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Discussions

Interactive comment on "On the isolation of elemental carbon for micro-molar ^{14}C accelerator mass spectrometry; evaluation of alternative isolation procedures, and accuracy assurance using a hybrid isotopic particulate carbon reference material" *by* L. A. Currie and J. D. Kessler

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A. General Comments

In the manuscript "On the isolation of elemental carbon for micro-molar ^{14}C accelerator

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mass spectrometry; evaluation of alternative isolation procedures and accuracy assurance using a hybrid isotopic particulate carbon reference material", Currie and Kessler studied the behavior of a mixture of two standard reference materials (SRM 2975 Forklift Diesel Soot - nearly pure EC, negligible amounts of ^{14}C - and SRM 1515 Apple Leaves - nearly pure OC, ^{14}C/^{12}C on the contemporary level) for the purpose of quality assurance of two OC/EC separation procedures with the main focus on EC isolation for ^{14}C determination. The authors employed these methods: thermal optical transmittance (TOT) and in-house invented thermal optical kinetic (TOK), the latter eliminating OC in He/O_2 at 560 $^\circ$C and carbonate in pure He at 850 $^\circ$C prior to EC analysis using optical correction. Interpretation of isotopic, thermal-optical, and kinetic data indicated a) occurrence of artifacts from incomplete OC elimination during EC analysis for both methods, but more severe for the TOT method, b) reduction of charring for the TOK method due to the initial isothermal oxidation stage, and c) increased complexity of OC/EC separation by this simple mixture of two RMs compared to the pure materials alone.

Even if the title may suggest only a relevance for ^{14}C determinations of aerosols, this paper contributes to the identification of basic advantages and disadvantages of methods for OC/EC separation and analysis and, therefore, establishes substantial arguments on the way to the "best" procedure. Currie and Kessler, indeed, present with the TOK method an elegant solution of several problems of standard TOT methods.

B. Discussion

I think that this paper provides very valuable information. Nevertheless, it could be improved by adding some more results and discussions as follows:

1. It is important to note that the TOK method produces less charring than TOT and is, consequently, the superior procedure. However, the statement that OC elimination in an oxidizing environment results in less artificial EC was already given earlier (e.g. by Cachier et al., 1989, and Lavanchy et al., 1999), which should be mentioned.

2. The manual mixture of diesel soot and apple leaves aiming at equal amounts of fossil soot-C and biomass-C provides certain information compared to both components alone, but it is only a very rough estimate of ambient carbonaceous aerosols, which should clearly be discussed within the paper. The difference is evident due to several reasons: a) atmospheric OC and EC are internally mixed, whereas the RMs are externally mixed; b) Other studies reported on a small fraction of plant debris within the particulate matter, e.g. approximately 1.2 percent of PM_{10} (Szidat et al., 2004a) or approximately 1.8 percent for size fractions <25 μm (Puxbaum and Tenze-Kunit, 2003), whereas the applied mixture contains about half of it; thus c) the major fraction of ambient OC is not represented by this mixture; d) I assume that the particle size especially of SRM Apple Leaves is substantially larger than $PM_{2.5}$ or PM_{10}.

3. The TOK method reported in this manuscript has to me a major drawback: the temperature for stage I of 560 °C is too high. Several papers reported lower separation temperatures as optimum, namely 340 °C in pure oxygen (Cachier et al., 1989, and Lavanchy et al., 1999) or 375 °C in air (Gustafsson et al., 1997, and Szidat et al., 2004b). The lower fraction of oxygen within stage I of the TOK method (1 percent in He) compared to those methods do not justify such a temperature increase. Indeed, the authors observe a premature loss of EC (Figs. 2d and 3, discussion on page 3354, line 1) and suggest an enhanced oxidation power caused by oxygenated biomass carbon polymers (page 3354, line 7). Investigation of the OC/EC separation of the hybrid RM in dependence on the temperature of stage I is essential to proof the potential of the TOK method and should be reported in this paper. Unfortunately, the cited reference (Currie and Kessler, 1999) is hardly available. Therefore, any important additional result from that paper, which has an impact on this manuscript (especially the reason for the high temperature of stage I), should be repeated here.

4. For the TOK method, the influence of charring is only discussed for stage II, but not for stage I. It cannot be derived directly from the thermal-optical data, as this shows a monotonic decrease due to the premature losses of EC. But this doesn't mean that

there is no charring during stage I. Maybe, an isotopic balance helps. The upper estimate can be derived using the assumption that the 8 percent of RC before the split in stage III represented the charred fraction, which was introduced in stage II, leading to the case that the whole deviation of the expected and observed ^{14}C-EC was introduced during stage I; the lower estimate follows from the assumption that the 8 percent of RC before the split did not remove any of the charred fraction, leading to the case that this deviation can mainly be explained from the charring during stage II and that only a residual - if existing - can be attributed to charring during stage I.

5. The authors define a very complicated terminology. I recommend using as little terms as possible in the discussion, i.e. EC, RC, and IC. (BC is used by definition to describe the optically absorbing fraction but not any thermal or chemical resistance so that it should be avoided in this paper. The differentiation between EC and SC is confusing; only one term should be used. Carbonate-C should consequently be replaced with IC.)

6. The paper should only refer very shortly (1-2 sentences + internet site) to the work of the BC-RM Steering Committee (page 3345). The meeting mentioned in the text already took place.

7. The term “compound-specific ^{14}C measurement” for isotopic analysis of EC is misleading (e.g. 3346, footnote 2), as EC is not a compound but a sum parameter. It should be omitted.

8. The last paragraph of chapter 4.2 discusses an IC peak for RM Apple Leaves and states that no such peak was visible for RM Diesel Soot (page 3353, line 12). This is a contradiction to Fig. 1, which shows an IC peak for [D] and [A].

C. Technical corrections:

9. There is an “of” missing on page 3344, line 10.

10. The reference citation (page 3349, line 11) should be corrected to: Gustafsson et

al. (1997).

11. Page 3351, line 18: It should be “Table 1 shows”.

12. There should appear only one expression of “^{14}C measurement in EC” within the text, e.g. “^{14}C-EC”. (Compare page 3346, line 16 with page 3348, line 20.)

13. Fig. 1 can be improved using grid lines comparable to Fig. 2.

14. Captions of Figs. 5 and 6 contain detailed discussions, which should be included in the text.

D. References

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Lavanchy, V.M.H., Gäggeler, H.W., Nyeki, S., and Baltensperger, U.: Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch, Atmospheric Environment, 33, 2759 2769, 1999.

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3341, 2005.

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