

Interactive comment on “An Optimized Method for Determination of Water Soluble Organic Carbon and its Isotopic Composition in Aerosol Samples” by Wenqi Zhang et al.

Anonymous Referee #2

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General comments:

The manuscript shows the setup and thorough evaluation of a method to analyze ^{13}C in small amounts of water-soluble organic carbon (WSOC). This method is then applied in an interesting case study and demonstrates the high time resolution that can be achieved by analyzing such small sample amounts. Measuring ^{13}C accurately and precisely on aerosol samples as small as $5\text{ }\mu\text{g}$ is challenging and it is nice to see that the authors succeed in this. My recommendation is major revisions, because

(1) part of the system testing and of the analysis procedure needs to be explained

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much more clearly and in more detail, before it is really understandable (see specific comments), ie. Probably 1-2 additional figures are required for the supporting material

(2) All the reproducibility tests were done with standard only, but the reproducibility of actual filter samples is usually lower and this should be tested as well. Please select a couple filters (with high and low loading) and analyze them repeatedly to get a better idea of reproducibility for WSOC extracted from filter samples

(3) The writing clarity and the grammar need to be improved, see specific comments for examples, but try to proofread the whole manuscript

Specific comments:

Line 47/48: In don't understand what this sentence means and it seems out of context. What is meant by "surface layer" and does the transport refer to vertical transport (e.g. deposition) or some other transport, such as long-range transport? Unless you explain in much more detail, omit this sentence

Line 61: Please provide reference with respect to fractionation during biomass burning

Line 69-78: Please explain this in a bit more detail and avoid unclear formulations, e.g. "lighter isotopes (^{12}C) have the priority to be oxidized", eg mean that "molecules containing lighter isotopes usually react faster than molecules containing heavier isotopes" (and this is still an oversimplification, but more acceptable than what is written here; "isotope depleted matters": The matter is not depleted in isotopes, it is depleted in the heavy isotope (^{13}C), "secondary formed WSOC" = WSOC formed by secondary processes, "positive isotopic fractionation" = I think you mean enrichment here? Line 74: what does "these" refer to.

Please reformulate this entire paragraph and use as precise and correct language as possible

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Line 89: This sentence seems out of context here, please explain this in more detail in a separate paragraph

Paragraph 2.2: The description is not clear. The figure itself quite clear and informative, but the text is not. The figure contains several steps, it would help to make clear in the text, which step (e.g., 1, 2,3 . . .) you are talking about. I think for clarity, you should refer to the extract from the filters as “WSOC extract” instead of extraction. After you add the oxidizing solution you name the resulting mixture sometimes as “mixture”, sometimes as “solution”, this is confusing – choose one. Make clear that the removal of CO₂ from the mixture refers to dissolved ambient CO₂ (i.e. a cleaning step before oxidation). People, who don’t know the subject well might assume that just adding the oxidizing solution would lead to oxidation. Finally make clear (in the text) that heating in the sand bath results in the oxidation of WSOC to CO₂.

Line 126: What gases are typically in the headspace after oxidation?

Line 159: This sentence might fit better in the method section

Line 164: Here you speak about “oxidizing agents” in plural, but in the text only one (H₃PO₄), is discussed. What about the other components of the solution?

Line 167: “blank effect of H₃PO₄” unclear formulation – I think you mean that you determine the carbon content of H₃PO₄, which will introduce contamination (blank) in your analysis.

Line 170-172: To make this more clear state the procedural blank (average + std) before and after addition of H₃PO₄

Line 190: Mention again here again that KHP is a standard. It was introduced in the very beginning, but most people will not remember the abbreviation several pages later

Line 203: “overheated” sounds like too high temperature, not too long heating times

Paragraph 3.3/Figure 2: Looking at Figure 2, I cannot find the trends and effects de-

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scribed in the text. I think a statistical test would show no significant differences between concentration or $\delta^{13}\text{C}$ values at different heating times. I can also not detect that data are less scattered at 60min. Vs (10ug) is maybe more scattered at 120 min than for other heating times, but at the same time the isotope values at 120 min are much more stable. Vs - 30ug has some big outliers for 120, 90 and 30min, but no corresponding outliers in $\delta^{13}\text{C}$. On the other hand $\delta^{13}\text{C}$ (4ug) has outliers at 60 and 30 min, when Vs-4ug is particularly stable. Overall I see data point with comparable scatter and occasional outliers, I think the text over-interprets the results.

Line 221: Confusing formulation – the carbon content of the WSOC samples stays the same. Only the contamination detected during flushing is lower for samples stored less than 12 hrs ...

Line 225: purged? Do you mean “heated and analyzed”?

Line 226/227: “tested through reference gas detection” What do you mean by this?

Line 227/228: The sensitivity of a mass spectrometer does not depend on sample peaks and loading time. What do you mean by “sensitivity of mass spectrometry”?

Line 228/229: what do you mean by “decline in isotopic ratios”? A decrease in delta values (i.e. depletion)? Or a decrease in reproducibility? Or something else?

Section 3.5.1: This section describes the method for blank correction, but barely any results. Please also give the results at least in the supporting material

Line 248 – 251: Show a graph of $\delta^{13}\text{C}_{\text{meas}}$ vs $1/A$ in the appendix, what was the typical R^2 ?

Line 255-256: What were the values you obtained for $\delta^{13}\text{C}_{\text{blk}}$ and A_{blk} ? How does A_{blk} compare to A of a typical sample?

Section 3.5.2: This section is very superficially described and very difficult to understand, partially due to poor English. I’m not 100% sure what the authors are doing

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here. It definitely needs to be carefully rewritten with more precise language and more detail. But if I am not completely mistaken by the vague descriptions, this section just describes a calibration, where delta values are normalized against standard material that is treated the same way as the samples?

Line 259: I don't think "system errors" is the correct term to describe what you are investigating here, "systematic bias" is probably a better term.

Line 261/262: The logic here is reversed: Systematic errors are the cause of differences between measurements on different systems, not the other way around.

Line 264: I assume larger amounts of the standard material analyzed on the EA (presumably without pretreatment) are taken as the "correct value" against which the standard materials that have undergone the whole extraction procedure are evaluated. If this is correct, then please describe clearly.

Line 266: what do you mean by "isotope standard curve", a calibration curve? Please show an example, at least in the appendix.

Line 267: Which "two different peripherals"? This whole sentence does not make sense to me.

Line 269: I don't see raw values from EA in the figure, does the EA result not give the nominal value (horizontal line)? "Corrected results ..." In figure 3 the corrected data are labeled as: "blank corrected" but the text suggests that they are both blank corrected and normalized (calibrated). Which one is true?

Line 272: What do you mean by "dilution curves". Dilution curves do not have a precision ...

Section 3.6 This section contains a summary of the previous test results. What this section should contain is a description of how the quality of the unknown samples are assured. How is the blank correction done exactly, i.e. which values are taken for $\delta^{13}\text{C}_{\text{blank}}$ and A_{blank} ? How many and which working standards are measured

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with the samples, and how frequently i.e. was the calibration curve described above only established once, or is it measured every day? Etc . . . please re-write this section.

Line 349: At least for PM2.5, not for PM10

Line 355: What could such a source be?

Line 376: primary OC from coal combustion does not contain much WSOC

Minor comments:

Line 84: "Previous method*s*". Please have the manuscript proofread for similar grammar errors throughout

Line 162: "optimistic" – do you mean "optimal"?

Line 234: replace "blank effects of the" with "blank contribution to"

Line 235: " ..could represent" -> is proportional to

Line 411: "Exclusively" -> clearly

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1056>, 2018.

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