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Atmospheric Measurement Techniques Discussions

Interactive comment on "Towards the development of standard reference materials for soot measurements – Part 1: Tailored graphitized soot" *by* O. Popovicheva et al.

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Response to All Reviewers

We would like to than M. Viana and the two anonymous reviewers for their careful evaluation of the paper and their helpful comments and suggestions.

All three reviewers have asked for more information about the methodology that was used for sampling the reference material with the TOA technique. We have expanded that section with a more detailed description of how the material was sampled.

Secondly, two of the reviewers questioned the motivation for dividing the subject matter into two parts, i.e. the current paper being part I and a second paper, related to the first paper, as part II. As we explain in the new version of the paper, the first paper is organized to introduce the topic of soot reference materials (SRM) in general, to describe in specific detail a candidate SRM that is particularly suited for validating the TOA technique and then to illustrate how the SRM can be effectively used. The bulk of the paper is designed to convince the reader that the graphitized thermal soot (GTS) approach is a robust, repeatable technique that offers precise mixtures of EC and OC by which some of the basic differences between TOA techniques can be resolved. The second part of the theme of SRMs is a detailed evaluation of three TOA methodologies using the GTS as a means of identifying where the methodologies diverge and how the GTS can be used to reconcile the different TOA approaches. This evaluation is still in progress and may require at least another nine months to a year to complete. We felt that in the mean time it was important to publicize the availability of the GTS SRM so that interested parties could test this material with their own systems and to also offer immediate feedback to our suggestion that this approach offers the most reasonable method for testing the basic TOA methodology.

The question was also raised as to why we discuss other methods for measuring soot properties such as filter based or photoacoustic measurements of light absorption without demonstrating the response of any of these methods to the GTS. This is a valid criticism of the manuscript and we have removed most of the discussion of these techniques and focus primarily on the measurement of EC/OC.

The questions, comments and suggestions of the individual reviewers are addressed below.

Response to M. Viana

Reviewer's comment: Page 1758: The authors state the samples were "deposited" on the filters, and this is the key issue which shall determine the applicability of the

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proposed reference material. What exactly do they mean by this? Large errors may be introduced during dosage of the filters with the SRM. It is unclear to me at this point whether the SRMs are in liquid or solid form, and this should be specified. If they are solid, how is the SRM dust deposited onto the blank filter and fixed to avoid losses before the filter is introduced in the oven? If it is liquid, how is the SRM dosed to minimize losses?

Response: The revised version of the manuscript now has a more detailed description of how samples are prepared prior to the TOA. In short,

1. A clean Pallflex Quartz filter was prefired and several segments were punched from this filter with dimensions of 1.5 x 1.0 cm

2. Each punch was weighed.

3. The reference material, stored in a glass test tube was gently mixed and then a small spatula used to remove a small amount that just covers the surface of the spatula.

4. The material is transferred to the filter punch by gently tapping the spatula and spreading the material with the edge of the spatula over the center portion of the filter where the laser transmission.

5. The punch is weighed again to determine the sample weight.

6. The punch is placed in the analyzer and evaluated using the protocol that is used in all Sunset Laboratory analysis.

7. After the analysis, the punch is weighed again to determine the weight of refractory materials.

Reviewer's comment: Page 1758, line 8: it would be useful to have a measure of the "very good precision" reported, the standard deviation, number of repeats, etc.

Response: At least two punches per reference material were analyzed. The stan-

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dard deviations in the table of measured versus nominal values represent the precision of the measurement.

Reviewer's comment: Page 1758, line 10: what is the uncertainty of the nominal OC values?

Response: It is written on page 1752 of our paper: "Experience indicates that a 1-3% variation in the coating can be expected"

Reviewer's comment: Page 1758: it would be useful if the authors could provide additional data on which specific SRM they suggest to be used as an international standard, out of those listed in Table 1. Do they suggest to provide all, and each lab should pick one? Or are the different SRMs suited for different purposes? From the end-user perspective, it would be useful to know exactly which standard to use.

Response: In the summary we have now recommended that the range of OC/TC ratios that we used in the initial tests would be a reasonable set of standards. All ten would not necessarily be needed as there does not seem to be any sensitivity to the the type of OC. It is necessary to choose a set of the smaller percentages of OC/TC to establish the sensitivity of a particular TOA methodology and as high a percentage as possible to look for non-linearities.

Reviewer's comment: Page 1759, line 12: the authors state that results after 6 months were "very close to nominal". Could they provide specific data, what concentrations were measured and what ratios to the originally measured concentrations (or the nominal values).

Response: In the revised text we explain that a sample of GTS-80 that had been stored for more than six months at the Moscow University laboratory was sent back to Sunset for reanalysis. The OC/TC ratio measured for the first GTS-80 sample was 0.000549 and for the second sample it was 0.000575, compared to the 0.000 for nominal value.

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Reviewer's comment: Page 1752, line 29: "higher" should be "the highest"

Response: No. Higher means that more OC can be deposited if required.

Reviewer's comment: Page 1753, line 8: "EM" should be "SEM"

Response: Corrected

Reviewer's comment: Page 1754, line 22: "chromatogramme" should be "chromatogram". Same on page 1755, line 1

Response: Corrected

Reviewer's comment: Page 1755, line 26: the sentence "leading to a negligible amount" seems to be incomplete.

Response: Rewritten for clarification.

"The heat treatment of GTS reduces the oxygen content and water soluble fraction to 4 and 0.45 wt%, respectively, such that there are neglibible amounts of O_2 or water soluble material in GTS-6 soot (within the measurement accuracy)."

Reviewer's comment: Page 1760, line 12: insert space between "evaluation" and "of".

Response: Corrected.

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Response to Reviewer #1

Reviewer's comment: The authors present a detailed description of several instruments that allow the measurement of soot, EC, BC but without using those instruments in the validation processes. Did the authors test those techniques with the reference material? Why not including the SP2? Are those tests planned to be presented in the paper Part II? If yes, why including, in this paper, so many details about the other instruments?

Response: The authors concur and have removed the majority of the text related to the instruments that measure soot properties other than TOA that measures EC/OC. Given that at the moment the GTS SRM is best suited for excercisng TOA techniques, the Part II paper will be an extensive evaluation of these techniques using the GTS SRM and an evaluation of the SP2 and optical properties instruments will be reserved for a later time.

Reviewer's comment: What are the EC concentrations measured? It is well known that the split between EC and OC in this instrument is the major uncertainty, and from Figure 5 and 6 it can be observed that the EC concentration are far higher than those observed in the atmosphere. Is there a reference material with the level of atmospheric concentrations?

Response: EC concentration is determined as TC-OC since there is no other carbon in the produced samples. All samples of SRM were fabricated with the purpose of validating the measurement protocol for separating EC from OC, not with the idea of replicating atmospheric relevant material. In the future, the fabrication technique will allow more complex, atmospherically relevant material to be produced.

Reviewer's comment: Page 1746: It is not really clear from this paper (and from this paragraph) if there will be a common reference for all techniques or if the conclusion is already that several references will have to be used and thus the different techniques

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will not be intercompared?

Response: this point is now clarified in the introduction and the summary, i.e. that the reference material developed for TOA will not necessarily be best for validating other measurement techniques.

Reviewer's comment: Part Evaluation of SRM properties: Please indicate on which form is the ECRM and SRM, are they solid? Liquid?

Response: The SRM are always powder. This is clarified now in the text.

Reviewer's comment: Page 1758: The authors present results indicating a "good agreement". It would be useful to get a bit more information about it, for instance how many repeats have been made, what are the standard deviations between those repeats.

Response: At least two punches per reference material were analyzed. The standard deviations in the table of measured versus nominal values represent the precision of the measurement. This is now clarified in the text.

Some technical corrections:

Reviewer's comment: Page 1747, line 25: Add a "." After "al. (2008)"

Response: This section has been removed.

Reviewer's comment: Page 1755, line 12: "system of benezene" should be "system of benzene"

Response: Corrected

Reviewer's comment: Page 1756, line 18: please give a reference for the SMPS system.

Response: TSI Inc. is already referenced in the sentence.

Reviewer's comment: Page 1756, line 10: remove the "," after Gregg.

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Response: Corrected

Reviewer's comment: Page 1757, line 14-15: it is limit of qualification or limit of quantification?

Response:Corrected to be "quantification"

Reviewer's comment: Page 1760, line 11: change "evaluationof measurement" to "evaluation of measurement".

Response: Corrected

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Response to Reviewer #2

Response: The reviewer's response was primarily associated with the opinion that then paper was not sufficient to stand on its own and should not be published without the follow-on paper. Although we have addressed this opinion in general, in our opening response to the reviewers, and have also expanded the introduction of the paper to justify the separation of the two parts, we would like to address a number of the reviewer's points that we think are critical for arguing our case.

Reviewer's comment: I don't see much value in this manuscript without the proposed follow-on work. While this manuscript does describe well-enough their approach to coating soot with organics, this alone is not of great value, in my opinion. The excitement lies, as acknowledged by the authors, in using the SRM to reduce uncertainty in measurements of OC/EC mass and absorption coefficient, and ultimately uncertainty in our understanding of air pollution health impacts and climate change. This manuscript doesn't begin to take that step, and more importantly, I am not convinced that the SRM that the authors have developed will be able to reduce measurement uncertainty.

Response: Whereas we understand the reviewer's opinion and the reasoning behind it, we respectfully disagree; however, given that other readers might share this viewpoint, we have modified the paper so as to make clear why we have only focused on the candidate SRM and not on the evaluation of the SRM beyond illustrating its capability. We believe that the application of this SRM will reduce the uncertainty in measurements of OC/EC because at the moment there is no technique for validating the protocols that are use in the currently used TOA methods.

Reviewer's comment: The main uncertainty in thermal-optical analysis of OC/EC lies in the complexity of ambient OC, which is refractory and prone to forming char when heated in the thermaloptical analyzer, as summarized by the manuscript and the stud-

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ies cited. The OC/EC ratio of ambient particles ranges from approximately 50% to >95%. The OC is partly refractory and possibly light-absorbing, especially when the OC is secondary-organic aerosol or from biomass burning, and, therefore, it turns to EC-like char during thermaloptical analysis. Since the OC"EC in ambient particles, the EC-like char can be much greater in mass than the EC originally present in the particle sample, leading the large uncertainty in quantification of EC. That, in brief, is why it is difficult to measure EC. My trouble with this manuscript is that the authors do not make a convincing argument –they really don't explain it at all – exactly how their SRM will tackle the problems of the thermal-optical analysis method.

Response: Thanks to the reviewer's observations, we have expanded the manuscript to more clearly describe how the GTS SRM can serve as the first stage validation of the TOA protocols. As we point out, there are at least three types of TOA that are currently implemented around the world and all three use different protocols with respect to how they analyze the sample yet there has never been any published data that tests these protocols against one another using well characterized mixtures of OC/EC that where one can say what the exact proportion of OC and EC is. What has been shown is that the techniques differ in their separation of EC and OC, sometime quite a lot, when using ambient samples or when using "reference material" like urban dust. What has not been shown is why. All of the techniques uses sucrose or other organic material to calibrate total carbon but none of the techniques have validated that they correctly separates EC from OC because there is no reference that can be used to determine what the true answer is. This is where the GTS SRM acts as the first stage reference for evaluating the validity of the TOA protocol.

Reviewer's comment: Since their SRM has OC/EC ratios that are mostly <1% and has relatively simple OC composition that is similar to products of fossil fuel combustion – rather than the more chemically complex, refractory, and prone to forming char OC of secondary-organic aerosol and biomass smoke – it is true that their SRM is unlike

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ambient carbon-containing aerosol in composition and it is likely true that their SRM will not challenge thermal-optical analysis methods as they need to be challenged to reduce measurement uncertainty. Their simplifying step of choosing off-the-shelf OC compounds is the main problem, in my opinion (and frankly, I'm not sure there is any way to get around this problem b/c it is the complexity of ambient OC that prevents us from putting it in a bottle and using it to coat reference soots).

Response: As is already discussed, the "off the shelf" OC compounds are considered valid surrogates for the different, general, functional groups of ambient OC, as described by McFiggan et al. As we now have added to the revised manuscript, there is nothing that prevents us from creating much more complex GTS SRMs in the future, or from increasing the depth of the coating. This first paper was to introduce a unique concept that has not been previously discussed in the open literature with respect to calibrating/validating TOA techniques. What we show in the current paper, for at least the case of the Sunset TOA the response does not appear to be affected by the type of organic.

Reviewer's comment: Second, the OC coverage is more than an order of magnitude lower than in ambient aerosols. The author's have chosen an important topic, but the major flaw of this manuscript is that the benefit of the developed SRM is, in my opinion, greatly overstated and certainly unsupported by its content.

In the end, it is not clear to me that the SRM will do more than help to strictly calibrate thermal-optical analysis instruments, i.e., confirm that they quantitatively count carbon atoms. The SRM is not needed for this b/c these instruments are already suitably calibrated with sucrose or glucose samples that are easily prepared in the laboratory.

Response: We respectfully disagree. The TOA methodology is NOT suitably calibrated with sucrose or glucose sample sine they do not have EC and they do not validate or calibrate the capacity of the TOA to separate EC from OC.

Reviewer's comment: It is not clear what is the form of the SRM: is it dry powder, dry

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powder on a filter, powder suspended in a solvent?

Response: As now included in the revised text, the SRM is always in the form of a dry powder.

Reviewer's comment: Similarly, the manuscript does not explain how the SRM was applied to filters for thermal-optical analysis or suspended for size-distribution measurement, but it should clearly explain these.

Response: As now included in the revised text, the procedure of preparing the sample has been provided in greater detail.

Reviewer's comment: The manuscript concludes with a statement that the next manuscript will discuss how the SRM will be used to calibrate the thermal-optical analysis instrument, but this has already been shown in the current manuscript, the results are shown in Figure 7.

Response: No, we have only used the preliminary evaluation with a single technique to illustrate how the SRM is used to validate the methodology for separating EC from OC.

Reviewer's comment: This current manuscript, in my opinion, should tackle the real issue – the difficult problem of separating correctly OC and EC in ambient samples (as already noted above). A much more minor concern, since the manuscript really focuses on thermal-optical analysis, is that the manuscript doesn't apply the SRM to methods of measuring absorption. The discussion of these absorption methods in the introduction could, therefore, be deleted.

Response: We have removed the discussion on absorption measurements from the manuscript and now focus only on TOA since we feel that the SRM that has been developed can be immediately applied for these techniques but further development is needed to use it to calibrate/validate measurements of light absorption.

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Reviewer's comment: I found the Methodology section somewhat cumbersome to read. Perhaps partly b/c I was unable to easy follow the progression of terminology: technical carbon, GTS, ECRM, SRM, modifier, probe molecules, and partly b/c of the style: it seems like some of this section should be in the introduction (such as the first sentence and the entire second paragraph of the Methodology section). I didn't find Figure 2 very helpful.

Response: This section has been somewhat modified for clarity although we keep Fig. 2 as it is very helpful to demonstrate the homogeneity of the ECRM and this one after deposition of organic coverage.

Reviewer's comment: What is the proof for the statement made in the caption of Figure 4 – that the apparent smaller sizes are due to changes in particle diffusivity and shape?

Response: We have removed this statement as it is not relevant to the general theme of the paper and is also only speculation, as the reviewer points out.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 1743, 2010.