

Interactive comment on “On-line derivatization for hourly measurements of gas- and particle-phase Semi-Volatile oxygenated organic compounds by Thermal desorption Aerosol Gas chromatography (SV-TAG)” by G. Isaacman et al.

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We thank the reviewers for their careful reading and consideration of this manuscript. Incorporation of their comments into the structure of the methods section and accompanying figure greatly improve the readability and clarity of the improvements and instrument description. More operational information has been added to the text wherever requested by reviewers. Short and typographical edits have been made where suggested. Larger edits in response to major comments are discussed below.

C3122

Reviewer 1:

1) The Introduction is clear and gives a good account of the science however fails to give any mention to GCxGC (P7498 lin 8) which has also shown to be useful for this kind of analysis.

GCxGC has indeed been used extensively and successfully in the study of atmospheric tracers and source apportionment, including by many of the co-authors of this work. However, it fundamentally still falls under the category of "GC" and is thus included in all the benefits and complications of GC that are discussed in the introduction. We have added a reference to Hamilton et al., 2010, a recent and excellent review of some of the advancements GCxGC has contributed to this field, but we do not believe an explicit discussion of GCxGC is necessary in this manuscript as it is covered in this context under the umbrella of "GC."

3) Section 2.1.2 describes the operation of the SV-TAG system. Although the text is well structured, Figure 1 could be further clarified to aid the reader with the description. From Figure 1 anything referred to in the text should be labelled to aid the reader work through the text explanation e.g P7503 lin 10 (VP1) I feel Figure could be further clarified with the addition of more flow indication arrows or by highlighting the lines that have flow during the desorption stage in a different colour. The diagram could also show the split ratio on the diagram to aid the reader in tracing the flow paths and further understanding the operation explained in the text (e.g highlighting the percentage of flow, with arrows, at the intersection of the “Tee-Box”). Figure 1 and the text within could be made larger to aid with clarity however, this may be a typesetting issue during upload to AMTD.

Figure 1 (and caption) has been edited to show flow paths and relative flow rates during CTD1 desorption. We think that this does indeed significantly improve the clarity of this figure and the accompanying discussion and thank the reviewer for their suggestion. Minor edits to the discussion have been made to reflect these changes in Fig. 1 and

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highlight flow splits.

8) P7503 lin 7 and P7504 lin 11. 1/16" should be given in SI units

Tubing and ferrules are typically purchased and described in inches, so 1/16" is a more useful and accurate description for the reader. The SI measurement (1.6 mm) has been added for readers unfamiliar with imperial units.

9) Figure 4. Could be made larger to aid with clarity

We agree. The figure has been provided with high enough resolution to be printed larger. This request has been made of the editor.

10) There are a few instances in the text where figure and fig are used please check for consistency.

The text has been edited to follow recommended conventions ("Fig." in mid-sentence, "Figure" at beginning of sentence).

C3124

Reviewer 2:

The possibility of gas-particle-partitioning should be mentioned more clearly within the abstract thereby interested readers get quick access to this paper when searching by keywords.

Made clear by editing abstract to read: "We present here an automated in situ instrument for the measurement of highly polar organic semi-volatile and low-volatility compounds in both the gas- and particle-phase with hourly quantification of mass concentrations and gas-particle partitioning"

Later the drawbacks of denuder sampling should be mentioned – at least by citation of papers discussing it.

The collection of gas-phase compounds in this instrument is based on the methods and instrumentation described by Zhao et al. (2013b) in a publication that focused in detail on the collection and measurement of gas-phase compounds, while this manuscript focuses on extension into simultaneous dual-sample collection and analysis with derivatization. Therefore, a detailed discussion of denuders is found in Zhao et al. as is appropriate. However, since partitioning measurements are a relevant and exciting feature of the instrument presented in this manuscript, a brief discussion of the relative issues in denuder vs filter measurements has been added:

"Gas-particle partitioning is measured using a denuder-difference technique, which is expected to result in lower error than a filter-difference measurement, as is discussed in detail by Zhao et al. (2013b). Briefly, filter-based removal of particles is expected to result in adsorption and possible re-volatilization of low-volatility gases resulting in positive artifacts (Storey et al., 1995). Negative artifacts from sampling through a denuder have been suggested as a potential source of error, such as removal of particle-phase compounds from volatilization in the denuder due to the removal of the gas phase (Kamens and Coe, 1997). These artifacts are minimized in this instrument by keeping denuder residence time low (1 s). Vapors are efficiently collected and retained on the

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F-CTD through long periods of sample collection, so loss of gas-phase compounds during sampling is expected to be negligible (Zhao et al., 2013b)."

The structure of the methodical part is straight forward but quite difficult to understand and the final details of the working procedure is missing:

Due to the separated description of the different parts of the instrument it is hard for the readers to get the working principle of the whole set-up. Therefore it would be helpful to give a first brief overview in section 2.1.1 and not to give a description of the original instrument. I think this would make it much easier for the readers to understand the subsequent descriptions of the different parts.

At the reviewer's suggestion, Section 2 (the methods section) has been re-organized to avoid relying on a reader's knowledge of previous instrumentation. The focus of the paper has been added to the section overview (Sect. 2.1):

"SV-TAG measures organic compounds in both the gas- and particle-phase through collection onto a custom collection cell containing a reusable, high-surface area metal fiber filter, the implementation and operation of which is described in detail by Zhao and co-workers (2013b). Two identical cells are used in parallel to collect simultaneous measurements with and without passing through a denuder to directly measure gas-particle partitioning. Thermal desorption of these compounds includes in situ derivatization and subsequent analysis by gas chromatography/mass spectrometry. Quantification of mass concentration and particle fraction is achieved with hourly time resolution. The implementation of two important novel instrument components are described and validated here: parallel dual-cell sampling system (Sect. 2.1.2) and in situ derivatization (Sect. 2.1.3)."

We hope that this helps set the tone and make clear the advancements and purpose of this manuscript. All subsections of Sect. 2.1 have been edited to avoid language focusing on the difference of this instrument from previous instruments, instead making clear the operations and details of this instrument.

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Final settings of derivatization (fdvz and derivatization time, ...) should be a part of the method section.

Flow and timing parameters have been made explicit in the text:

Sect. 2.1.1. "Samples are transferred from the CTD to the GC/MS in a two-step thermal desorption process. First, compounds are desorbed from the cell into a stream of helium saturated with a variable quantity of derivatizing agent, ramping between 30 oC and 315 oC over 8 minutes with relatively high helium flow rates (20-150 sccm two-stage desorption flow as described by Zhao et al., 2013b). . ."

Sect. 2.1.3. "Derivatization occurs during the first 7 minutes of the two-step thermal desorption process, with the final minute purged without derivatizing agent to reduce introduction of reagent onto the GC column."

Sect. 2.1.3. "...Despite these limitations, independent control of derivatized and non-derivatized flow provides a useful tool for probing derivatization efficiency (demonstrated in Sect. 3.1) and optimizing amount of reagent used. In typical collection of ambient data, fdvz is set to the practical maximum of 0.80 to ensure complete derivatization."

Please give a short note about the ongoing GC run (temperatures, flows, . . .) after thermal desorption or give a citation.

Detailed information has been added to Sect. 2.1.1. "GC analysis of each sample occurs in 14 minutes, with a ramp of 23.6 oC min⁻¹ from 50 to 330 oC (hold 2.2 min) and a helium flow rate of 1 sccm."

C3127

Addition of Supplementary Information:

Publication of this manuscript in AMTD spurred discussions amongst co-authors and collaborating researches regarding propagation of error and detailed uncertainty analysis. In response to these discussions, a very detailed section has been added to the Supplementary Information, Sect. S3. This section details the relevant application of NIST recommended error propagation equations for linear mass calibration. These methods are applied to the case of calibration of a single SV-TAG cell, as well as reconciling differences between the two SV-TAG cells and a quantitative assessment of uncertainty in measurements of particle fraction. These calculations and discussions have been added to the Supplementary Information as they go beyond the interest of the casual reader, but are a valuable resource for anyone desiring an in depth knowledge and understanding of SV-TAG data. The estimates of uncertainty are not significantly different than those presented in the original AMTD manuscript, but they are now substantiated and refined through formal assessment. This material is highlighted in an edit to Sect. 3.3:

“...uncertainty in mass concentrations is dominated by the correction for instrument and derivatization variability. As the ratio of signal from both cells, uncertainties in variability correction combine to yield approximately 20-25

The new Supplementary Information has been included as an attachment to this comment.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/7/C3122/2014/amtd-7-C3122-2014-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 7495, 2014.