, C., Alleman, L. Y., Panteliadis, P., Leoz, E., and Favez, O.: Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter, *Atmos. Meas. Tech.*, 7, 1649–1661, doi:10.5194/amt-7-1649-2014, 2014.
- Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IM10 PROVE and NIOSH carbon measurements, *Aerosol Sci. Tech.*, 34, 23–34, 2001.
- Huang, L., J.R. Brook, W. Zhang, S-M. Li, L. Graham, D. Ernst, A. Chivulescu and G. Lu.: Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment. *Atmospheric Environment* 40: 2690–2705, 2006.
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- Schmid, H., Laskus, L., Jürgen Abraham, H., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H. M., Giesen, K. P., Hitztenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J. P., Toom-Sauntry, D., and Puxbaum, H.: Results of the “carbon conference” international aerosol carbon round robin test stage I, *Atmos. Environ.*, 35, 2111–2121, 2001.
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