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,

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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 #3

General comments

This manuscript describes the development, characterization, and application of an optimized semi-quantitative method for toluene oxidation intermediates using iodide-adduct CIMS. The method was established based on the linear correlation between instrument sensitivity to the iodide addition and theoretically calculated binding enthalpies of the formed iodide-analyte adduct for different species categories. Compared to the previous semi-quantitative method based on binding enthalpies of iodide adducts, the categorized semi-quantitative method proposed in this study appears to have a higher quantification accuracy. Although this method was developed particularly for the toluene oxidation products, the concept can be also applied to the development of the quantification method for other oxidation system. This work is scientifically sound and the manuscript is well written. I recommend its publication in AMT after several minor comments are addressed.

Response:

We would like to thank reviewer #3 for carefully reading our manuscript and for the 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 appreciate the positive feedback from the reviewer.

Comment

L100: What was the TIC value of the iodide CIMS under typical operating conditions?

Response:

We appreciate the reviewer's comments, and we have added the information of TIC value. Now it reads as follows:

During the experimental operating conditions of this study, the iodide CIMS exhibited a total ion count (TIC) of approximately 2 ions per extraction (ions/ex.) and 32,000 counts per second (cps).

L109-110: It would be more informative and readable if the method for the generation of the calibration gas (i.e., using gas cylinders, permeation tubes, or atomizing standard solutions) can be added for each standard in Table S1.

Response:

We appreciate the reviewer's comments, and we have added the information of the calibration method in Table S1 according to the reviewer's suggestions.

In addition, we actually calibrate the I-CIMS sensitivities of 37 organic compounds using certified penetrant tubes (CPT) and a home-built liquid calibration unit (LCU). Additionally, gas standards from Spectra Gas Inc. were used for the calibration of PTR-QMS to accurately measure nonmethane hydrocarbons (HMHCs), aldehydes (such as benzaldehyde), and other oxidation products that cannot be quantified by I-CIMS during chamber experiments.

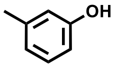
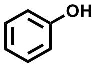
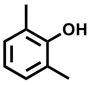
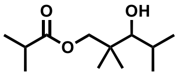
Therefore, we have improved the description of this section in the revised manuscript and the SI. Now it reads as follows:

Line 120-124 in tracked changes manuscript: In this study, 37 species with different functional group were directly calibrated using certified penetrant tubes (CPT) and a home-built liquid calibration unit (LCU), including monophenols, monoacids, polyphenols, diacids, phenolic acids, keto acids, furanones, and other species (Table S1). For OVOCs that can be customized to a standard gas and penetrant tubes, calibration is often performed using certified penetrant tubes (KinTek Inc.) at 5-6 gradient concentration levels (Huang et al., 2019).

SI: HMHCs and some oxidation products were calibrated using gas standards (Spectra gas Inc.) and certified penetrant tubes (KinTek Inc.) for PTR-QMS under experimental conditions.

Due to the length of the table, here is a brief display of the changes to the monophenol section of the table:

Table S1: Detailed information on the direct calibration of species associated with aromatic hydrocarbons and their oxidation products in this study. (Monophenol part)

Type	No.	Species	Formula	MW	Detection limit*	Sensitivity (ncps/ppb)	Structure	Methods
Monophenol	1	m-Cresol	C_7H_8O	108.06	0.083	1.3×10^2		CPT
	2	Phenol	C_6H_6O	94.04	0.108	1.5×10^2		CPT
	3	2,6-Xylenol	$C_8H_{10}O$	122.07	4.198	2		CPT
	4	Texanol	$C_{12}H_{24}O_3$	216.17	0.554	26		LCU

* The Detection limit unit is ppb in 1-seconds, S/N=3

CPT represent certified penetrant tube, LCU represent home-built liquid calibration unit.

L114: Suggest also providing the corresponding RH values at ambient pressure.

Response:

We appreciate the reviewer's comments, and we have added the corresponding RH values at ambient pressure. Now it reads as follows:

To investigate the influence of humidity on calibration, both CPT and LCU calibration system are equipped with a humidification section that can control humidity within the range of 0.12 to 22.00 mmol/mol, which corresponds to a relative humidity (RH) of 0.4% to 70% at a temperature of 25°C and a pressure of 101.325 kPa.

L117-119: Did all the standards dissolved into the solvent turn into the gaseous form after atomization? Were any particles detected in the atomized gas flow?

Response:

We are sorry for the unclear expression. In this study, all the standards dissolved in the solvent were mixed with nitrogen of a large flow rate at a microliter-level flow rate to completely evaporate the atomized droplets. No liquid condensation was observed on the wall of the mixing unit, and no particulate matter was present. After sufficient equilibration time, stable signals of standard samples could be detected in I-CIMS. We have carefully revised this statement in the revised manuscript. Now it reads as follows:

The standard sample was mixed with a soluble solvent, including water, dichloromethane, or acetone, and the solvent was atomized at a given flow rate. Subsequently, the atomized gas was mixed with high-flow nitrogen to ensure the complete evaporation of the atomized droplets, which were then injected into the sampling port. No liquid condensation was observed on the wall of the mixing unit, and no particulate matter was present. After sufficient equilibration time, stable signals of standard samples could be detected in I-CIMS.

L185: As the sensitivity of iodide ionization is strongly dependent on the RH, the authors should clearly indicate the RH conditions (dry or wet) under which the sensitivity values shown in Figures 1-3 were estimated.

Response:

We appreciate the reviewer's comments and have accordingly included the RH conditions information in the titles of Figures 1-3. The primary humidity note for the titles of Figures 1-4 is as follows:

All sensitivity values presented in the figures were acquired under the RH condition of approximately 55 ± 5%.

L307-308: Figure S8 provides a nice validation of the proposed semi-quantitative method, I would suggest moving the figure to the main text.

Response:

We appreciate the reviewer’s comments, and we have moved Figure S8 into the main text and incorporated additional validation analyses for the semi-quantitative method. The revised figure is presented as follows:

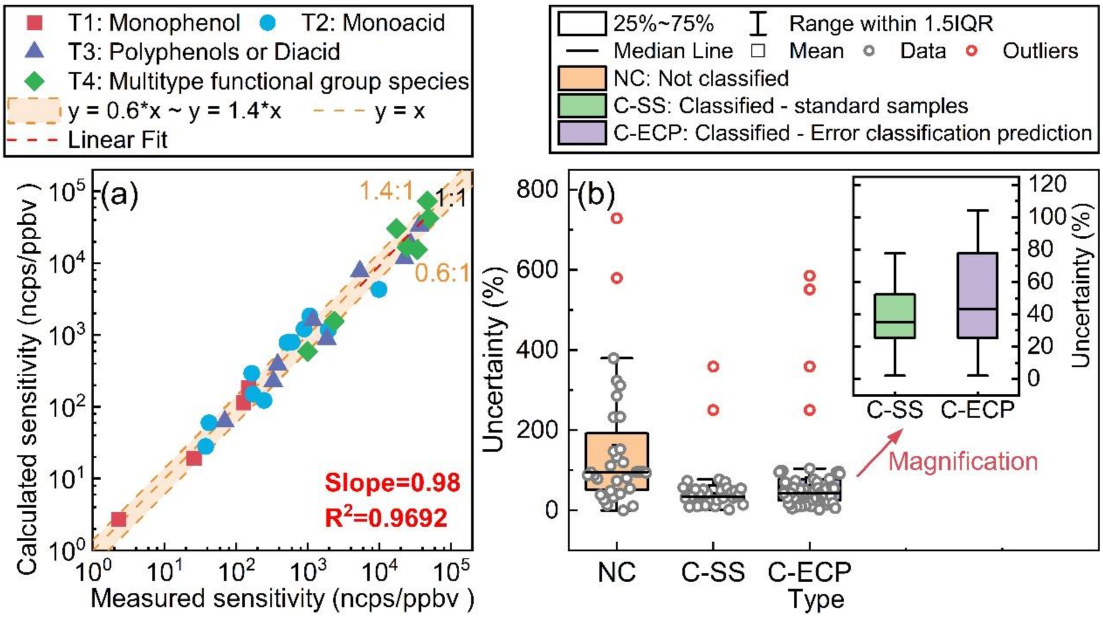


Figure 3: (a) The difference between the measured sensitivity and the calculated sensitivity for standards at the B3LYP/Def2TZVP (D3) level. (b) The uncertainty of classification-based semi-quantitative methods at the B3LYP/Def2TZVP (D3) level. The uncertainty is computed by dividing the absolute difference between the measured sensitivity and the calculated sensitivity by the measured sensitivity. All sensitivity values presented in the figures were acquired under the RH condition of approximately 55 ± 5%.

L309: "with absolute deviations below 40%". This value is actually the relative deviation.

Response:

"absolute deviations" has been replaced by "relative deviations"

L312-313: How were these uncertainties quantified?

Response:

We appreciate the reviewer's comments. In the revised paper, we have included a detailed analysis of uncertainty quantification. Now it reads as follows:

Based on the above discussion, we use the interquartile range (IQR) from the uncertainty box plot in Figure 3b to evaluate the classification-based semi-quantitative method. For species with standards, the uncertainties in sensitivity are approximately 25%-50%. For species without standards, semi-quantitative sensitivity uncertainty may increase due to improper classification. This is represented by the IQR of the error classification uncertainty prediction box plot (C-ECP in Figure 3b), ranging from 25% to 80%. Additionally, our previous studies have shown that mass spectrometric sampling losses can introduce uncertainties of approximately 10%-20% in the measurement of oxidation intermediates (Huang et al., 2019). In this study, the overall uncertainty for oxidation intermediates ranged from 30% to 85%, which is calculated as the quadrature addition of individual uncertainties.

L338-339: There may be isomers for the oxidation products identified here. Did the sensitivity values estimated here take into account the sensitivity differences between potential isomers?

Response:

We appreciate the reviewer's comments. Isomers pose a significant challenge in mass spectrometry data analysis. We have included a discussion on isomers in the revised manuscript. Now it reads as follows:

During the photo-oxidation process of precursors such as aromatics, I-CIMS measurements reveal that each formula may have many isomers (Bi et al., 2021). Therefore, in the semi-quantitative study of toluene oxidation products using a binding energy-based method, it is crucial to reasonably infer their structures. For the oxidation products of toluene, including $C_4H_4O_2$, $C_5H_6O_2$, $C_7H_8O_4$, $C_7H_{10}O_4$, $C_7H_{10}O_5$, and $C_7H_8O_6$,we first excluded furanones or aldehyde species that cannot be measured by I-CIMS among their isomers. Additionally, we excluded isomers originating from lower concentration multi-generation oxidation products. For example, in the toluene system, the $C_7H_8O_4I^-$ signal measured by CIMS reveals three isomers: first-generation products in the bicyclic RO_2 pathway, a minor fourth-generation product hydroxyquinol derived from the phenolic pathway, and a second-generation epoxy hydroxy compound from the epoxide pathway. Laboratory experiments have revealed a negligible contribution from the epoxy pathway(Zaytsev et al., 2019), and the impact of second-generation epoxy hydroxy compounds on the $C_7H_8O_4I^-$ signal can be considered negligible. Based on the reasonable inference above, we propose that the signals of $C_4H_4O_2$, $C_5H_6O_2$, $C_7H_8O_4$, $C_7H_{10}O_4$, $C_7H_{10}O_5$, and $C_7H_8O_6$ detected by I-CIMS primarily originate from the major first-generation products of the bicyclic RO_2 pathway as depicted in Figure S9. Due to their diverse functional groups, the multitype functional group species semi-quantitative equations based on the binding energy method is employed for their quantification.

For the multi-generation products $C_7H_8O_3$, $C_4H_4O_3$, and $C_5H_6O_3$, by excluding furanones and aldehydic compounds that are difficult to detect by I-CIMS, it can be inferred that the signal of $C_7H_8O_3$ primarily originates from trihydroxytoluene, the signal of $C_4H_4O_3$ primarily comes from (Z)-4-oxobut-2-enoic acid, and the signal of $C_5H_6O_3$ primarily comes from (Z)-4-oxopent-2-enoic acid and (Z)-2-methyl-4-oxobut-2-enoic acid. $C_7H_8O_3$ quantification involves semi-quantitative equations with polyphenol or diacid species, while for $C_4H_4O_3$ and $C_5H_6O_3$, which are keto acids, semi-quantitative equations incorporating multiple functional group species are used for quantification..

Furthermore, we attempted to employ voltage scanning techniques for the auxiliary identification of isomers. Isaacman et al. preliminarily explored the possible differences in the dV_{50} of isomers (Isaacman-Vanwertz et al., 2018), which may serve as an important means to distinguish and quantify isomers measured by I-CIMS. In the toluene system, the C_7H_8O produced during the reaction could originate from cresol in the phenolic pathway or from benzyl alcohol, a byproduct of the aldehyde pathway. Through voltage scanning, we observed a small difference in the voltage variation of C7H8OI- in the toluene system compared to the cresol standard samples, with dV50 values of -0.97 and -1.12, respectively. This difference may stem from the significantly higher yield of cresol, the primary product in the toluene system, compared to benzyl alcohol (Smith et al., 1998; Baltaretu et al., 2009; Ji et al., 2017), suggesting that the influence of this type of isomerization can be disregarded during the quantification process. Therefore, C_7H_8O quantification is performed using semi-quantitative equations specific to monophenol species. By comparing the voltage scanning results of $C_7H_8O_2I^-$, the oxidation products from the toluene and the dihydroxy toluene sample, and dV_{50} was 0.75 and 0.72, respectively. Therefore, these results indicated that the signal for $C_7H_8O_2I^-$ could be approximated as dihydroxy toluene in the toluene system. Therefore, C_7H_8O quantification is performed using semi-quantitative equations specific to polyphenol or diacid species.

L349: Replace "less" by "small". Also, "absolute deviations" should be "relative deviations".

Response:

Revised accordingly.

L357: How was the "satisfactory" defined or determined here? 4

Response:

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

In this study, the fitting of the experimental and simulated peak shapes exhibited a high degree of correspondence ($R^2 > 0.99$), indicating that fitting species' molecular ion peak areas using high-resolution mass spectrometry can represent the measured species signal effectively.

L360: Were the concentrations of toluene oxidation products corrected for the RH effect?

Response:

We appreciate the reviewer's comments. When establishing the semi-quantitative equation, we accounted for the impact of humidity. However, during the chamber experiments, since the humidity was consistently maintained at approximately 55 ± 5%, which coincides with the humidity condition specified for the semi-quantitative equation depicted in Figure 3, the correction factor (RH_{corr}) in the semi-quantitative process can be designated as 1. We have carefully revised this statement in the revised manuscript. Now it reads as follows:

During the chamber experiment, the humidity was maintained at approximately 55 ± 5%, which is consistent with the humidity condition established for the semi-quantitative equation in Figure 3, the correction factor (RH_{corr}) in the semi-quantitative process can be set to 1. Time series of the oxidation products in the toluene + OH system at different concentrations of NO is shown in Figure 4 and Figure S11.

L371-372: References should be provided for this statement.

Response:

We appreciate the reviewer's comments, and we have the reference in the revised manuscript. Now it reads as follows:

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 (Xu et al., 2020).

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

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