Response to the Comments of the Reviewers

Dear Editor and Reviewers,

We would like to thank you and the reviewers for the great efforts and elaborate work on this manuscript.

We revised the manuscript by responding to each of the suggestions in the reviews. In our response, the questions of the reviewers are shown in *Italic* form and the responses in standard form. The corresponding revisions to the manuscript are marked in blue. All updates to the original submission are tracked in the revised manuscript.

We appreciate your help and time.

Sincerely yours,

Xin Li and Co-authors.

College of Environmental Sciences and Engineering
Peking University
100871 Beijing China
E-mail: li_xin@pku.edu.cn
Tel: +86-185 1358 6831

Manuscript Number: AMT-2024-1203.

Manuscript Title: Optimizing Iodide-Adduct CIMS Quantitative Method for Toluene Oxidation Intermediates: Experimental Insights into Functional Group Differences.

Response to Reviewer #1

General comments

In this manuscript, the authors present an attempt to quantify toluene oxidation intermediates by establishing quantitative and semi-quantitative calibration methods for I-CIMS. Specifically, the authors established semi-quantitative equations for four distinct categories: monophenols, monoacids, polyphenol or diacid species, and species with multiple functional groups. This classification method enhances the accuracy of the semi-quantitative approach (R^2 from ~0.50 to >0.88). Overall, the research goal of this manuscript is novel and has practical atmospheric significance. The description of the calibration methods and experimental results is logical and comprehensive. After the authors address the minor comments below, the manuscript can be published in AMT.

Response:

We would like to thank reviewer #1 for carefully reading our manuscript and for your valuable and constructive comments. The manuscript was carefully revised according to the reviewer's suggestions. Listed below are our point-by-point responses to reviewer's comments. In our response, the questions of the reviewers are shown in *Italic* form and the responses in standard form. The corresponding revisions to the manuscript are marked in blue. All updates to the original submission are tracked in the revised manuscript. Lastly, we would like to thank reviewer for the positive comments again.

Comments

1. Line 42, "H3O+ ions are used for the detection of VOCs". This description here is not accurate. Conventional PTR has the ability to detect some I/SVOCs, although not many species. The newly developed Vocus or Fusion PTR can detect more I/SVOCs, some of which are oxygenated compounds (e.g., Atmos. Meas. Tech. 2019, 2403-2421).

Response:

We are sorry for the inaccurate expression. We have carefully revised this statement in the revised manuscript. Now it reads as follows:

Among them, H_3O^+ ions in conventional PTR instrument are designed to primarily measure VOCs (Yuan et al., 2017; Riva et al., 2019). However, with the inlet modifications introduced in the newly developed VOCUS or FUSION PTR instruments, the H_3O^+ ions were able to measure a large range of OVOCs (Reinecke et al., 2023; Riva et al., 2019). Moreover, NH_4^+ ions are used for the detection of oxygenated organic compounds, including alcohols, aldehydes, ketones (Hansel et al., 2018; Xu et al., 2022), NO_3^- ions are used for the detection of highly oxygenated organic molecules (HOMs) (Xu et al., 2020), I^- ions are used for the detection of compounds containing many different functional groups, including monophenols, polyphenols, monoacids, diacids, phenolic acids, keto acids, and inorganic species (Lee et al., 2014), $CH_3CH(O)O^-$ ions are used for the detection of organic acids (Hansel et al., 2018), and CF_3O^- ions are used for the detection of oxygenated organics, including hydroperoxides (Schwantes et al., 2017).

----

2. Lines 53-76, some key references are missing when introducing the calibration method of CIMS and its research progress. For example, Li et al. (Environ. Sci. Technol. 2021, 12841-12851) used 22 organic standards to calibrate I-CIMS and reduced the uncertainty in total organic carbon concentrations to ~20%-35% when combining the voltage scanning approach.

Response:

We appreciate the reviewer's comments, and we have added some literature introductions of CIMS calibration methods in the revised manuscript. Now it reads as follows:

First, the quantification of oxidation intermediates requires calibration using commercial standards. Direct calibration plays a crucial role in exploring the sensitivity characteristics of instruments and reducing the uncertainty of quantitative methods. Common direct calibration methods include the utilization of standard gas cylinders (SGC), penetrant tubes (CPT), and liquid calibration units (LCU) (Xu et al., 2022; Huang et al., 2019). Xu et al. employed 60 organic compound standards utilizing SGC and a home-built LCU method to calibrate NH_4^+ CIMS, revealing its differential sensitivity to diverse organic compounds (Xu et al., 2022). Additionally, Li et al. implemented 22 organic standards with the LCU method for I-CIMS calibration, achieving a significant reduction in total organic carbon concentration uncertainty to approximately 20%-35% when coupled with the voltage scanning approach (Li et al., 2021). However, most intermediates measurable by I-CIMS are difficult to synthesize effectively as pure standards.

----

3. Line 172, "humidity" should be "relative humidity".

Response:

Revised accordingly.

----

4. Section 3.1, it would be more straightforward to list the sensitivities in a table, probably in Table S1.

Response:

We appreciate the reviewer's comments, and we have listed the sensitivities in Table S1 in the revised manuscript.

----

5. Line 230, the sections and figures in the SI should be presented in order in the manuscript.

Response:

We appreciate the reviewer's comments, and we have combined the sections related to humidity, thereby ensuring the correct order of presentation for sections and figures. Now the sentence reads as follows:

Through the establishment of humidity-dependent parametric equations, species sensitivity under different humidity conditions can be obtained, as detailed in Section S3, Figure S3 and Figure S4. These humidity-dependent parametric equations correspond to RH_{Corr} in Equation (2), (4), and (S2).

Additionally, we have meticulously reviewed the sequence of sections and figures throughout the SI file, ensuring they were presented in order in the manuscript.

---

6. Figure 2, it is difficult to match the data points to compound names. Adding some arrows may help.

Response:

We appreciate the reviewer’s comments, and we have added some arrows in the Figure 2 to match the data points to compound names. The revised Figure 2 is depicted as follows:

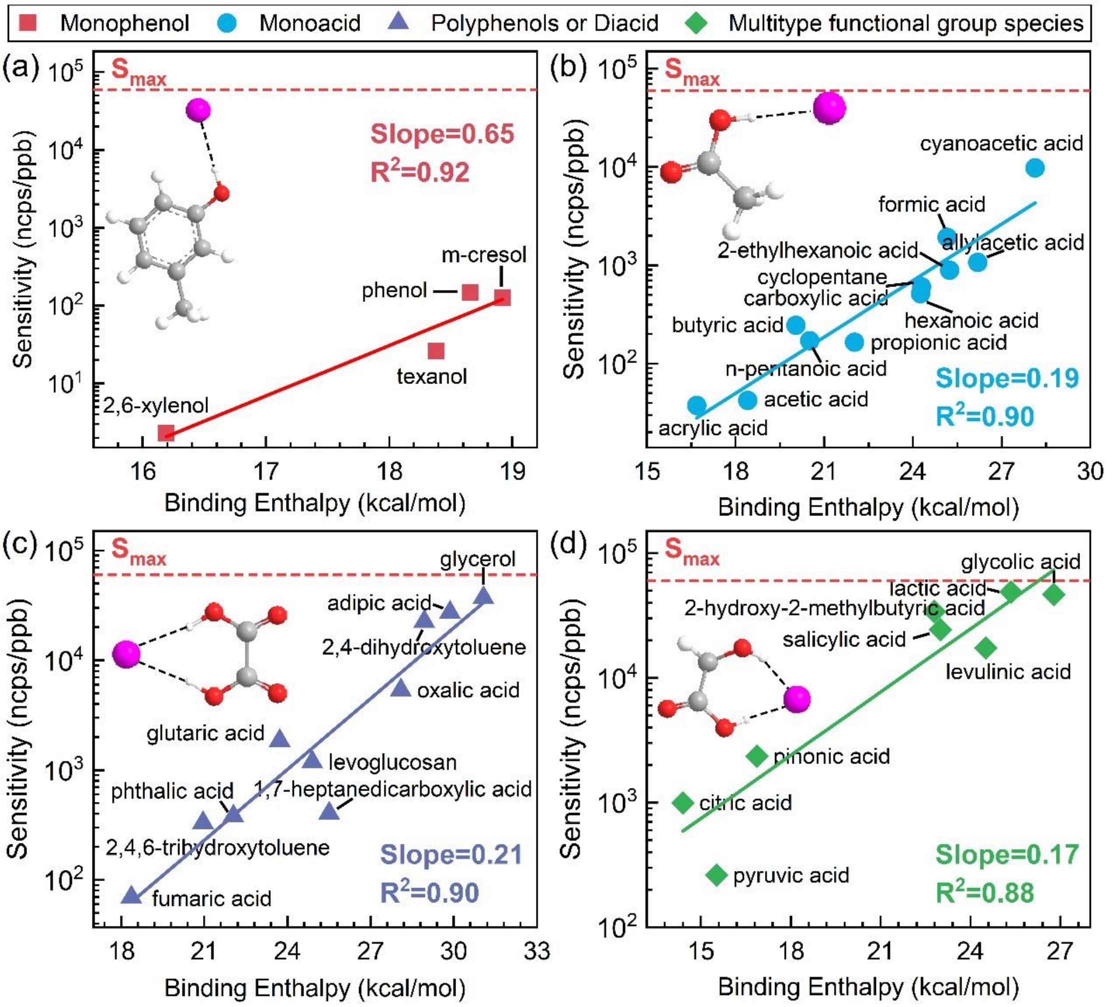

Figure 2: Fitting curve for cluster binding enthalpies and logarithmic sensitivities of (a) monophenol species (b) monoacid species, (c) polyphenol or diacid species, and (d) multitype functional group species at the B3LYP/Def2TZVP (D3) level. All sensitivity values presented in the figures were acquired under the RH condition of approximately 55 ± 5%.

---

7. Lines 363-370, could the authors show the time series of C7H8O4, C7H10O4, C7H10O5, C4H4O3, and C5H6O3 separately somewhere in the SI? It would be helpful to see the ratio of C5H6O3 to C4H4O3 as well.

Response:

We appreciate the reviewer’s comments, and we have added the time series of $C_7H_8O_4$, $C_7H_{10}O_4$, $C_7H_{10}O_5$, $C_4H_4O_3$, and $C_5H_6O_3$ separately in Figure S11. Now it shows as follows:

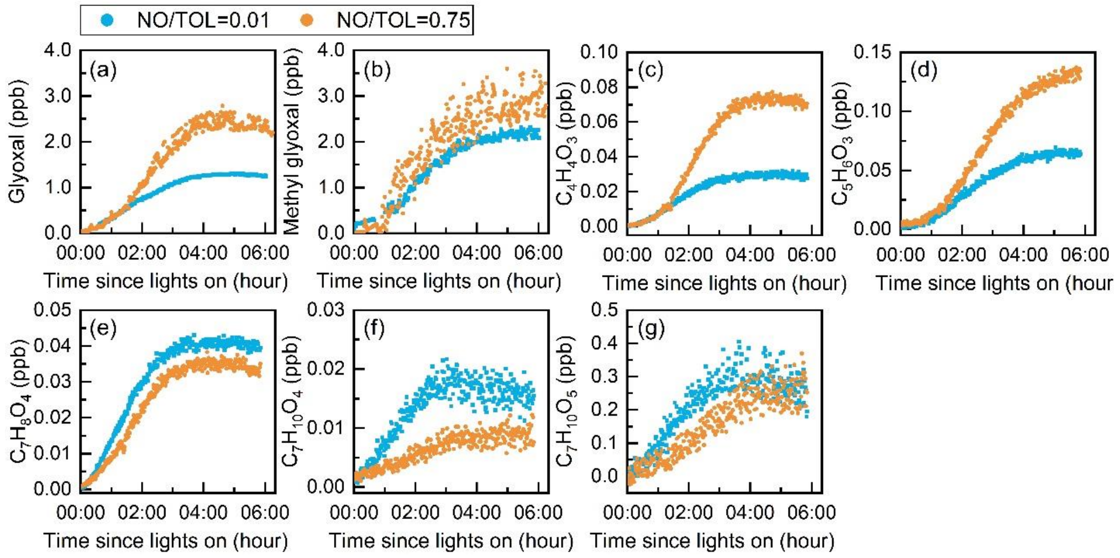

Figure S11: Time series of (a) glyoxal, (b) methyl glyoxal, (c) $C_4H_4O_3$, (d) $C_5H_6O_3$, (e) $C_7H_8O_4$, (g) $C_7H_{10}O_4$, and (g) $C_7H_{10}O_5$ during the oxidation of toluene without NO injection (blue) and with NO injection (orange). Note: glyoxal and methyl glyoxal were measured by CEAS instrument.

In addition, we calculated the ratio of $C_5H_6O_3$ to $C_4H_4O_3$, which were 3.77 and 1.70 under low and high NO conditions, respectively. Now it reads as follows:

Additionally, the study found that the ratio of $C_5H_6O_3$ to $C_4H_4O_3$ under low NO and high NO conditions was 3.77 and 1.70, respectively. These compounds were recently identified as ring-opening products originating from the 1,5-aldehydic H-shift of alkoxy radicals during the bicyclic peroxy radical pathway. The ratio of $C_5H_6O_3$ to $C_4H_4O_3$ exhibited an inverse relationship with NOx levels, similar to the case of the traditional ring-opening products $C_5H_6O_2$ to $C_4H_4O_2$ (He et al., 2023). The assumption of fixed ratios of ring-opening products in previous studies may have been due to a lack of measurement and quantification of oxidized intermediates.

---

8. Lines 401-403, there is no need to repeat these numbers in the conclusion.

Response:

We appreciate the reviewer's comments, and we have removed the duplicated sentences regarding the ratios described in the conclusion (Lines 401-403) in the revised manuscript.

---

9. Check the capitalization of the first letter. Some examples: Line 60, "Discovered"; Line 149, "Computational"; Line 213, "2,6-Xylenol and Texanol"; Compound names in Figure 2; Line 288, "Salicylic acid, Citric acid".

Response:

We appreciate the reviewer's comments. We have carefully checked the capitalization of the first letter in the manuscript and carefully revised according to the reviewer's suggestions.

Lastly, we would again express our appreciation to the reviewers and editor for their warm-hearted help. Thank you very much!!!!

References

Hansel, A., Scholz, W., Mentler, B., Fischer, L., and Berndt, T.: Detection of RO2 radicals and other products from cyclohexene ozonolysis with NH4+ and acetate chemical ionization mass spectrometry, Atmos. Environ., 186, 248-255, https://doi.org/10.1016/j.atmosenv.2018.04.023, 2018.

He, S., Liu, Y., Song, M., Li, X., Lu, S., Chen, T., Mu, Y., Lou, S., Shi, X., Qiu, X., Zhu, T., and Zhang, Y.: Insights into the Peroxide-Bicyclic Intermediate Pathway of Aromatic Photooxidation: Experimental Yields and NOx-Dependency of Ring-Opening and Ring-Retaining Products, Environ. Sci. Technol., 57, 20657-20668, https://doi.org/10.1021/acs.est.3c05304, 2023.

Huang, G., Liu, Y., Shao, M., Li, Y., Chen, Q., Zheng, Y., Wu, Z., Liu, Y., Wu, Y., Hu, M., Li, X., Lu, S., Wang, C., Liu, J., Zheng, M., and Zhu, T.: Potentially Important Contribution of Gas-Phase Oxidation of Naphthalene and Methylnaphthalene to Secondary Organic Aerosol during Haze Events in Beijing, Environ. Sci. Technol., 53, 1235-1244, https://doi.org/10.1021/acs.est.8b04523, 2019.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurten, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, Environ. Sci. Technol., 48, 6309-6317, https://doi.org/10.1021/es500362a, 2014.

Li, K., Wentzell, J. J. B., Liu, Q., Leithead, A., Moussa, S. G., Wheeler, M. J., Han, C., Lee, P., Li, S.-M., and Liggio, J.: Evolution of Atmospheric Total Organic Carbon from Petrochemical Mixtures, Environ. Sci. Technol., https://doi.org/10.1021/acs.est.1c02620, 2021.

Reinecke, T., Leiminger, M., Jordan, A., Wisthaler, A., and Müller, M.: Ultrahigh Sensitivity PTR-MS Instrument with a Well-Defined Ion Chemistry, Anal. Chem., 95, 11879-11884, https://doi.org/10.1021/acs.analchem.3c02669, 2023.

Riva, M., Rantala, P., Krechmer, J. E., Peräkylä, O., Zhang, Y., Heikkinen, L., Garmash, O., Yan, C., Kulmala, M., Worsnop, D., and Ehn, M.: Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species, Atmos. Meas. Tech., 12, 2403-2421, https://doi.org/10.5194/amt-12-2403-2019, 2019.

Schwantes, R. H., Schilling, K. A., McVay, R. C., Lignell, H., Coggon, M. M., Zhang, X., Wennberg, P. O., and Seinfeld, J. H.: Formation of highly oxygenated low-volatility products from cresol oxidation, Atmos. Chem. Phys., 17, 3453-3474, https://doi.org/10.5194/acp-17-3453-2017, 2017.

Xu, L., Moller, K. H., Crounse, J. D., Kjaergaard, H. G., and Wennberg, P. O.: New Insights into the Radical Chemistry and Product Distribution in the OH-Initiated Oxidation of Benzene, Environ. Sci. Technol., 54, 13467-13477, https://doi.org/10.1021/acs.est.0c04780, 2020.

Xu, L., Coggon, M. M., Stockwell, C. E., Gilman, J. B., Robinson, M. A., Breitenlechner, M., Lamplugh, A., Crounse, J. D., Wennberg, P. O., Neuman, J. A., Novak, G. A., Veres, P. R., Brown, S. S., and Warneke, C.: Chemical ionization mass spectrometry utilizing ammonium ions (NH4+ CIMS) for measurements of organic compounds in the atmosphere, Atmos. Meas. Tech., 15, 7353-7373, https://doi.org/10.5194/amt-15-7353-2022, 2022.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117, 13187-13229, https://doi.org/10.1021/acs.chemrev.7b00325, 2017.