

## ***Interactive comment on “Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden” by S. Szidat et al.***

**S. Szidat et al.**

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The discussion of the optimum procedure for analysis of OC and EC started about 30 years ago and is still ongoing. Cadle et al. (1980) proposed the evaporation of OC in an inert atmosphere and the determination of EC as the remaining fraction. In order to correct for the positive artifact in EC determination ("charring"), Huntzicker et al. (1982) coupled the thermal procedure with on-line attenuation measurements. Today, this principle technique is widely accepted for determination of OC and EC concentrations in different optical modes (TOT vs. TOR). However, it is clear that common procedures based on the evaporation of OC in helium cannot be used for chemical isolation of EC, as the charring produces additional EC so the EC measured will then be a mixture of OC and EC. Cachier et al. (1989) observed that charring is largely reduced

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if oxygen is used for the OC step, which introduces oxidation as removal process instead of evaporation. Only a few groups in the world are applying this technique for determination of OC and EC concentrations. However, a European intercomparison revealed that two-step oxidation (without optical correction) gained comparable results to TOT (with optical correction) for ambient urban PM<sub>10</sub> aerosols (Schmid et al., 2001), which underlines the reduced tendency of charring under oxidizing conditions. Another important development was the introduction of water-extraction of the filters prior to the chemothermal treatment. This procedure substantially reduces charring due to the removal of inorganic catalytic compounds and WSOC (Novakov and Corrigan, 1995; Mayol-Bracero et al., 2002; Szidat et al., 2004). The requirement of water extraction was addressed by Andreae and Gelencsér (2006) in particular for wood-burning aerosols.

Currently, we are investigating in detail the influence of charring on EC isolation for <sup>14</sup>C analysis using on-line attenuation determination (Perron et al., in preparation). With on-line monitoring of the optical properties of the filter during the thermal treatment, the effect of charring on <sup>14</sup>C analysis can be detected continuously and quasi-quantitatively. For this, we applied an OCEC analyzer (Sunset Laboratory) so that results are comparable to the TOT method. In this way, the quality of our procedure refers to a standard technique so that traceability of the results is guaranteed. Furthermore, our observation may help to uncover chemical and physical processes occurring during TOT analysis. In order to determine the impact of charring, the attenuation of filters, which is introduced additionally at the beginning of the analysis, is estimated by optical monitoring.

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Here, first results from Perron et al. (in preparation) are presented in brief.

With an OCEC analyzer (Sunset Laboratory) using typical thermal protocols, three different methods of OC removal were compared:

- 1) Evaporation in helium, i.e. according to the TOT principle [Helium],
- 2) Oxidation in pure oxygen without water extraction prior to the thermal treatment, i.e. based on Cachier et al. (1989) [O2dry],
- 3) Oxidation in pure oxygen with water extraction prior to the thermal treatment, i.e. our method of choice (Szidat et al., 2004) [O2wat].

These methods were applied to three different filters from the Göte-2005 campaign:

A) Winter/urban: 11-14 Feb 05

B) Winter/rural: 18-25 Feb 05

C) Summer/urban: 13-20 Jun 06

Attenuation was determined from on-line light transmittance measurements. In order to estimate the percentage importance of charring ( $\text{pATN}_{char}$ ), the difference of the maximum attenuation within the thermal procedure ( $\text{ATN}_{max}$ ) and the initial attenuation at the beginning of the analysis ( $\text{ATN}_i$ ) was divided by the initial attenuation:

$$\text{pATN}_{char} = (\text{ATN}_{max} - \text{ATN}_i) / \text{ATN}_i$$

We observed these values for  $\text{pATN}_{char}$  in dependence of the method (filter codes in brackets):

[Helium]: 69% (A), 121% (B), 98% (C)

[O2dry]: 7% (A), 47% (B), 32% (C)

[O2wat]: 2% (A), 4% (B), 4% (C)

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These measurements demonstrate that charring is negligible for  $^{14}\text{C}$  analysis of EC for all filter types (i.e. winter/urban, winter/rural, and summer/urban), if OC removal is performed in oxygen after water extraction of the filters. This method was applied to all the filters of the Göte-2005 campaign. (To state more precisely: Filters of the Göte-2005 campaign were analyzed using off-line attenuation measurements of the filters, which monitored attenuation changes for each pretreatment step, but not continuously. On-line attenuation measurements have been introduced only just recently. However, the results shown here indicate that charring is generally negligible with our procedure so that on-line attenuation measurements were dispensable.) Furthermore, results reveal that OC isolation in helium is inappropriate for  $^{14}\text{C}$  analysis of EC. Here, charring induces an excess of up to 121% of artificial EC. It must be noted that charred OC may have a largely different isotopic signal than EC (Szidat et al., 2004). Unfortunately, the concept of OCEC determination with the TOT procedure, which considers a split point when attenuation reaches the initial value, cannot be adapted to  $^{14}\text{C}$  analysis, because it is not clear, whether the artificial EC is totally removed before the split point or remains partially on the filter afterwards. Therefore, the main goal of the OC removal for  $^{14}\text{C}$  analysis of EC is the suppression of charring, which was optimized with our technique.

We clearly emphasize, however, that our results have to be regarded as method-dependent, as it is generally valid for all kind of OCEC analysis. Both carbonaceous particle fractions are defined by the method that is applied for their determination or, in our case, separation. Especially, the general obscurity, if and how OC and EC - two compound classes with overlapping physical and chemical properties - can be distinguished at all (Pöschl, 2005), remains further on. To our opinion, complexity of nature cannot be met perfectly by any OCEC separation approach. Nevertheless, regarding the commonly accepted simplicity of today's OCEC techniques, our method of OCEC separation for  $^{14}\text{C}$  analysis meets the current state of the art.

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