

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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Manuscript revisions have been made taking into account the referee's remarks, as indicated below, together with suggestions from four official reviewers at NIST. Included in the preparation are brief corrections, new paragraphs addressing specific comments, new data for TOK concerning the effect of the isothermal oxidation temperature (includ-

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ing added Table 3), new references, a re-examination of data and uncertainty evaluations, and a minor technical correction we discovered for Fig. 7. The basic structure and substance of the paper, however, remain unchanged. Thanks are expressed to the referee and to the NIST reviewers for their many helpful questions and suggestions; thanks also to all for their courtesy in acting as “attributed” reviewers.

Responses to specific comments by the referee follow.

B. Discussion

1. The referee's suggestion has been incorporated in a slight revision of Section 3, and the reference to Lavanchy, et al., has been added to the discussion and list of references.

2. The Hybrid RM composition issues are addressed in an added note to section 2 of the manuscript. Our use of the expression “compositional relevance” was not intended to convey compositional identity. The objective in preparing the Hybrid RM was to provide a means to explore quantitatively certain measurement artifacts, linked to EC isolation for ^{14}C AMS, that may help identify and control isotopic particulate carbon EC measurement problems in a variety of environmental disciplines. To a certain extent the “compositional relevance” is analogous to that of the NIST urban dust SRM (1649, 1649a), which has served as a valuable means to explore inter-laboratory and inter-method particulate carbon measurement quality for more than a quarter of a century. Just as SRM 1649a “is not intended to be representative of the area in which it was collected,” the exploratory Hybrid RM is not intended to mirror the composition of any particular sample of real carbonaceous particles. Mean particle diameters, for example, are quite large compared to those of typical ambient carbonaceous aerosols, both for SRM 1649a (34.6 μm), and for Hybrid RM end members: SRM 1515 (ca. 75 μm), SRM 2975 (31.9 μm). Regarding the mixing ratio of the end member SRMs, this was addressed already in the third paragraph of Section 2. A relatively large proportion

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of a natural biopolymer, highly susceptible to charring, was used to emphasize the artifact, in the sense of ruggedness testing, and to ensure that a relatively small extent of biomass-C leakage would be detectable. We noted also that the end member mixing ratio employed in our exploratory study was just one of many possible combinations that may merit future study.

3. In response to the referee's request for information on the effects of the isothermal oxidation temperature, we have added a new subsection 4.2.1 (Isothermal oxidation temperature) and Table 3 (Performance characteristics as a function of isothermal oxidation temperature). Based on our experiments with the three stage TOK procedure, 560 C appears to be a good choice. Decreasing the default temperature is interesting, however, for those situations where matrix effects (as with the Hybrid RM) lead to premature EC combustion. This, incidentally, is a conclusion that Gustafsson and coworkers have come to in recent studies.

4. Charring was observed during the isothermal combustion stage for all three materials: Diesel Soot, Apple Leaves, and DiesApple – as evidenced by a common local minimum in laser transmission near the start of the isothermal region of Stage I (ca. 95 s after the start of analysis). This was most noticeable with SRM 1515, because pyrolytic char from this material was the only source of optical attenuation. We suggest that the short-lived ($\tau = 35\text{--}40$ s) kinetic component found for all three materials may represent the burn-off of the OC char, relatively early during the isothermal stage. Increased char in final stage RC for lower (isothermal) temperature TOK is consistent with an extended mean life for OC char combustion at lower temperatures, and increased char production in Stage II (IC). In a small addition to the text in Section 4.3, we show that mass balance is achieved between the OC char components of the end member SRMs and the Hybrid RM. There remain some interesting questions about the source of the biomass-C contamination RC (stage-III), which we had surmised to be primarily fossil. This ^{14}C deduced contamination was equivalent to about 3 % of the biomass-C present. These issues are addressed in a substantive addition to the

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discussion in section 4.1 of the manuscript.

5. We agree with the referee that our (EC, SC, etc.) terminology is complicated. We have followed his suggestion to simplify it, notably with the omission of BC (where possible) and SC. The “EC” determined by the two test procedures (TOT, TOK) could be considered BC, since it is identified optically (using the thermal optical split time). Our refractory carbon (RC) fractions, on the other hand, are equivalent to the residual carbon that non-optical oxidation techniques (as referenced in the third paragraph of Section 3) seek to isolate while avoiding charring. (It is noted, however, that this refractory component is labeled BC by some, even in the absence of direct optical data.) Where the revised terminology results in possible confusion, we have resorted to (transparent) subscripts: e.g., EC_TOT and EC_TOK. IC, incidentally, is not synonymous with carbonate-C. One of the primary reasons for including a high temperature inert gas decomposition stage (IC) is that extremely resistant highly condensed non-EC species exist in both fossil and biopolymer source materials – e.g (perhaps) cutin in natural vegetation. A lower IC temperature (as with TOR, as practiced) may be responsible for a systematic positive bias compared to conventional TOT – i.e., IC organic matter that escapes decomposition may then masquerade as EC in the final EC oxidation stage of analysis. (A similar observation has been published by Novakov and Corrigan (1995), as noted in a small addition we made to section 2 of our manuscript.)

6. Since a central focus of our manuscript relates to black carbon reference materials and black carbon measurement quality, mention of the International Steering Committee for Black Carbon Reference Materials is appropriate. The paragraph has been shortened and updated, however, including information on the newly opened public discussion of results of the BC Ring Trial, which is perhaps the most extensive international comparison to date of BC reference materials.

7. The “compound specific” oxymoron has been deleted.

8. The statement made at the end of section 4.2 was that no carbonate peak was

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visible for SRM 2975; it did not state that no IC peak was visible. This relates to one of the issues treated in our response to referee comment-5. The peaks visible for [A], [D], and [DA] in Fig. 1 include a carbonate component for [A] and [DA]; but the IC peak for [D] appears to reflect only the decomposition of highly refractory organic matter. Differences in the structure of these IC peaks are evident when the thermograms are enlarged, as in Fig. 4. For [D], the IC thermogram is broad and featureless, like the baseline in Fig. 4; whereas [A] and [DA] display rather narrow carbonate peaks sitting atop this relatively smooth IC baseline.

C. Technical corrections

9 - 12.. Thank you; the several corrections have been made.

13. We prefer to avoid the clutter that gridlines would bring to Fig.1. A particular problem would be interference with the vertical dashed lines used for demarcation of stages I (OC), II (IC), and III (RC).

14. We compressed the captions for Figures 5 and 6 at the referee's request, already at the earlier "technical correction" stage. In response to the current comments by the referee, we have further reduced the caption for Fig. 5; but further reduction for Fig. 6 would remove information that we believe would be immediately helpful to the reader upon viewing the figure.

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