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

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Abstract. Iodide-Adduct time-of-flight chemical ionization mass spectrometry (I-CIMS) has been developed as a powerful tool for detecting the oxidation products of volatile organic compounds. However, the accurate quantification of species that do not have generic standards remains a challenge for I-CIMS application. To accurately quantify aromatic hydrocarbon oxidation intermediates, both quantitative and semi-quantitative methods for I-CIMS were established for intermediate species. The direct quantitative experimental results reveal a correlation between sensitivity to iodide addition and the number of polar functional groups (keto groups, hydroxyl groups, and acid groups) present in the species. Leveraging the selectivity of I-CIMS for species with diverse functional groups, this study established semi-quantitative equations for four distinct categories: monophenols, monoacids, polyphenol or diacid species, and species with multiple functional groups. The proposed classification method offers a pathway to enhance the accuracy of the semi-quantitative approach, achieving an improvement in R^2 values from 0.50 to beyond 0.88. Overall, the categorized semi-quantitative method was utilized to quantify intermediates formed during the oxidation of toluene under both NO-free and NO-applied conditions, revealing the differential variations in oxidation products with varying levels of NOx concentration.

1 Introduction

Volatile organic compounds (VOCs) react with oxidants (e.g., hydroxyl radical OH, ozone O_3, nitrate radical NO_3, etc.) in the atmosphere and contribute significantly to the formation of secondary organic aerosols (SOAs) (Hu et al., 2007). However, accurate prediction of SOAs remains a challenge, partly due to an insufficient understanding of SOA precursors which mainly consist of oxidation intermediates of VOCs (Bloss et al., 2005; Li et al., 2019a; Nehr et al., 2014; Ng et al., 2007). As one of

the most important VOCs in the urban atmosphere, aromatic hydrocarbons react with OH producing various intermediate products (Li et al., 2019b; Wu and Xie, 2017; Molteni et al., 2018; Schwantes et al., 2017; Wu et al., 2014), most of which are oxygenated volatile organic compounds (OVOCs). According to oxidation pathways, the intermediates can be divided into four categories (Song et al., 2021): (1) aldehyde pathway: aromatic aldehyde compounds such as benzaldehyde and methyl

35 benzaldehyde; (2) phenolic pathway: phenol, cresol, and polyhydroxy aromatic phenols, (3) bicyclic peroxy radical pathway: furanone, glyoxal, methyl glyoxal, and (4) epoxide pathway: epoxides. The intermediate oxidation products of these four pathways contain many different functional groups; therefore, the products are challenging to measure.

Chemical ionization mass spectrometry (CIMS) techniques can be used to identify nearly all semi-volatility and low volatility intermediate species (Bianchi et al., 2019; Riva et al., 2019), but appropriate ion sources need to be selected for different types

40 of intermediate products. CIMS ion sources mainly include positively charged H_3O^+(Schwantes et al., 2017) and NH_4^+(Riva et al., 2019), and negatively charged NO_3^- (Xu et al., 2020), I^- (Lee et al., 2014),$CH_3CH(O)O^-$ (Hansel et al., 2018), and CF_3O^- (Schwantes et al., 2017), etc. Among them, H_3O^+ ions are used for the detection of VOCs (Yuan et al., 2017), 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

45 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). I-CIMS has often been used in field observations and laboratory research in recent years (Lee et al., 2014; Ye et al., 2021; Isaacman-Vanwertz et al., 2018; Zhang and Zhang, 2021; Coggon et al., 2019; Wang

50 et al., 2020) because it induces minimal fragmentation (Lee et al., 2014) and shows a good detection capacity for HNO_3, N_2O_5, halogenated organic matter, and OVOCs containing carboxyl, epoxide, and multifunctional groups (Iyer et al., 2016; Dorich et al., 2021; Veres et al., 2015).

Although numerous I-CIMS applications exist for investigating VOC atmospheric chemistry, challenges associated with the qualitative / quantitative detection of critical reaction products persist (Riva et al., 2019). First, the quantification of oxidation

55 intermediates requires calibration using commercial standards. However, most intermediates are difficult to synthesize effectively as pure standards. Second, during the direct calibration process, because most of standard samples belong to semi-volatility species, they are present a liquid or solid state, which are difficult to calibrate. Some studies use Filter Inlet for Gases and AEROsols (FIGAERO) to calibrate species with very low volatility (Ye et al., 2021; Lopez-Hilfiker et al., 2014), but this process presents challenges with controlling the calibrated humidity status. In a squantificationemi-quantitative process, Iyer

60 et al. Discovered the linear relationship between the cluster binding enthalpies and logarithmic instrument sensitivities (Iyer et al., 2016). Then, Lopez-Hilfiker et al. discovered that ionization declustering analysis of iodine additions could be performed by changing instrument voltage (Lopez-Hilfiker et al., 2016). The above two semi-quantitative methods have, for the first time, achieved an approximate sensitivity analysis for species that cannot be calibrated using traditional standard calibration methods. However, the wide range of sensitivities of an iodide CIMS to different species poses a significant challenge to accurately

65   assess the sensitivity of species with different functional groups(Bi et al., 2021a). Compared to Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS), which exhibits sensitivity variations of only 0.3-0.4 orders of magnitude when measuring OVOCs (Bi et al., 2021a; Sekimoto et al., 2017), I-CIMS shows sensitivity changes of 4-5 orders of magnitude (Lee et al., 2014; Ye et al., 2021). The sensitivity of I-CIMS varies significantly across different functional group types of species, indicating that a single semi-quantitative equation is insufficient for quantifying all detected species with this

70   technique. Additionally, the complex theoretical calculation methods underlying binding energy calculations, as well as the requirement for stable product concentrations in voltage scanning, impose limitations on semi-quantitative methods. Moreover, the presence of isomers affects all mass spectrometry quantification. This results in an uncertainty in the sensitivity obtained by these methods could reach 0.5-1 order of magnitude for a single compound (Bi et al., 2021b). Even when estimating the uncertainty in measuring total oxidation product concentrations, it reaches about 60% (Isaacman-Vanwertz et al., 2018). To

75   obtain values closer to the actual sensitivity, this semi-quantitative process needs to be improved (Isaacman-Vanwertz et al., 2018; Heinritzi et al., 2016).

In this study, an in-depth exploration of quantitative and semi-quantitative methods within the I-CIMS measurement process was undertaken to enhance the identification and quantification of intermediates in the oxidation process of aromatic hydrocarbons. Direct quantitative calibration was conducted with 37 OVOC species associated with the oxidation products of

80   aromatic hydrocarbons. Based on the obtained direct quantitative sensitivity data set, we discussed the corresponding differences in the sensitivity of I-CIMS to different functional groups OVOCs. The semi-quantitative equation was established using theoretical computational methods. In order to enhance the accuracy of the semi-quantitative approach for species, a classification method was applied to species with different functional groups. In addition, the quantitative and semi-quantitative methods were applied to the experimental study on the oxidation of aromatic hydrocarbons in the chamber

85   experienments, which ensured the feasibility of this method. Additionally, this method quantified the challenging-to-quantify ring-retaining and ring-opening products formed during the oxidation of toluene, and discussed their differences in proportions under different NOx conditions.

2 Experimental Description

2.1 CIMS measurement

90   The iodide-adduct high-resolution time-of-flight chemical ionization mass spectrometry (I-CIMS) used in this study was a commercial product from TOFWERK. The sample flow was approximately 2 L/min, comparable to the primary ion flow rate. The primary ion I$^-$ was generated by introducing 3 ml/min 300 ppm methyl iodine standard gas in 2.3 L/min pure nitrogen through an X-ray source in an ion molecule reaction (IMR) chamber. The volume of the IMR chamber was 47 cm^3 and the working pressure was maintained at approximately 380 mbar. During measurements, the variation in IMR pressure is

95   controlled within ±3 mbar. In the IMR chamber, neutral molecules (X) reacted with iodine reagent ions (I$^-$) to produce different product ions (XI$^-$). The main reaction path is shown in R1:

$$X + I^- \rightarrow XI^- \tag{R1}$$

In the IMR, the sample and primary ions were mixed and interacted for approximately 120 milliseconds. Then, the mixed flow was passed through an orifice into the high-resolution time-of-flight mass spectrometry and arrived at the detector to be identified. The resolving power of the I-CIMS was 5300–5600. The data acquisition frequency of the I-CIMS instrument was 1 s.

TofWare software version 3.2.2 (Tofwerk Inc.) was used for high-resolution peak fitting of I-CIMS data. For mass spectrometry analysis, we used the single-ion peaks for I^-, H_2OI^-, HNO_3I^-, and I_3^- for mass calibration, and making the absolute in-flight deviation of the m/Q was below 5 ppm (2σ), which was much lower than the instrument guideline of 20 ppm. Then, the molecular ion peak was standardized to obtain the final signal data. The signal standardization methods are obtained using Equation (1) (Lee et al., 2014; Ye et al., 2021).

$$\text{Normalized Signal (ncps)} = \frac{\text{Signal}}{I^- + H_2OI^-} * 10^6 \tag{1}$$

2.2 Calibration method

In this study, 37 species with different functional group were directly calibrated, 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 a gas standard (Spectra gas Inc.) and certified penetrant tubes (KinTek Inc.) at 5-6 gradient concentration levels (Huang et al., 2019). The calibrated concentration ranges from dozens of ppt to several ppb levels. To investigate the influence of humidity on calibration, the calibration system is equipped with a humidification section, which can control humidity within the range of 0.12 – 22.00 mmol/mol. However, because many standard samples are liquid or solid, it is challenging to make permeable tubes that have stable permeability. Because this study focused on the gas phase reaction, an appropriate calibration system was designed so the OVOCs could be calibrated in the gasous form under normal temperature and pressure. We mixed the standard sample with a soluble solvent (such as water, carbon dichloride, or acetone), atomized the solvent at a given flow rate, and then mixed the atomized gas with nitrogen to inject into the sampling port. This calibration system is also equipped with a humidification section. The specific calibration method can be found in a study by Qiu et al (Qiu et al., 2021). In this study, the molecular weight range of directly calibrated species was 46.01 to 216.17, which covered the molecular weight range of the principal gaseous intermediates of toluene and o-cresol (48.04-203.15). The linear correlation between the normalized signal values of the directly calibrated species and the concentration was excellent, with R^2 values greater than 0.99 for most species. For species whose sensitivities could be directly calibrated, concentrations can be calculated using Equation (2):

$$[X\_ppb] = \frac{\text{Normalized signal}}{\text{Sensitivity from direct quantification} \times RH_{Corr}} \tag{2}$$

where RH_{Corr} represents the humidity correction equation.

Assuming that the random uncertainty of the CIMS detector counts follows Poisson statistics, the signal-to-noise ratio (S/N) and the detection limits for calibrated species can be calculated using Equation (3) (Bertram et al., 2011):

$$\frac{S}{N} = \frac{C_f[X]t}{\sqrt{C_f[X]t + 2Bt}} \tag{3}$$

130   Where [X] represents the detection limits (ppbv), C_f is the sensitivity factor from calibration (ncps s^{-1} ppbv^{-1}), t is the integration time (s), B represents the background normalized signal rate (ncps s^{-1}). In this study, we calculate the detection limits for all 37 calibrated species under 1 second averaging and a signal-to-noise ratio of 3. The data results are listed in Table S1.

2.3 Binding Energy Calculation Method

The semi quantitative method of I-CIMS can be established by two approaches. The first approach, referred to as the
135   binding enthalpy method, utilizes the binding energy between a given species and iodide ions to construct a parametric equation for the sensitivity. This method is extensively discussed and implemented in this study. The second approach, known as the scanning voltage method, relies on leveraging the instrument's transmission efficiency of molecular ions through the electric fields to establish the parameterized equation of sensitivity and the mass-to-charge ratio. The details of the scanning voltage method are shown in Section S1. The binding energy method for the I-CIMS instrument requires four
140   factors to be considered, i.e., the normalization of the instrument signal, binding characteristics of species and reagent ions,(Iyer et al., 2016) mass transmission correction (Isaacman-Vanwertz et al., 2018; Heinritzi et al., 2016) and humidity correction (Ye et al., 2021; Lee et al., 2014). These four factors are combined to generate a detailed semi-quantitative expression, as shown in Equation (4):

$$[X\_ppb] = \frac{\text{Normalized signal}}{\text{Sensitivity from binding enthalpy} \times \text{MassTrans} \times \text{RH}_{\text{Corr}}} \tag{4}$$

145   where MassTrans represents the mass transmission correction equation.

In this study, theoretical and computational approach were used to calculate the binding energy between the species and iodide anion. The study demonstrates that iodide anion binds with species through hydrogen bonding(Zhang et al., 2020). The primary types of hydrogen bonds that can bind with iodide anion are N−H, O−H, and C−H. The type, quantity, and various hydrogen bond binding geometries in species all influence the magnitude of binding energy. The theoretical and Computational
150   calculations were carried out using the Gaussian 16 package(Gaussian 16, 2016). The standard species and oxidation intermediates were optimized at the B3LYP/6-31G* (Petersson et al., 1988; Petersson and Al-Laham, 1991) level of theory. In density functional theory (DFT), the PBE(Perdrew et al., 1997) and B3LYP methods have been reported to perform well in the calculation of iodide anion binding energies(Zhang et al., 2020; Iyer et al., 2016). In the calculation of binding energies between iodide ions and their respective standard species and oxidation intermediates, the London-dispersion effects cannot
155   be neglected. Since B3LYP and PBE lack a description of dispersion corrections and significant improvements are achieved

with the addition of D3 dispersion corrections(Goerigk et al., 2017), this study incorporated DFT-D3 for correction in the theoretical calculation process.

Therefore, all geometrical optimization of standard species, products, and iodide ions using there theoretical methods: PBE/SDD (Schaefer, 2013), PBE/SDD-D3, and B3LYP/Def2TZVP-D3 (Weigend and Ahlrichs, 2005; Weigend, 2006) levels.

160 Vibrational frequency analyses were employed on the optimized structures to verify their representation as true energy minima on the potential energy surface, ensuring the absence of any imaginary frequency. The binding energy of the product ion (XI^-) can be defined by subtracting the computed electronic energies of iodide ions (I^-) and reference species (X) from XI^-, and taking the absolute value (Iyer et al., 2016).

2.4 Chamber Experiments

165 To test whether the oxidation intermediates of aromatic hydrocarbons could be quantitatively identified using I-CIMS, oxidation experiments were carried out in a chamber for toluene. The chamber consisted of a Teflon FEP bag with a cylindrical shape. The chamber was 3.2 meters long and 2 meters in diameter, with a practical volume of 10 m^3. It was equipped with 60 black light sources (330-400 nm) to simulate solar radiation. Nitrogen dioxide (NO_2) was used to characterize the photolysis performance of the chamber. The photolysis rate of NO_2 was estimated by a steady-state chemical actinometry method (Zou

170 et al., 2016). The photolysis rate of NO_2 (jNO_2) was 2.59×10^{-3} s^{-1} when the black light tube was fully operated. The experimental chamber layout is shown in (Figure S1). Before the experiment, the chamber was cleaned with 100 L/min dry synthetic air (made from liquid N_2 and O_2 with a ratio of 80:20, purity > 99.999%) for at least 10 hours. The humidity of the chamber was humidified to approximately $55 \pm 5\%$, while the temperature was maintained at 26 ± 1 °C. Then, VOC precursor and NO were introduced into the chamber, leading to initial toluene concentrations of 100 ppbv (without NO injection) and 80

175 ppbv (with 60 ppb NO) in the chamber. After the chamber air became stable (within 10-20 min), the lights were turned on. The wall of the chamber formed nitrous acid (HONO), and the reaction was dependent on humidity and UV radiation. The photolysis of HONO led to the formation of OH radicals ranging from 1.23×10^6 molecule cm^{-3} to 3.55×10^6 molecule cm^{-3}, which triggered the atmospheric oxidation reaction of aromatic hydrocarbons. During the chamber experiment, we often introduced synthetic air to compensate for the sampling instrument to keep the chamber volume and pressure constant (Novelli

180 et al., 2020; Poppe et al., 2007). Usually, stable and reaction-independent tracers such as acetonitrile (C_2H_3N), hexafluorobenzene (C_6F_6), and sulfur hexafluoride (SF_6) are utilized to correct for dilution in the chamber.(Chu et al., 2022) In this study, we choses acetonitrile as the dilution tracer. During the chamber experiments, I-CIMS was employed for measuring intermediate oxidation products of aromatic hydrocarbons. For detailed information on the measurement methods for precursors, NOx, O_3, and temperature-humidity, refer to Section S2.

3 Result and discussion

3.1 Sensitivity of typical toluene oxidation intermediates in I-CIMS
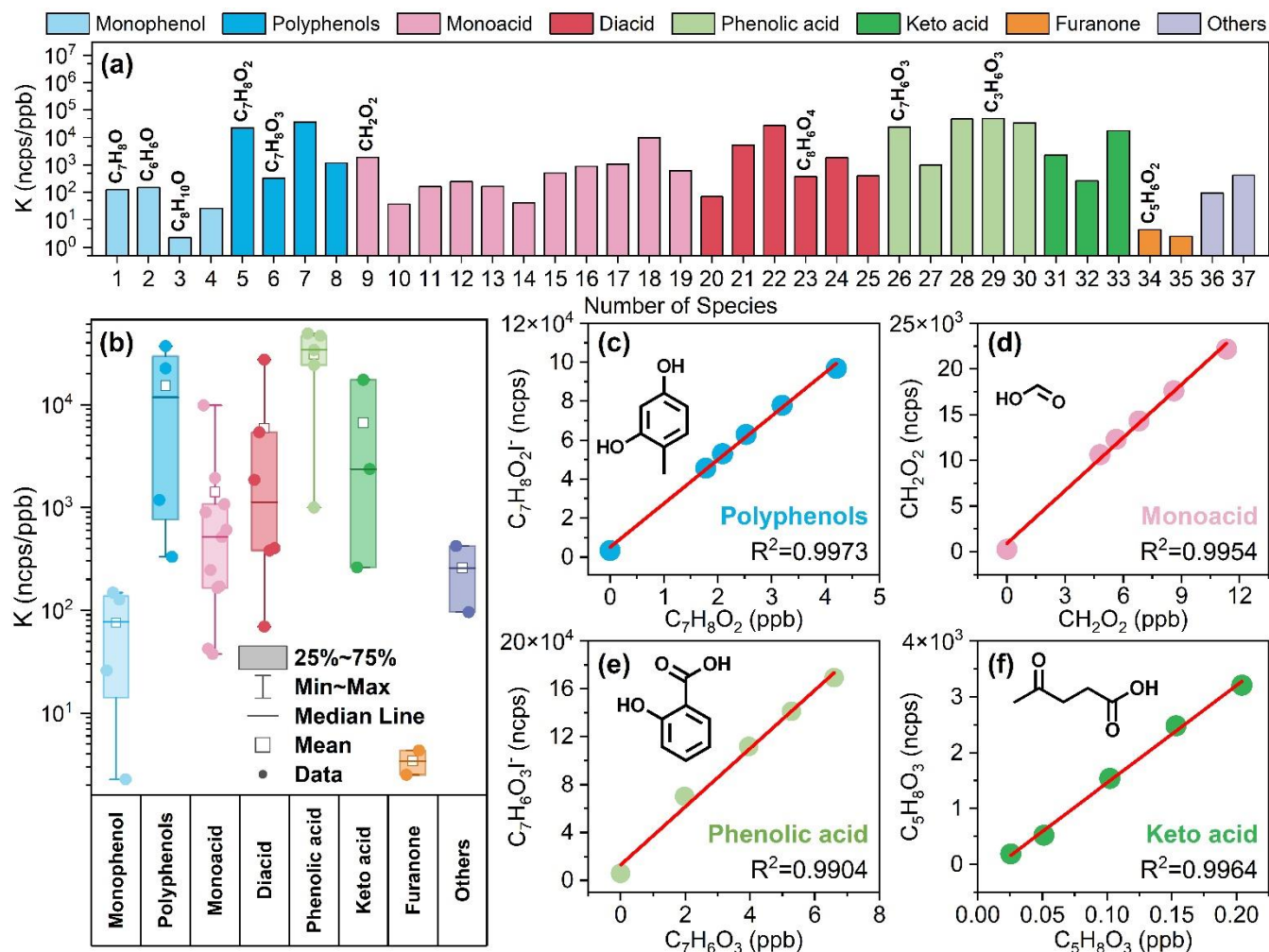
Figure 1: (a) Direct quantitation sensitivity results of 37 standard materials (b) Sensitivity statistics for standard materials containing different functional groups (c)-(f) Calibration curves of 2, 4-dihydroxytoluene ($C_7H_8O_2$), formic acid (CH_2O_2), salicylic acid ($C_7H_6O_3$), and levulinic acid ($C_5H_8O_3$). Note. Details of species with corresponding serial numbers in figure (a) are available in TableS1.

For toluene oxidation intermediates with standards, such as m-cresol, 2,4-dihydroxytoluene, and 2,4,6-trihydroxytoluene, the directly calibrated sensitivity in I-CIMS is 127.02 ncps/ppb, 22455.01 ncps/ppb, and 330.89 ncps/ppb, respectively (Figure 1). In the case of toluene oxidation intermediates lacking standards, this study explores their sensitivity characteristics through calibration with species possessing similar active functional groups. Typical oxidation products of toluene include aromatic phenols, ring-retaining phenols, ring-opening acids, ring-opening keto acids, ring-opening phenolic acids, and ring-opening

furanones, among others (He et al., 2023). To accurately investigate the sensitivity characteristics of toluene oxidation intermediates lacking standards, this study calibrated the sensitivity of the iodine adducts of monophenols, polyphenols, monoacids, diacids, phenolic acids, keto acids, furanones, and other species in I-CIMS, as shown in Figure 1 and Table S1.

200   By quantifying the sensitivity of the iodine adduction of monophenols, polyphenols, monoacids, diacids, phenolic acids, keto acids, furanones, and other species in I-CIMS (Figure 1), it was shown that iodide ions have different sensitivities for species with different functional groups due to differences in binding energies (Iyer et al., 2016). The sensitivity difference for these species ranged from 10^0-10^4 ncps/ppb, spanning over 4 orders of magnitude. Based on a comparison with previous studies (Ye et al., 2021; Lee et al., 2014), this study identified distinct sensitivity characteristics of I-CIMS towards various functional groups. As illustrated in Figure 1 and Figure S2, the sensitivity to iodine addition is correlated with the type and quantity of
205   polar functional groups present in the species, including keto groups, hydroxyl groups, and acid groups.

Among the species that contained only one active group, those containing keto groups, hydroxyl groups, and acid groups showed increased sensitivity in the order listed (Figure 1). Among them, furanone containing keto groups were the least sensitive, and the sensitivities of furfural and 3-methyl-2(5H)-furanone were 2.51 ncps/ppb and 4.34 ncps/ppb, respectively. The detection limits for furfural and 3-methyl-2(5H)-furanone are also very high (Table S1), indicating that I-CIMS does not
210   have an advantage in measuring furanones. The sensitivities of monophenolic compounds such as phenol and m-cresol were 148.48 ncps/ppb and 127.02 ncps/ppb, respectively. I-CIMS demonstrates good detection capability for phenol and m-cresol, with low detection limits of 0.11 and 0.08 ppb (in 1-second, S/N=3), respectively. However, it exhibits relatively lower sensitivity for larger mass compounds such as 2,6-Xylenol and Texanol, resulting in higher detection limits. Previous studies have also shown that I-CIMS has good sensitivity toward compounds containing carboxylic acid groups (Mcneill et al., 2007;
215   Le Breton et al., 2012; Lee et al., 2014). Similarly, here we found that the sensitivity of monoacids was higher, and the sensitivities of formic acid, allylacetic acid, and 2-ethylhexanoic acid were 1933.91 ncps/ppb, 1075.39 ncps/ppb, and 894.61 ncps/ppb, respectively. I-CIMS exhibits low detection limits for monoacids, ranging from a few to 400 ppt (Table S1), enabling the detection of species at the molecular level.

For species containing more than one hydroxyl group, sensitivity also increased with the addition of ketone, hydroxyl, and
220   carboxyl groups in the order listed (Figure 1 and Figure S2). Keto acids, with a keto group and an acid group, show significantly lower sensitivity compared to phenolic acids, which feature a hydroxyl group and an acid group. The sensitivities of pyruvic acid, citric acid, salicylic acid, and glycolic acid were 261.69 ncps/ppb, 994.43 ncps/ppb, 24308.85 ncps/ppb and 46603.18 ncps/ppb, respectively. Moreover, the sensitivity toward dicarboxylic compounds was higher than that toward monocarboxylic compounds due to the increase in the number of active groups (Figure S2). The sensitivities of oxalic acid, adipic acid, and
225   glutaric acid were 5365.33 ncps/ppb, 27280.29 ncps/ppb, and 1852.96 ncps/ppb, respectively. Species with multiple reactive functional groups exhibit high sensitivity and low detection limits, with detection limits ranging from a few ppt to 150 ppt (Table S1), demonstrating the excellent detection capability of I-CIMS for these species.

Humidity has a significant influence on the sensitivity of iodine adducts (Ye et al., 2021; Lee et al., 2014). Through the establishment of humidity-dependent parametric equations, species sensitivity under different humidity conditions can be

230 obtained, as detailed in Section S4 and Figure S4. These humidity-dependent parametric equations correspond to RH_{Corr} in Equation (2), (4), and (S1).

3.2 Establishment of classification-based semi-quantitative equations

For toluene oxidation intermediates lacking standards, semi-quantitative methods are utilized to estimate their sensitivity in I-CIMS. When establishing the semi-quantitative method based on experimental sensitivity in the toluene system, consideration

235 must be given to the four factors mentioned in Section 2.3. Alongside the previously discussed signal normalization and humidity correction, attention must be paid to mass transmission correction and the binding characteristics of species and iodide ions.

For the toluene oxidation system under investigation, this study analyzed the mass transmission effects of species within the mass range (180-350 m/z), where the primary gaseous oxidation products of toluene are located (Figure S5). It is shown that

240 within the specified mass-to-charge ratio range, the mass discrimination effect has minimal influence on the sensitivity of the target species. This impact remains similarly negligible when comparing with mass transmission curves from prior studies (Ye et al., 2021) in the 180-350 m/z range. However, for products with higher mass-to-charge ratios, it is crucial to account for mass correction using the mass transmission curves reported by Heinritzi et.al (Heinritzi et al., 2016) and Ye et. al (Ye et al., 2021).

245 When considering the binding characteristics of species and reagent ions, this study utilizes a reasonable linear relationship between the cluster binding enthalpy and logarithmic instrument sensitivity of iodine adducts (Iyer et al., 2016). This suggests that a relatively straightforward method could be used to predict the sensitivity of I-CIMS toward species with calculated binding energies. While this method is relatively simple, existing research has primarily focused on acidic species(Iyer et al., 2016). This study computed the binding energies of various functional group types, including

250 monophenols, polyphenols, monoacids, diacids, phenolic acids, keto acids, etc. However, when the logarithmic relationship was directly fitted, the correlation was poor. The correlation between experimentally observed sensitivities and calculated binding enthalpies at the PBE/SDD level did not exhibit a strong relationship (R^2=0.38). Upon correction for D3 effects at B3LYP/Def2TZVP level, the performance was enhanced, resulting in an improved R^2 of 0.50 (Figure S6). However, the correlation remained relatively weak, introducing a large degree of uncertainty to the subsequent calculations of intermediate

255 product yield. For example, when taking the phenolic pathway for toluene was examined, the yield of cresol obtained by the semi-quantitative analysis was 2.5 times lower than that obtained by direct calibration. The poorer correlation may be attributed to significant differences in the sensitivity of iodine ions to different functional group species. Earlier studies have primarily focused on acidic species, showing favourable correlations.

Given the significant selectivity distinctions of I-CIMS towards various reactive functional groups, the measured species were

260 classified into four groups: monophenols, monoacids, polyphenol or diacid species, and species with multiple functional groups for semi-quantitative analysis (Figure 2 and Figure S6). It was observed that the categorization of these species enhances the

accuracy of logarithmic fitting between binding energy and sensitivity. Higher theoretical level calculations and the inclusion of dispersion corrections enhance the quality of logarithmic fitting between binding energy and species sensitivities, as depicted in Figure S6. The B3LYP/Def2TZVP (D3) level of calculation is computationally less expensive compared to
265   DLPNO-CCSD(T) method (Iyer et al., 2016) and has shown favourable performance in describing the relationship between binding energy and experimental sensitivity of species. Therefore, this theoretical calculation level was chosen to establish a semi-quantitative equation for binding enthalpies and sensitivity.
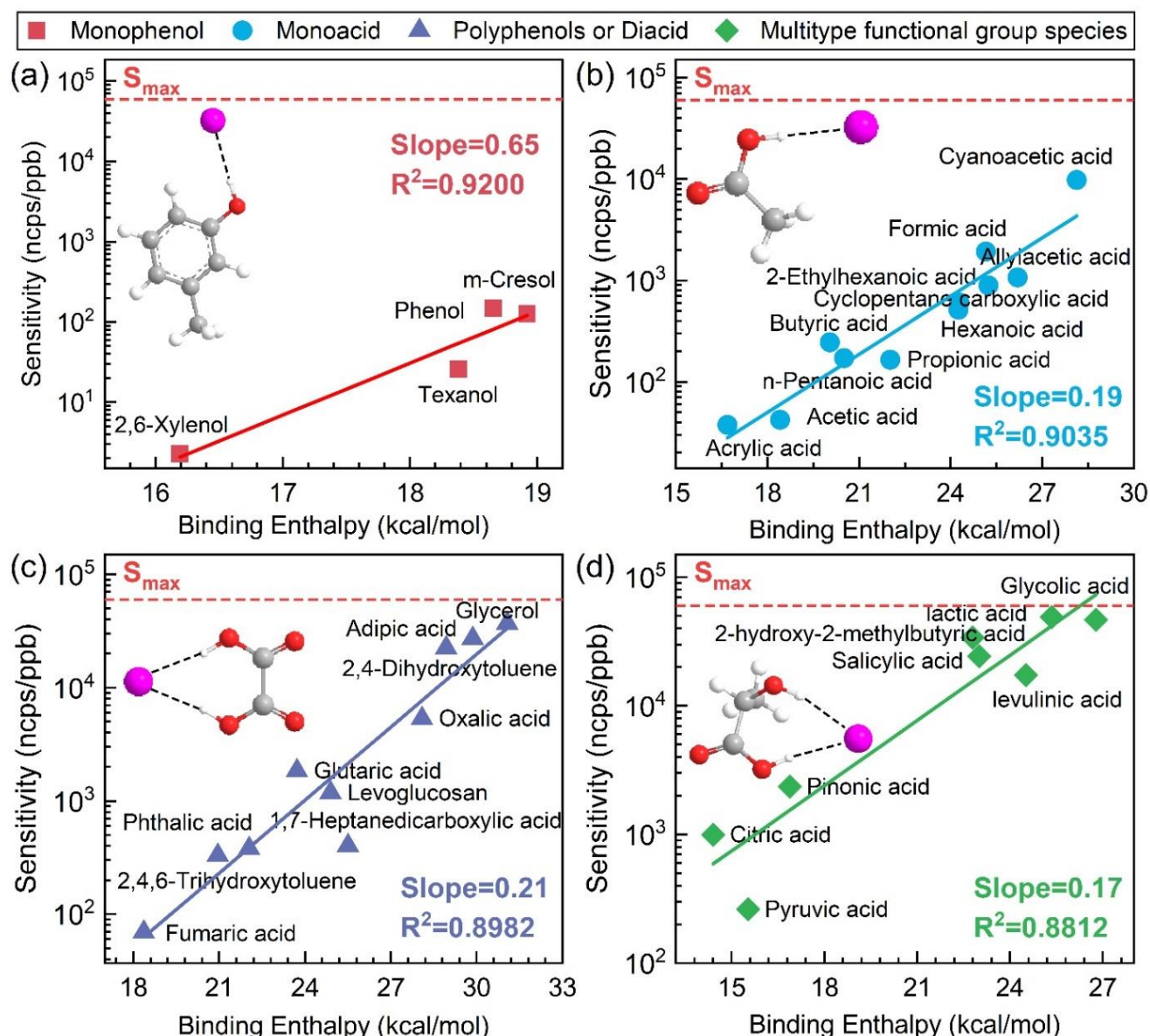
Figure 2: Fitting curve for cluster binding enthalpies and logarithmic sensitivities of (a) monophenol species (b) monoacid species,
270 **(c) polyphenol or diacid species, and (d) multitype functional group species at the B3LYP/Def2TZVP (D3) level.**

For monophenol species, with a single hydroxyl group, the most energetically favourable cluster geometry involves the attachment of the iodide ion to the hydroxyl group H via a single hydrogen bond (Figure 2a). These species include phenol, m-cresol, 2,6-xylenol, and texanol, with binding enthalpies to iodide ion between 16 to 19 kcal/mol. A strong logarithmic linear correlation is observed between binding enthalpies and sensitivity, with R^2 values of 0.92 (Figure 2a). These species
275 exhibit relatively low binding enthalpies and sensitivities. The slope of the fitting between binding enthalpies and sensitivities is higher compared to other categories, indicating a significant impact of binding energy variations on sensitivity.

For monoacid species, with a single acid group, the most energetically favourable cluster geometry involves the attachment of the iodide ion to the acid group H via a single hydrogen bond (Figure 2b).These species, such as formic acid, acrylic acid, and propionic acid, have binding enthalpies to iodide ions ranging from 17 to 28 kcal/mol. It shown a good logarithmic linear
280 correlation exists between binding enthalpies and sensitivity, yielding R^2 values of 0.90 (Figure 2b). The sensitivity and binding energy to iodide of these species are significantly higher than those of monophenol species.

Polyphenol or diacid species, compounds with multiple carboxyl and acid groups, exhibit a tendency for iodide-adduct to form two hydrogen bonds, as illustrated in Figure 2c. These species, such as fumaric acid, phthalic acid, and 2,4-dihydroxytoluene, with binding enthalpies to iodide ion between 19 to 31 kcal/mol. The fitting performance (R^2) for the correlation between
285 binding enthalpies and sensitivity is 0.90 (Figure 2c). These species, characterized by identical reactive functional groups, generally form two symmetric hydrogen bonds, resulting in higher binding energy and sensitivity.

In the case of species with multiple functional groups, typically consisting of one carboxyl group paired with either a hydroxyl or a ketone group. In the case of species containing one carboxyl group and one hydroxyl group, such as Salicylic acid, Citric acid, and lactic acid, iodide-adduct tend to form two hydrogen bonds (Figure 2d). The fitting performance (R^2) for the
290 correlation between binding enthalpies and sensitivity is 0.88 (Figure 3d). The sensitivity of these compounds is significantly higher than that of other categories, with binding enthalpies to iodide ion ranging between 15 to 27 kcal/mol.

When using semi-quantitative equations to calculate species sensitivity, the maximum sensitivity (S_{max}) is considered a reasonable upper bound limit. The maximum sensitivity of I-CIMS was empirically found to be 19-22 cps/ppt under the operating conditions of the instruments employed by Lee, Iyer, and Lopez-Hilfiker et al. (Lee et al., 2014; Iyer et al., 2016;
295 Lopez-Hilfiker et al., 2016). The maximum sensitivity (60 ncps/ppt) selected in this study refers to the findings reported by Ye et al. under similar IMR working conditions. In Figure 2, we use red dashed lines to indicate the maximum sensitivity of the I-CIMS instrument. Similarly, I-CIMS exhibits a minimum sensitivity. When the binding energy between the analyte species and I- approaches or falls below the binding energy of H_2OI^- at 12 kcal/mol at the B3LYP/Def2TZVP (D3) level, the instrument cannot detect the species.

300 By applying a classification-based approach to establish semi-quantitative equations according to different functional groups, this study significantly improved the fitting effect of the equations, raising the R^2 from 0.50 to above 0.88 and reducing the uncertainty of the semi-quantitative method. This classification method also applies to previous research findings (Figure S7), enhancing the accuracy of quantification for both monoacid and multiple functional group species, with R^2 increasing from

0.66 to above 0.90. Particularly noteworthy is the more than fivefold improvement in the semi-quantitative coefficient for
305   monoacid species (Figure S7). Therefore, classifying semi-quantitatively based on the selective differences of I-CIMS among
different species is crucial for improving the accuracy of semi-quantitative methods.

The semi-quantitative uncertainty was evaluated by comparing the difference between the theoretical and measured sensitivity
response factors, as illustrated in Figure S8. The findings indicated a satisfactory concordance between the calculated and
experimental sensitivity factors, with absolute deviations below 40%. However, the uncertainty in sensitivity obtained by
310   previous studies could reach 0.5-1 order of magnitude for a single compound (Bi et al., 2021b). Therefore, we conclude that
this method is reliable for estimating the sensitivity factors of oxidation intermediates in the absence of standards. For species
with standards, the uncertainties in sensitivity for monophenol, monoacid, polyphenol or diacid, and species with multiple
functional groups are within 5%, 10%, 5%, and 12%, respectively. For species without standards, the uncertainty in semi-
quantitative sensitivity is represented by an upper limit of 40% on the relative deviations between the theoretical and measured
315   sensitivities of calibrated species. 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 15% to 45%.

3.3 Quantification of oxidation intermediates during toluene + OH reactions

The schematic diagram of the oxidation intermediates in the toluene + OH system is shown in Figure S9. Toluene rapidly
320   reacted with OH radicals after the light was turned on. The fates of toluene with OH radicals involved hydrogen abstraction
and addition reactions (Roger and Janet, 2003). The OH hydrogen abstraction reaction was the main source of benzaldehyde.
According to the oxidation mechanism of toluene (Wu et al., 2014; Schwantes et al., 2017; Wang et al., 2017; Xu et al., 2020;
Vereecken, 2018; Song et al., 2021), the OH hydrogen addition reaction is the main pathway for toluene oxidation. The addition
product of the toluene-OH reaction (toluene-OH adducts) has more active nonaromatic double bonds which can react with O_2
325   by hydrogen abstraction and addition reactions (Suh et al., 2002; Wu et al., 2014). Toluene-OH adducts can form an aromatic
phenolic compound (cresol) by hydrogen abstraction with O_2, which is the dominant pathway for the formation of phenolic
products (Wu et al., 2014; Ji et al., 2017). Toluene-OH adducts can react with O_2 over several generation cycles to form a
series of bicyclic peroxy radical (RO_2) radicals. The bimolecular reactions of RO_2 radicals with NO, RO_2, and HO_2 can give
rise to alkoxy radicals (RO) (Jenkin et al., 2018) and ring-retaining products ($C_7H_8O_4$, $C_7H_{10}O_4$, $C_7H_{10}O_5$, and $C_7H_8O_6$), and
330   then the RO radical can form ring-opening products (glyoxal, methyl glyoxal, $C_4H_4O_2$, $C_4H_4O_3$, $C_5H_6O_2$, and $C_5H_6O_3$) through
a ring breakage reactions (Nishino et al., 2010; Wu et al., 2014). This study chose C_7H_8O, $C_7H_8O_2$, $C_7H_8O_3$, $C_4H_4O_2$, $C_4H_4O_3$,
$C_5H_6O_2$, $C_5H_6O_3$, $C_7H_8O_4$, $C_7H_{10}O_4$, $C_7H_{10}O_5$, $C_7H_8O_6$ and glyoxal, methyl glyoxal as the tracers for the oxidation of toluene
(Figure S9).
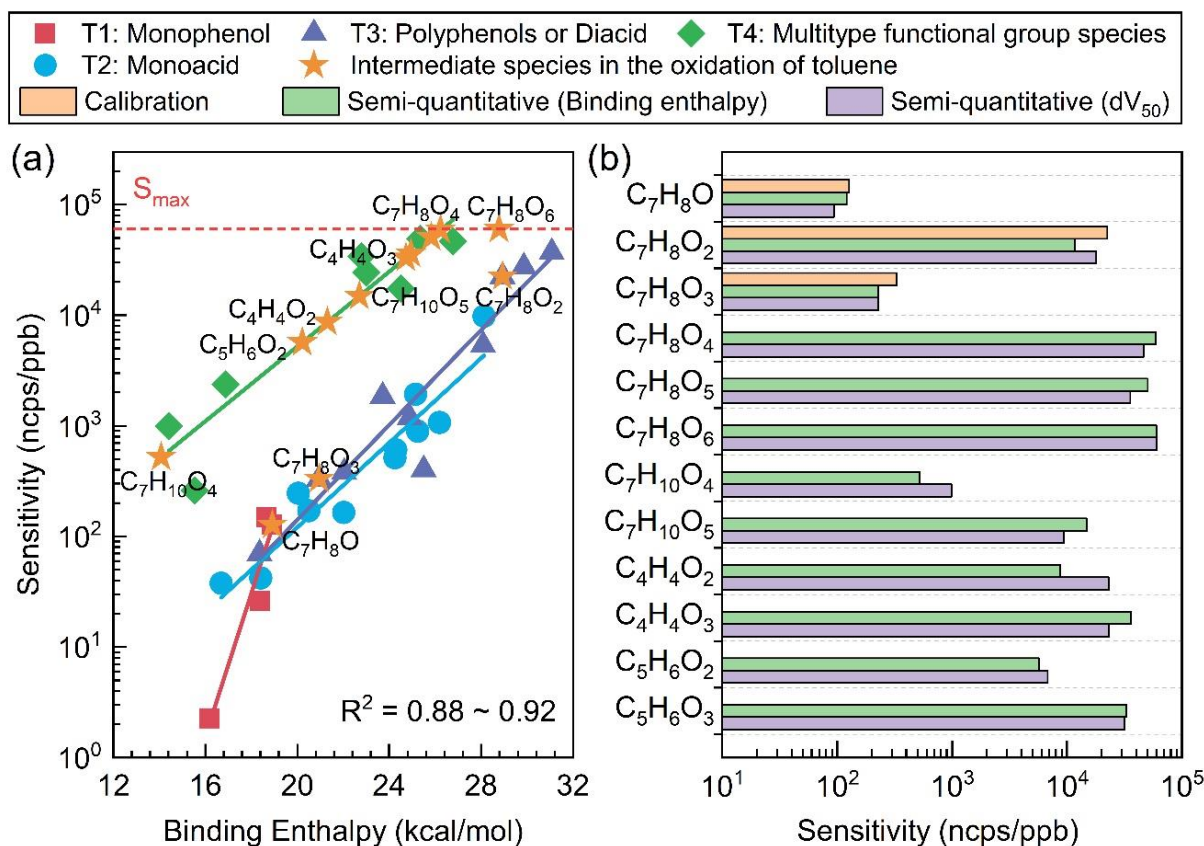
Figure 3: (a) The sensitivity results of toluene oxidation intermediates obtained at the B3LYP/Def2TZVP (D3) level. (b) The sensitivity of key toluene oxidation intermediates obtained by direct calibration, binding energy semi-quantitative, and voltage scan semi-quantitative methods.

Based on the quantitative and semi-quantitative method established in this study, sensitivity results for key oxidation products during the toluene oxidation process were obtained, as illustrated in Figure 3. This study also utilized voltage scanning as a semi-quantitative method (Section S1 and Figure S10) to validate the classification theory calculation's semi-quantitative approach. The main difference between the two semi-quantitative methods lies in their sensitivity to the concentration of the target species and its isomers. The semi-quantitative approach based on binding enthalpy relies on the rational estimation of the structure of oxidation intermediates to obtain the sensitivity of specific products. The voltage scanning method estimates sensitivity for specific formulas but faces significant uncertainties with isomers. These two methods are both influenced by the presence and distribution of isomers of the target species, which is also a bottleneck issue in all mass spectrometry semi-quantitative studies (Bi et al., 2021b). Furthermore, it is difficult to obtain voltage scan results for low-concentration products. Hence, it's challenging to provide an absolute assessment of the advantages and disadvantages of the two methods using current technology. In this study, a comparison between the two semi-quantitative methods (Figure 3) reveals that the calculated

sensitivities exhibit less differences (with absolute deviations about 40%), thereby supporting the feasibility of the

350 aforementioned semi-quantitative methods.
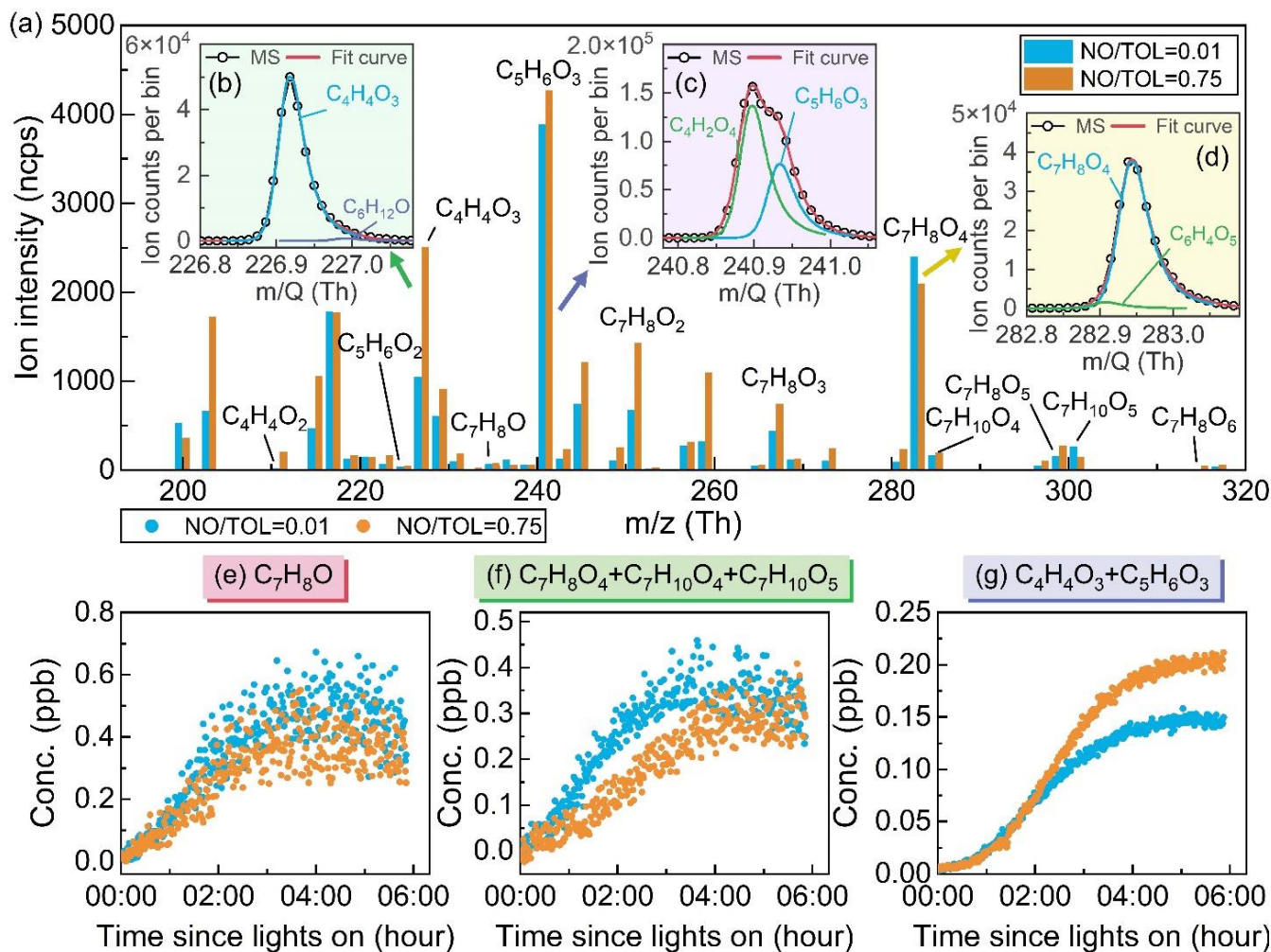
Figure 4: (a) A one-second averaged high-resolution mass spectrum of intermediates during the oxidation of toluene. Identification of toluene oxidation products: (b) $C_4H_4O_3$, (c) $C_5H_6O_3$, and (d) $C_7H_8O_4$ in the mass spectrum. Time series of (e) C_7H_8O, (f) $C_7H_8O_4$ + $C_7H_{10}O_4$ + $C_7H_{10}O_5$, (g) $C_4H_4O_3$ + $C_5H_6O_3$ during the oxidation of toluene. Note: NO-free condition (blue), NO-applied condition

355 **(orange).**

The toluene oxidation intermediates were identified through high-resolution peak fitting analysis using the TofWare software, as illustrated in Figure 4. In this study, the fitting of experimental and simulated peak shapes was satisfactory, indicating that fitting species' molecular ion peak areas using high-resolution mass spectrometry can represent the measured species signal effectively. Time series of the oxidation products in the toluene + OH system at different concentrations of NO is shown in

360 Figure 4 and Figure S11. After the light is turned on, the rapid generation of cresol can reach a peak of 0.4-0.5 ppb within 4 hours (Figure 4e), followed by a subsequent decline as it reacts with OH radicals. The trend of cresol formation shows little

variation with different NO/TOL ratios. However, there is a significant difference in the trend of formation and concentration for typical ring-retaining products, such as $C_7H_8O_4 + C_7H_{10}O_4 + C_7H_{10}O_5$, and typical ring-opening products, such as $C_4H_4O_3 + C_5H_6O_3$, glyoxal, and methylglyoxal in bicyclic peroxy radical pathway (Figure 4f-g and Figure S11). To remove the
365 influence of precursor concentration, a ratio method was employed for comparative analysis. Under NO-free conditions, the ratios of $C_7H_8O_4 + C_7H_{10}O_4 + C_7H_{10}O_5$ to $C_4H_4O_3 + C_5H_6O_3$, glyoxal, and methylglyoxal were 2.40, 0.27, and 0.16, respectively. Under NO- applied conditions, the ratios of $C_7H_8O_4 + C_7H_{10}O_4 + C_7H_{10}O_5$ to $C_4H_4O_3 + C_5H_6O_3$, glyoxal, and methylglyoxal were 1.17, 0.10, and 0.09, respectively. This indicates that in the presence of high NO concentrations in the toluene oxidation system, the distribution of bicyclic RO_2 products tends to favour the ring-opening pathway. Additionally, the study found that
370 the ratio of $C_5H_6O_3$ to $C_4H_4O_3$ under NO-free conditions and NO-applied 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
375 intermediates. The impact of NO concentration on oxidation products has been a focal point in aromatic hydrocarbon oxidation studies, but this is beyond the scope of this work. It is hoped that the quantitative method proposed in this study will hold significance for subsequent research in quantifying the influence of NO concentration on oxidation products.

4 Conclusion

In this study, tracers for oxidation intermediates in the toluene + OH reaction system were identified and quantified by an
380 iodide time-of-flight chemical ionization mass spectrometer. Based on the experimental results and intermediate product characteristics of toluene oxidation system, detailed quantitative and semi-quantitative studies were conducted. Direct quantitative methods were used to measure intermediates that had available standards, such as cresol, dihydroxy-toluene, and trihydroxy-toluene. This study directly calibrated the sensitivity of various species including monophenols, polyphenols, monoacids, diacids, phenolic acids, keto acids, furanones, etc., with sensitivity ranging from 10^0-10^4 ncps/ppb, and detection
385 limits mostly ranging from a few to 300 ppt. The study indicates a correlation between sensitivity to iodine addition and the type and quantity of polar functional groups in the species, including keto, hydroxyl, and acid groups. For species with a single active group, sensitivity is observed to be in the order: keto group < hydroxyl group < acid group. Similarly, for species containing more than one hydroxyl group, sensitivity increased with the addition of polar functional groups in the order: keto group < hydroxyl group < acid group.
390 A detailed semi-quantitative method based on binding energies was established for intermediates for which standards were not available. Given the significant selectivity differences of I-CIMS towards various reactive functional groups, this study employs a classification approach to optimize the binding energy-based semi-quantitative method. The measured species were classified into four groups: monophenols, monoacids, polyphenol or diacid species, and species with multiple functional groups

for semi-quantitative analysis in the B3LYP/Def2TZVP (D3) level. The categorization method improves the accuracy of

395 logarithmic fitting between binding energy and sensitivity, yielding R^2 values exceeding 0.88. This categorization method simultaneously reduces the uncertainty of semi-quantitative sensitivity. For species with standards, sensitivity uncertainties range from 5% to 12%. For species without standards, the upper limit of uncertainty in semi-quantitative sensitivity is 40%, determined by relative deviations between theoretical and measured sensitivities. After accounting for sampling losses, the overall uncertainty for oxidation intermediates ranged from 15% to 45%.

400 Using the optimized I-CIMS quantitative method, quantitative measurements of intermediates formed during toluene oxidation under both NO-free and NO-applied conditions were obtained. Without NO, the ratios of $C_7H_8O_4 + C_7H_{10}O_4 + C_7H_{10}O_5$ to $C_4H_4O_3 + C_5H_6O_3$, glyoxal, and methylglyoxal were 2.40, 0.27, and 0.16, respectively. With NO, these ratios shifted to 1.17, 0.10, and 0.09, respectively. The research findings experimentally demonstrate the perspective that increasing NO concentration in the toluene oxidation system enhances the ring-opening pathway of bicyclic RO_2 products. The ratio of

405 $C_5H_6O_3$ to $C_4H_4O_3$ was 3.77 under NO-free conditions and 1.70 under NO-applied conditions, showing an inverse correlation with NOx levels. This contrasts with findings from traditional MCMv331 mechanism studies. Therefore, optimizing semi-quantitative methods for precise quantification of oxidation products can facilitate deeper exploration of aromatic hydrocarbon oxidation mechanisms.

This study aims to provide an optimized approach for establishing quantitative and semi-quantitative equations for measuring

410 sensitivity with I-CIMS from a classification perspective. As this study primarily examines aromatic hydrocarbon oxidation systems, the choice of calibration species tends to prioritize aromatic hydrocarbon oxidation products or standard species with analogous functional groups. However, for other experimental systems, more experimental calibration data on species are needed for verification.

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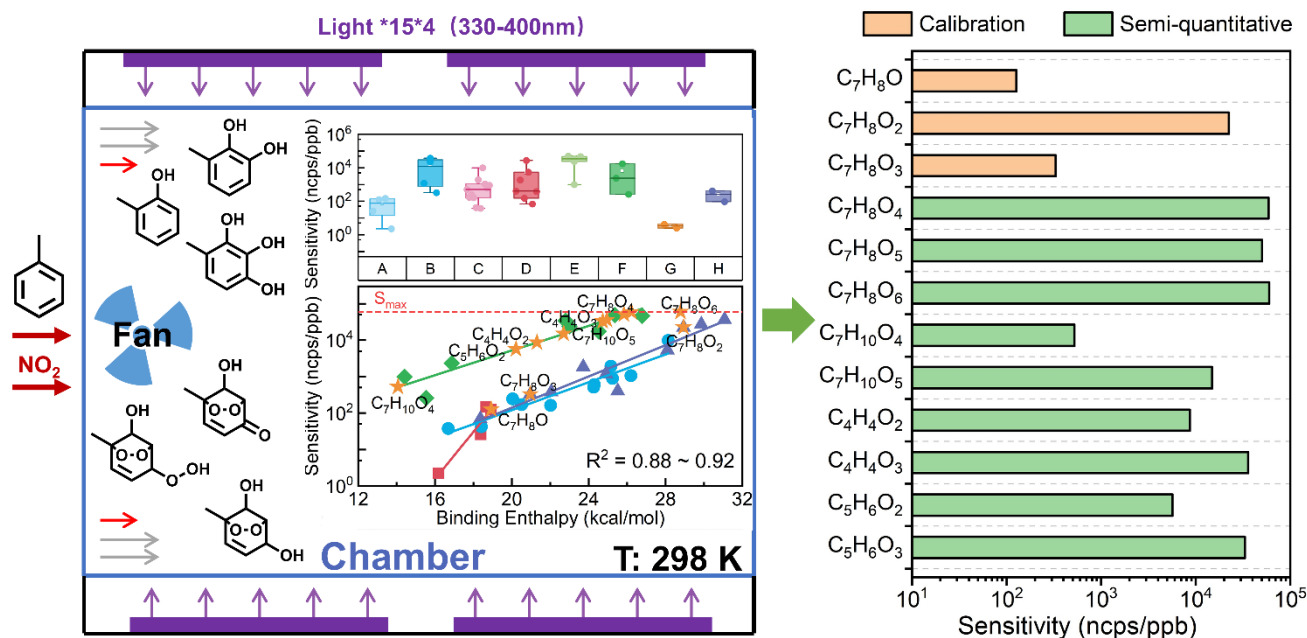
Graphical abstract

Data availability

The underlying research data can be accessed upon contact with the corresponding author (Xin Li: li_xin@pku.edu.cn).

Author contribution

X. L. and Y.L. designed and organized the experiments, supervised the data analysis, and edited the manuscript. M.S. and S.H. performed the experiments and analyzed the data. M.S. prepared the manuscript. Y.L., S.R.L., and Y.Z. contributed to the conception of this study. S.H.L., L.Z. contributed to the data reduction of VOCs measurements.

Competing interests

The contact author has declared that none of the authors has any competing interests.

Acknowledgements

This work was supported by the Beijing Municipal Natural Science Fund (JQ21030) and by the National Natural Science Foundation of China (Nos. 91844301, 91644108).

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