1 2	Response factor of a Q-ACSM to chamber generated SOA with different average oxygen content
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18	Abstract
19	The response factor (RF) of a quadrupole based aerosol chemical speciation monitor (Q-ACSM) for
20	secondary organic aerosols (SOA) has been investigated in this work. SOA were generated under simulated
21	photochemical oxidation conditions in a 4.5 m ³ Teflon chamber from three different volatile organic compounds
22	(VOC): α -pinene, isoprene and toluene, representing both biogenic and anthropogenic VOCs. For some

23 experiments, different degrees of average oxygen content of SOA, indicated by the ratio of m/z 44 signal over total

24 organic ion signal intensity (f_{44}), were obtained by changing the ratio of the VOC precursors to the oxidants (O₃ or 25 OH). An aerosol particle mass analyzer (APM) and a scanning mobility particle sizer (SMPS) were used to 26 determine SOA effective density (ρ_{eff}) and volume concentrations. Relative response factor (RRF) of the Q-ACSM 27 to organics was determined by dividing Q-ACSM measured mass (the relative ionization efficiency (RIE_{ore}) and 28 organic collection efficiency (CEorg) were set to default values of 1.4 and 0.5, respectively) by SMPS-APM deduced 29 mass (amended by aerodynamic lens transmission efficiency (E_L) and particle loss due to non-spherical shape (E_s)). 30 Our results showed that RRF for a specific type of SOA anti-correlated with f_{44} regardless of the VOC precursors. RRF decreased from 2.16 to 0.81 when f_{44} increased from 0.057 to 0.191. Meanwhile, ρ_{eff} increased from 1.09 to 31 1.34 g cm⁻³, implying more compact structure for more oxidized SOA. The anti-correlation between RRF and f_{44} 32 33 might be due to the decreased RIE_{org} or CE_{org} for more oxidized SOA. To further explore the actual cause, 34 ammonium sulfate (AS) seed particles were injected into the chamber before SOA were produced. After the 80 nm 35 AS particles were fully coated with SOA (coating thickness > 18-25 nm), CE of the aerosol changed from CE_{AS} 36 (0.285 ± 0.067) to CE_{org} of the SOA shell. The experiment showed that CE_{org} decreased from 0.882 to 0.313-0.475 37 when f_{44} increased from 0.127 to 0.209, possibly caused by a phase change of SOA from liquid to solid/glassy. The variation of CE_{org} with f_{44} could explain a large fraction of the observed decrease in RRF, while the influence of 38 39 RIE_{org} cannot be excluded. The trends in RRF and CE_{org} for Q-ACSM were in accordance with those done with the 40 high-resolution aerosol mass spectrometer (AMS), demonstrating the capability of the low-resolution Q-ACSM in 41 doing SOA laboratory studies and the necessity to calibrate RF when conducting laboratory SOA experiments.

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43 Key words: Organic Aerosols; ACSM Calibration; Relative Response Factor; Collection Efficiency; Average
44 Oxygen Content

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46 **1. Introduction**

47 Organic aerosols (OA) have been recognized as a major component of ambient particulate matters, 48 contributing 20-90% to the total submicron particles around the world (Kanakidou et al., 2005; Salcedo et al., 2006; 49 Zhang et al., 2007; Hallquist et al., 2009), which can substantially affect the climate directly by interacting with 50 solar radiation and indirectly by affecting cloud microphysics (IPCC, 2014). Recent studies demonstrated that haze 51 events in China were largely driven by secondary organic aerosols (SOA) (Huang et al., 2014) and may exert 52 significant adverse effects on human health (Poschl, 2005; Poschl and Shiraiwa, 2015). The chemical composition 53 and the dramatic changes of OA in ambient aerosol remain less understood compared to the inorganic species. 54 Measurement of OA has been a challenging task not only for the fact that OA contains nearly countless chemical 55 species but also due to its relatively short lifetime and rapid transformation in the atmosphere.

56 A powerful method, known as aerosol mass spectrometry (AMS) has been successfully developed and 57 widely deployed to do real time size-resolved aerosol measurements (Jayne et al., 2000). A typical AMS is equipped 58 with a set of aerodynamic lens (Liu et al., 1995a, b) to effectively focus and transmit particles (~50-1000 nm) (PM₁) 59 into the instrument, a time-of-flight (ToF) chamber to determine the aerosol size, a thermal vaporizer (heated to 60 $\sim 600^{\circ}$ C) to evaporate non-refractory (NR) components into the gas-phase, and a 70 eV electron impact (EI) 61 ionization source to ionize the gaseous samples before they can be analyzed by a mass analyzer (either a quadrupole 62 or a time-of-flight mass spectrometer) (Jayne et al., 2000; DeCarlo et al., 2004). Evidently, compared to previous 63 filter-based techniques, AMS can provide elemental composition of the organic species and can achieve much 64 higher time and size resolution. More recently, a newer version of AMS, i.e., the aerosol chemical speciation 65 monitor (ACSM) was developed (Ng et al., 2011a). ACSM is basically a simplified AMS without the aerosol ToF 66 chamber and thus is much smaller and affordable. Although ACSM cannot obtain high resolution mass spectra, 67 elementary information can still be readily recovered from some symbolic fragments, such as $C_n H_{2n\pm 1}^+$ (*m/z* 27, 29, 41, 43, 55, 57, 69...) and CO_2^+ (*m/z* 44), representing hydrocarbon-like organic aerosol (HOA) and oxygenated 68 69 organic aerosol (OOA) (Ng et al., 2011a). Specially, f_{44} is widely used to reflect the average oxygen content in OA 70 (Ng et al., 2010; Ng et al., 2011b; Canagaratna et al., 2015). Therefore, ACSM is especially suitable for long term field operation. Nevertheless, Aerodyne AMS/ACSM have been widely used to conduct researches on NR-PM₁
around the world in both field and chamber studies (Zhang et al., 2007; Mohr et al., 2009; Zhou et al., 2016).

73 Although the performance of AMS/ACSM has been demonstrated to be in accordance with many other 74 measuring techniques (Drewnick et al., 2003; Takegawa et al., 2005; Kondo et al., 2007; Jimenez et al., 2016), the 75 quantification of aerosol composition by AMS/ACSM still needs to be further refined. In theory, the accuracy of 76 AMS/ACSM measurements is affected by particle collection efficiency (CE), molecule ionization efficiency (IE), 77 fragmentations during thermo-vaporization and EI ionization (70 eV) processes, and ion transmission efficiency 78 inside the mass analyzer (Jayne et al., 2000; Allan et al., 2003; Jimenez et al., 2003; Canagaratna et al., 2015). With 79 the last two influencing factors well understood and calibrated, response factor (RF) of AMS/ACSM to a specific 80 species is mainly determined by CE and IE. In practice, AMS calibrations in terms of CE and IE were mostly 81 conducted with inorganic species. The calibration factors for organics were indirectly inferred and could be highly 82 uncertain for laboratory generated SOA (Jimenez et al., 2016). Typically, RF for OA (RF_{org}) is determined indirectly 83 using ammonium nitrate as reference and could be mathematically expressed as the product of three factors:

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$$RF_{org} = IE_{NO3} \cdot RIE_{org} \cdot CE_{org}$$
(1)

i.e., IE_{NO3} is the ionization efficiency of nitrate; RIE_{org} is the relative ionization efficiency of OA to nitrate and CE_{org} is the collection efficiency of OA. IE_{NO3} can be calibrated with SMPS and is independent from the properties of OA. However, the other two terms may vary with different OA species.

CE is mainly composed of three parts: E_L (the transmission efficiency of particles as a function of vacuum aerodynamic diameter (d_{va}) through the aerodynamic lens), E_s (to account for the disperse loss of non-spherical particles from the main air stream), E_b (to account for the bouncing loss of particles from the vaporizer surface). Among these, E_L can be explicitly taken into account by applying transmission efficiency in the aerodynamic lens, E_s is usually near unit for most particle types according to previous beam width measurements, and E_b is usually the most variable and uncertain part (Huffman et al., 2005; Salcedo et al., 2007). Based on inter-comparisons in sulfate measurements among AMS, particle-into-liquid-sampler/ion chromatography system (PILS-IC) and other

95 instruments, a default CE of 0.5 for all compounds has been recommended with the assumption that particles are 96 internally mixed (Drewnick et al., 2003; Takegawa et al., 2005). Although organics quantified using a default CEorg 97 of 0.5 has been found correlating well with independent organic carbon (OC) or VOC measurements in most field 98 works (Allan et al., 2004; de Gouw et al., 2005; Takegawa et al., 2005; Venkatachari et al., 2006; Middlebrook et 99 al., 2012), studies have shown that CE_{org} can vary substantially for various chamber generated organic particles (Bahreini et al., 2005; Docherty et al., 2013). Similarly, OA is assigned with a default RIE_{org} of 1.4. However, RIE_{org} 100 101 has been suggested to be significantly different for different OA species (Jimenez et al., 2016; Murphy, 2016). For 102 instance, it appears that RIE_{org} for primary OA (POA) are significantly different from those for SOA (Slowik et al., 103 2004; Dzepina et al., 2007; Jimenez et al., 2016). Any uncertainty associated with RIE_{org} may lead to erroneous 104 AMS/ACSM measurement results, especially in the case of interpreting aerosol samples from various environments 105 around the world. Therefore, comprehensive researches on the CE_{org} and RIE_{org} for different SOA species are of 106 practical importance to constrain the AMS/ACSM measurements.

Some methods have been introduced to quantify or constrain the side-effects of RIEorg and CEorg in AMS 107 108 measurements. For example, light scattering-based detections make it possible to directly measure aerosol CE 109 (Cross et al., 2007; Docherty et al., 2013; Robinson et al., 2017; Xu et al., 2018). However, the laser can only be 110 used for larger particles ($d_{va} > 200$ nm). Most recently, a new type of capture vaporizer has been developed to achieve a unit CE (Hu et al., 2017). RIE_{org} can be directly measured with this capture vaporizer (Xu et al., 2018). 111 112 Nevertheless, the determination of RIE_{org} and CE_{org} appears to be a complicated but essential issue for accurate 113 AMS/ACSM OA measurements that necessitate further investigations, including to explore new ways of SOA 114 standard generation and to constrain the measurement uncertainty with various measurement techniques.

In this work, RF of a quadrupole based ACSM (Q-ACSM) for chamber-generated SOA under atmospheric relevant conditions was investigated. Three different VOC precursors (i.e., α -pinene, isoprene, and toluene) were chosen to represent biogenic (α -pinene and isoprene) and anthropogenic (toluene) VOC. The mass concentrations of the SOA standards were precisely determined by a SMPS-APM system according to the first principle. RF_{org} and CE_{org} of Q-ACSM to SOA with different average oxygen content were quantified by comparing Q-ACSM measured mass concentrations with SMPS-APM deduced mass concentrations for SOA produced by both homogeneous nucleation of organics or condensation of organics on dry AS seed particles. The effects of SOA average oxygen contents, roughly indicated by f_{44} , on RF_{org} and CE_{org} of the Q-ACSM were investigated.

123 2. Experimental Methods

124 2.1 Chamber Setup

A 4.5 m³ collapsible atmospheric-pressure fluoropolymer (Teflon) smog chamber (L = 1.8 m; W = 1.5 m; 125 H = 1.7 m (see Fig. 1) was used to generate SOA. The chamber was essentially the same as the one used in our 126 127 previous work and has been described in detail elsewhere (Yao et al., 2014; Yuan et al., 2017). Before each 128 experiment, the chamber was flushed with pure air generated by a zero-air generator (Aadco 737, USA) until the particle concentration was less than 10 cm⁻³. Reactants and scavengers (if used) were introduced into the chamber 129 130 through a T-shaped glass bulb by zero air. The glass bulb was heated gently to ensure complete injections. A Teflon-131 coated fan was installed at the bottom center of the smog chamber. It was operated for 15 seconds after all reactants 132 were injected to the chamber to achieve rapid mixing. The chamber temperature and RH were maintained at $20 \pm$ 1°C and 10-15%, respectively. 133

All the detection instruments were sampling from the same outlet which was located in the opposite side of the inlet. The sampling tubing of SMPS, APM and Q-ACSM were kept at the same length to achieve identical diffusion losses. During the experiments, no zero air was injected into the chamber and the amount of air in the chamber would decrease over the time. The total sampling flow rate was ~1.6 liters per minute (LPM). The experiments usually lasted for 4-7 hours, resulting the total consumption of chamber air of ~0.7 m³. Therefore, a constant pressure inside the collapsible Teflon bag could be maintained during the experiments.

140 2.2 SOA Generation

During each experiment, known amount of α-pinene (Sigma-Aldrich, >98%), isoprene (Sigma-Aldrich,
 >99%), or toluene (Sigma-Aldrich, >99.5%) was firstly dissolved into cyclohexane (TEDIA Inc., HPLC grade

143 >99.5%) and then was injected into the chamber through a stream of zero air. Ozone was generated by exposing 144 pure oxygen (O₂) to a low-pressure mercury (Hg) lamp (Jelight, Model 600). When O₃ was used as the oxidant, an 145 OH radical scavenger, cyclohexane, was injected into the chamber before the experiment. When OH was used as 146 the oxidant, trace amount of methyl nitrite was firstly injected into the chamber and then the black light bulbs around 147 the chamber were turned on (Yao et al., 2014). The mixing ratios of O₃ inside the chamber were monitored 148 continuously by a Thermo Fisher Scientific ozone monitor (Model 49i) throughout each experiment. Different f_{44} 149 were achieved by changing the ratio between the VOC precursor and the oxidants (O₃ or OH).

150 2.3 Instrument Operation

151 The sampling interval of the Q-ACSM was set to be 8-15 minutes, depending on the particle mass 152 concentration generated in the chamber. The sampling line was a piece of stainless steel tubing with an inside 153 diameter (ID) of ~0.4 cm and a length of 0.8 m. The vaporizer temperature of the Q-ACSM was set to be 585 ± 2 154 [°]Cwhich was within the recommended operation temperature range for aerosol measurements (Jimenez et al., 2003). 155 The sampling flow rate, aerodynamic lens alignment, m/z calibration, m/z-dependent ion transmission efficiency 156 of the quadrupole mass spectrometer were well calibrated by following the manufacture's recommendation (see 157 Supplementary Information for details). The lens pressure was kept at 1.22 ± 0.02 throughout the experiment. The 158 response factor of NO₃⁻ (RF_{NO3}) was calibrated before the experiment using atomized 300 nm NH₄NO₃ particles 159 following the procedure described in previous studies (Fig. S1) (Jayne et al., 2000; Ng et al., 2011a). E_L as a function 160 of d_{va} was calibrated with 200-600 nm (d_m) NH₄NO₃ particles (Fig. S2).

161 A scanning mobility particle sizer (SMPS), consisting of a differential mobility analyzer (DMA, TSI Model 162 3081) and an ultrafine condensation particle counter (UCPC, TSI Model 3776), was used for real-time monitoring 163 of the particle number size distribution with mobility diameter (d_m) ranging between 15 nm and 650 nm. The 164 sampling time interval was 3 min. An aerosol particle mass analyzer (APM, Kanomax Model 3601) combined with 165 a DMA (TSI Model 3081) and an ultrafine condensation particle counter (UCPC, TSI Model 3776) were used to 166 determine the particle effective density (ρ_{eff}) (McMurry et al., 2002; DeCarlo et al., 2004). During each experiment,

167 the diameter of the particles analyzed by APM was manually set to be the same as the peak value of the particle 168 number size distribution measured by the SMPS, as the particles were continuously growing in the chamber. Before 169 applying this measured ρ_{eff} to the whole size distribution, ρ_{eff} of particles in all sizes at the same moment were 170 assumed to be the same. Each DMA-APM scan took ~5 min. The flow rates and the voltages applied to the DMAs were well calibrated before the experiments. Three sizes of polystyrene latex (PSL) spheres (81 ± 3 nm, 147 ± 3 171 nm, 269 ± 5 nm) with a density of 1.05 g cm⁻³ were nebulized with an atomizer (TSI, Model 3076) and then dried 172 by a diffusion dryer filled with silica gel for size calibration of the SMPS system. The same PSL spheres were also 173 174 used for the calibration of APM (see Fig. S3). The bias of SMPS size and APM effective density measurements 175 were within $\pm 4\%$ and $\pm 3\%$, respectively.

176 2.4 Calculation Method

To elucidate how Q-ACSM measured mass concentration (PM_{ACSM} , using default $RIE_{org} = 1.4$ and $CE_{org} =$ 0.5) may deviate from the true mass concentration for particles entered Q-ACSM (PM_{SMPS} , the product of E_L and E_S -amended SMPS-measured volume concentration and APM-measured ρ_{eff}), relative response factor (RRF) is defined as the ratio of PM_{ACSM} to PM_{SMPS} . The calculated RRF is thus proportional to the real RIE_{org} and CE_{org} . Any non-unit value of RRF might be caused by the deviation of RIE_{org} or CE_{org} from the default values.

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$$RRF = \frac{PM_{ACSM}(assuming \ def \ ault \ RIE_{org} = 1.4, CE_{org} = 0.5)}{PM_{SMPS}(amended \ by \ \rho_{eff}, Es, E_L)} = \frac{RIE_{org} \cdot CE_{org}}{1.4 \cdot 0.5}$$
(2)

183
$$PM_{SMPS} = V_{SMPS} \cdot \rho_{eff} \cdot E_L \cdot E_s = \sum_{i=1}^n \{\frac{\pi}{6} d_{m,i}^3 \cdot dN_i \cdot \rho_{eff,i} \cdot E_{L,i} \cdot E_{s,i}\}$$
(3)

Eq. (3) is used to calculate PM_{SMPS} , where V_{SMPS} is the volume concentration calculated with SMPS measured size distribution; n is the total number of bins for SMPS measurements; $d_{m,i}$ and dN_i are respectively the geometric mean diameter and the number of counts in size bin i; $E_{L,i}$ and $E_{S,i}$ are the aerodynamic lens transmission efficiency and the non-spherical shape influence for particles of $d_{m,i}$. After taking into account the effects of $E_{L,i}$ and $E_{S,i}$, any deviation in CE_{org} should be caused only by particle bounce on the vaporizer surface (E_b). The measured E_L in this work (Fig. S2) is in reasonable agreement with previous studies (Jayne et al., 2000; Knote et al., 2011; Hu et al., 2017), while larger than other reports (Liu et al., 2007) as for 300-1000 nm (d_{va}) particles. d_m and d_{va} are inter-convertible via $d_{va} = d_m \cdot \rho_{eff} / \rho_0$ for a reference density ρ_0 of 1000 kg m⁻³ (Jayne et al., 2000; DeCarlo et al., 2004). The uncertainties of $d_{m,i}(\pm 4\%)$, $dN_i(\pm 10\%$ for 20-200 nm and $\pm 20\%$ for 200-800 nm particles) (Wiedensohler et al., 2012; Wiedensohler et al., 2018), ρ_{eff} ($\pm 3\%$), E_L ($\pm 10\%$) and E_s ($\pm 5\%$) were all considered in the calculation. As a result, the relative uncertainties of PM_{SMPS} were between 19.4-26.0%, depending on the actual size distribution. Details of the uncertainty analysis can be found in Section 2 of the Supplementary Information.

196 **3. Results and Discussion**

197 3.1 RRF for Chamber Generated SOA

198 The evolution of SOA during a typical chamber experiment (Exp. 1) is shown in Fig. 2, where 80 ppby O_3 199 and 20 ppby α -pinene were injected into the chamber. Shortly after injection, a strong nucleation event occurred 200 and was marked by a typical banana-shaped number size distribution plot (Fig. 2a). As the ozonolysis reaction 201 proceeded, PM_{ACSM}, PM_{SMPS}, particle sizes, and peff swiftly increased during the initial two hours (Fig. 2b). The initial high values of f_{44} could partially due to f_{44} calculation bias in low concentration (0-5 µg m⁻³) or the fact that 202 203 initially formed SOA particles were highly oxidized because of gas to particle partitioning (Shilling et al., 2009). 204 PM_{ACSM} kept slightly higher than PM_{SMPS}, indicating an over-unit RRF. After 2-3 hours, the gas phase reaction and 205 the gas to particle phase partition slowed down, a "relative stable state" was reached. During the "relative stable state", PM_{SMPS} slightly increased from \sim 32 µg m⁻³ to \sim 37 µg m⁻³, ρ_{eff} slightly increased from \sim 1.17 to \sim 1.22 g cm⁻³, 206 207 f_{44} fluctuated between ~0.118 and ~0.134, indicating that both the SOA mass and the composition were relative 208 stable. Therefore, an averaged RRF (1.32 \pm 0.30) and f_{44} (0.126 \pm 0.005) within the "relative stable state" were 209 obtained.

Following the similar procedure, fourteen independent chamber experiments were conducted in this work Table 1 listed the detailed experiment conditions. The mixing ratios of the VOC precursors ranged from 10 to 200 ppbv. The oxidant concentrations were 50-80 ppbv for O₃ and 50-300 μ L for methyl nitrite. Each experiment typically lasted for 4-7 hours. In each experiment, a "relative stable state" was defined as f_{44} , ρ_{eff} , and mass concentration all reached relatively constant values and the average values within the "relative stable state" were used for analysis. Evidently, the characteristics of the generated SOA appeared to be significantly different among various oxidation conditions as for the generated wide ranges of mass concentrations (7.8-137.0 μ g m⁻³) and f_{44} (0.057-0.191).

RRF for the chamber-generated SOA decreased from 2.16 to 0.81 as f_{44} increased from 0.057 to 0.191 (see Fig. 3a). Although nearly half of the points were still within the measurement uncertainties of Q-ACSM for organics (±38%) (Bahreini et al., 2009; Middlebrook et al., 2012), RRF were higher than unit for most of the points, especially for the three points when $f_{44} < 0.10$. The highest two points were from isoprene oxidation and the third highest was from toluene oxidation. The over-unit RRF indicated that either CE_{org} or RIE_{org}, or both of them were higher than the default values (1.4 and 0.5, respectively). RRF value was slightly lower than unit for one of the toluene oxidation experiment, which might indicate lower CE_{org} or RIE_{org} values.

225 ρ_{eff} increased from 1.09 to 1.34 g cm⁻³ with increasing f_{44} , as shown in Fig. 3b. Although our APM 226 calibration with standard PSL spheres indicated some systematic positive deviations for larger particles, the ±3% 227 systematic errors could not explain such big positive trend observed in Fig. 3b. Similarly, George and Abbatt (2010) 228 observed an increasing trend of ρ_{eff} during simulated atmospheric aging of α -pinene oxidized SOA, where f_{44} 229 increased substantially. α -pinene oxidation experiments conducted by Kuwata et al. (2011) also indicated that ρ_{eff} 230 increased from 1.23 to 1.46 g cm⁻³ as oxygen to carbon ratio (O/C) increased from 0.38 to 0.48. In short, it appeared 231 that organics with higher oxygen contents tended to be more compact.

232 *3.2 Effects of CE*

To investigate and evaluate the contribution of variation of CE_{org} to the observed anti-correlations between RRF and f_{44} in this work, a set of chamber experiments using $(NH_4)_2SO_4$ (AS) as seed particles were conducted. The difference between this set of experiments from the previous experiments was that dry AS seed particles were injected into the chamber with an atomizer (model 3076 TSI) followed by a diffusion dryer before SOA were generated. After AS concentrations were stable in the chamber, VOC and the oxidants were injected. The gas phase oxidation products condensed onto the AS seeds instead of initiating new particle formations. As soon as AS seeds were coated with SOA, the Q-ACSM measured sulfate mass concentrations would change. A default RIE_{SO4} (1.15) was used here as suggested by previous studies (Canagaratna et al., 2007; Ng et al., 2011a; Petit et al., 2015). As RIE_{SO4} would not change after coated with SOA, any changes in sulfate signal was due to variations in CE_{AS} (Matthew et al., 2008). After AS particles were fully coated with SOA shell, CE_{AS} was equal to CE_{org} for the pure SOA particles (Bahreini et al., 2005; Docherty et al., 2013).

244 Figure 4 displayed the evolution of a typical AS coating experiment (Exp. 19), where 80 ppbv toluene and 245 150 µL methyl nitrite were used to generate SOA. The experiment started when AS was first injected into the chamber. The initial geometric mean diameter (d_g) of AS seed particles in the chamber were 70-80 nm. ρ_{eff} of the 246 dry 80 nm AS particles was measured to be 1.64 ± 0.08 g cm⁻³, which was consistent with 1.65 g cm⁻³ (Zelenyuk et 247 al., 2006) or slightly lower than 1.66-1.70 g cm⁻³ measured for 200 nm (d_m) dry AS particles in a previous study 248 (Matthew et al., 2008). Initially, the Q-ACSM measured sulfate mass concentrations were \sim 35 µg m⁻³. The initial 249 250 CE_{AS} was calculated to be 0.277 ± 0.066. An hour later, toluene and methyl nitrite were injected and the black light 251 bulbs were turned on. The Q-ACSM measured sulfate signal increased substantially as SOA gradually condensed 252 onto AS seeds, implying that the SOA cover caused CE_{AS} to gradually increase as coating layer became thicker. 253 Two hours after the experiment started, the Q-ACSM measured organic concentration was still increasing but the 254 measured sulfate stopped increasing and kept constant during the rest of the experiment. By the time when sulfate signal stopped increasing, d_g increased to 115 nm, the average coating thickness (growth in particle radius) was 255 256 about 18 nm assuming uniform coating. This indicated that an 18 nm SOA shell was already enough to cover the 257 80 nm seed particles in this experiment. Similarly, f_{44} did not change significantly as SOA increased, indicating 258 nearly identical particle chemical compositions during the entire experiment. The period when both sulfate and 259 organic concentration reached relative constant was considered as the "relative stable state" in this experiment (area 260 between Arrow 3 and Arrow 4 in Fig. 4). Points after Arrow 4 were obviously affected by wall losses and thus were 261 not included in the calculation. Average PMACSM of AS in "relative stable state" divided by average PMSMPS of AS

was used to calculate the CE_{AS} after coating with SOA. Since AS was fully covered, CE_{org} should be equal to CE_{AS}, which was 0.441 ± 0.110 for an average f_{44} value of 0.209 ± 0.011 .

264 Eight experiments using AS seeds were conducted in total (see Table 2). In each experiment, similar mass concentrations (76.0-98.2 μ g m⁻³) and sizes (d_g = 70-80 nm) of AS seeds were injected into the chamber. The slightly 265 different initial AS mass concentrations among different experiments were caused by the different initial AS seed 266 267 number concentrations. ρ_{eff} of AS measured in all experiments were very much the same as in Exp. 19, with an average of 1.64 ± 0.04 g cm⁻³. CE_{AS} for dry AS particles varied from 0.265 to 0.298 in different experiments, with 268 269 an average value of 0.285 ± 0.067 which was slightly higher than the reported 0.24 ± 0.03 (Matthew et al., 2008). The bias could come from the large uncertainties of SMPS measurement or the bias from the default RIE_{SO4} (1.15). 270 271 For most of the experiments, all condensable organic vapor seemed to condense directly onto seed particles instead 272 of forming new particles. While in one experiment (Exp. 22), there were small amounts of new particles formed, 273 which was indicated by a smaller mode on the size distribution (Fig. S6) and further confirmed by a sudden increase 274 in total particle number concentration. However, the newly formed particles only contributed slightly to the total 275 particulate mass for their much smaller sizes. In addition, to avoid the influence of new particle formation on CE_{org} or RIE_{org} deduction, only PM_{ACSM} and PM_{SMPS} associated with AS signals were used to deduce the actual CE_{org} in 276 277 our experiments.

278 Figure 5 showed the variation of CE_{org} as a function of f_{44} . For most of the experiments, the SOA coating 279 layer was thick enough (18-25 nm) to cover AS seed particles. This was supported by the fact that after coating with 280 18-25 nm SOA, the Q-ACSM measured sulfate concentration stopped increasing with further organic increase. 281 While CE_{org} from Exp. 16, 20, and 21 (coating layer < 18-25 nm) might be the result of a combination of AS and organic particles because the Q-ACSM measured sulfate increased all the way until organics stopped increasing. 282 283 For α -pinene initiated SOA, high CE_{org} (0.882 ± 0.207) was observed when $f_{44} = 0.127 \pm 0.003$ at the beginning. CE_{org} decreased sharply to 0.313 ± 0.076 when f_{44} increased to 0.147 ± 0.009, then kept at 0.338 as f_{44} further 284 increased to 0.202. For toluene initiated SOA, CE_{org} varied between 0.441 and 0.475 when f_{44} varied between 0.190 285

and 0.219, which was the highest level of f_{44} obtained in this work. Nevertheless, it could be observed that SOA with the lowest f_{44} (0.127) was associated with the highest CE, which largely explained the trend in RRF.

288 3.3 Possible Effects of RIE

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289 The effects of RIE_{org} can be evaluated using Eq. 5 (Jimenez et al., 2003; Canagaratna et al., 2007):

$$RIE_{org} = \frac{MW_{NO3}}{IE_{NO3}} \cdot \frac{IE_{org}}{MW_{org}}$$
(5)

291 Where, MW_{NO3} and MW_{org} are the molecular weights of nitrate and a specific organic compound, respectively. 292 Theoretically, IE_{NO3} is directly proportion to σ , the electron impact ionization cross section of the molecule, which 293 is linearly related to the number of electrons in the molecule for molecules with similar structure and functionality. 294 Since the number of electrons is roughly proportional to the molecular weight, RIE_{org} for molecules with similar structure and functionality are suggested to be similar to each other. RIE_{org} for hydrocarbons and oxygenated 295 296 species, thus, are believed to be different since their oxygen contents can vary substantially (Canagaratna et al., 297 2007). With our experiments, we still cannot rule out the contribution of RIE_{org} to the overall RRF trend even though 298 the variation of CE_{org} with f_{44} could largely explain the observed RFF changes.

299 3.4 Comparison with AMS Calibrations

300 Since the Q-ACSM has similar characteristics as an AMS (aerodynamic lens followed by thermal 301 vaporization, electron impact ionization, and MS detection), the calibration results obtained from this work are 302 expected to be comparable with those done with the AMS.

In previous studies conducted by AMS, CE was demonstrated to be variable for particles with different chemical composition, phase state and under different RH, with CE_{org} ranging from less than 0.15 to ~1 (Alfarra, 2004; Matthew et al., 2008; Docherty et al., 2013; Robinson et al., 2015). However, during field studies AMS measurement results based on default RIE = 1.14 and CE = 0.5 appeared to be in reasonable agreement with other aerosol measurement techniques (Slowik et al., 2004; Zhang et al., 2005; Middlebrook et al., 2012). CE for biogenic SOA has been reported to be close to 1 based on both chamber experiments (Kiendler-Scharr et al., 2009) and field 309 measurements conducted in Amazon, where aerosols were dominated by liquid SOA (Chen et al., 2009; Allan et 310 al., 2014). However, it has been proposed in theoretical, chamber, and field studies that besides liquid state, organic 311 particles can exist in semi-solid or solid state (Vaden et al., 2010; Virtanen et al., 2010; Shiraiwa et al., 2011), which 312 might lead to lower CE_{org} . For example, CE_{org} of liquid squalane (CE = 1) decreased after SOA condensed on the 313 particle (Robinson et al., 2015). Most recent CE_{org} calibration with light-scattering single-particle (LSSP) module 314 also suggested that CE_{org} (0.25-0.4) could be much less than 1 (Robinson et al., 2017). An inverse relationship 315 between CE_{org} and f_{44}/f_{57} ratio in chamber SOA generation experiments (Docherty et al., 2013) was very similar to 316 our results. However, our results could not be quantitatively compared with the previous ones because the Q-ACSM 317 might report comparably higher f_{44} than the AMS (Fröhlich et al., 2015).

318 One possible explanation of the observed decreasing CE_{org} with f_{44} was the phase change. Particle 319 morphology research based on glass transition temperature (T_{e}) indicated that during oxidation, the SOA products 320 might vary between liquid state, semi-solid state and solid (glassy) state, resulting from a combined effect of 321 increasing molecular weight and O/C ratio (Koop et al., 2011). As a result, it was reasonably to assume that HOA particles were initially "sticky" liquid droplets with CE_{org} close to 1. As O/C ratio increases during oxidation 322 process, the liquid droplets changes into "bouncing" semisolid or solid ball with sharp or slow decrease in CE_{org}. 323 324 As the phase changes were not only determined by oxygen contents but also the molecular weight that was related 325 to the precursor gases, i.e., CE_{org} changes might be different for different VOC precursors. The phase change 326 speculation is partially supported by the positive relationship between ρ_{eff} and f_{44} .

Previous studies have shown that RIE_{org} ranged from less than 1 for SOA to more than 3 for HOA (Slowik et al., 2004; Dzepina et al., 2007; Jimenez et al., 2016). A most recent research showed that RIE_{org} for hydrocarbonlike organic aerosol might vary from 2 to 7. While RIE_{org} for organic with $-1.0 < \overline{OSc}$ (average carbon oxidation states) < 0.5 varied between 1.6 ± 0.5 (2σ) (Xu et al., 2018), which is relatively higher than the widely used default value (RIE_{org} = 1.4). Clearly, a higher than default RIE_{org} value is consistent with the overall positive deviations of RRF observed in our experiments.

333 4. Conclusions

334 The quantification of SOA using a Q-ACSM has been investigated in a photochemical chamber. We found 335 an anti-correlation between RRF, defined as PM_{ACSM} divided by PM_{SMPS}, and SOA f₄₄, regardless of the type of VOC precursors. RRF decreased from 2.16 to 0.81 as f_{44} increased from 0.057 to 0.191, while ρ_{eff} increased from 336 1.09 to 1.34 g cm⁻³. In SOA coating experiments, an SOA coating layer with a thickness of 18-25 nm (in radius) 337 was found to be sufficient to fully cover the AS seed particles with mobility diameters of 70-80 nm. Collection 338 efficiency of organics-coated aerosols (CE_{org}) was found to decrease from 0.882 to 0.313-0.475 as f_{44} increased 339 340 from 0.127 to 0.174-0.210. Decreasing CE_{org} with f_{44} might be explained by the phase transition from liquid-state 341 into more solid-like/glassy state of SOA particles consisting of more oxidized organic compounds that normally 342 assume a higher ρ_{eff} . Although RIE_{org} was not directly measured in our experiments, it seemed that the variation of CE_{org} with f_{44} could largely explain the RFF changes with f_{44} , indicating that the effect of f_{44} on RIE_{org} might be 343 344 limited for SOA.

Our results strongly indicate that chamber measurements of OA with various f_{44} by a Q-ACSM using constant conversion factors may induce significant errors in aerosol mass concentration measurements. The exact values of these factors most likely will vary with different individual instrument. Accordingly, the Q-ACSM response factor for OA should be systematically calibrated with laboratory-generated SOA with various average oxygen contents. It is also important that quantification of laboratory and ambient OA by a Q-ACSM with size distribution information should include measurements of effective density instead of assuming a constant value.

Due to the low-cost and durability, Q-ACSMs have been widely used in both ambient and laboratory experiments to quantify aerosol chemical compositions, especially for long-term observations in highly polluted regions (such as in China). However, the performance of Q-ACSM in organics measurement was rarely evaluated because of its low time and m/z resolution and the lack of particle size selection. To the best of our knowledge, this study represents the first comprehensive chamber calibration of CE_{org} and RRF_{org} for a Q-ACSM. Our results of RRF, and CE_{org} calibration were generally in line with previous studies conducted with the AMS. Although the

357	results of this work were not directly applicable to ambient Q-ACSM measurements, it is suggested that more
358	accurate and comprehensive calibrations of Q-ACSM for complicated ambient conditions shall be done to further
359	lower the uncertainties of OA measurement, which is still relatively high (±38%) currently.
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Precursor	#	VOC(ppbv)	O ₃ /OH ^[1] (ppbv or μL)	PM _{SMPS} (µg m ⁻³) ^[2]	$ ho_{eff}$ cm ⁻³) ^[3]	f ₄₄ ^[4]	RRF ^[5]
	1	20	80 ppbv	35.9±7.2	1.19±0.05	0.126±0.005	1.32±0.30
a-pinene	2	60	75 μL	106.9±25.6	1.25±0.04	0.136±0.005	1.49±0.37
a pinene	3	10	80 ppbv	9.7±2.23	1.29±0.05	0.146±0.018	1.31±0.37
	4	60	60 ppbv	9.6±1.92	1.25±0.05	0.152±0.011	1.23±0.30
	5	30	75 μL	15.6±3.1	1.19±0.05	0.146±0.012	0.99±0.23
toluene	6	60	150 μL	38.2±7.6	1.34±0.04	0.191±0.012	0.81±0.19
	7	30	50 µL	14.2±2.8	1.10±0.04	0.079±0.010	1.58±0.38
	8	60	75 μL	10.6±2.8	1.24±0.05	0.127±0.006	1.45±0.40
	9	200	300 µL	137.0±32.9	1.09±0.04	0.057±0.003	2.16±0.51
	10	100	150 μL	15.1±3.2	1.11±0.05	0.080±0.025	1.81±0.43
isoprene	11	60	90 µL	7.8±1.6	1.26±0.05	0.138±0.031	1.42±0.34
	12	80	120 µL	10.2±2.0	1.20±0.05	0.129±0.023	1.47±0.33
	13	160	60 µL	20.6±4.5	1.22±0.04	0.160±0.005	1.28±0.31
	14	200	60 µL	36.7±7.3	1.28±0.04	0.157±0.006	1.47±0.30

593 Table 1. Summary of SOA Chamber Experiments without Seed Particles

^[1] The amount of OH is expressed as the amount of methyl nitrite (μL) injected into the chamber.

 $^{[2]}$ PM_{SMPS} was calculated from the average sized distribution (Fig. S4) in "relative stable state", PM_{SMPS} was amended by E_L of ACSM aerodynamic lens (Fig. S2) and Es (100 ± 5%). Details of the uncertainties calculation can be found in SI.

597 ^[3-4] ρ_{eff}, f_{44} were the average values in "relative stable state", uncertainties were standard deviations of all the points during "relative stable state".

598 ^[5] RRF was calculated with the average PMSMPS and PMACSM in "relative stable state". Details of the uncertainties calculation can be found in SI.

Precursor	#	VOC (ppbv)	O ₃ /OH (ppbv or μL)	PM _{ACSM-AS1} ^[1] (μg m ⁻³)	PM _{ACSM-AS2} ^[2] (μg m ⁻³)	PM _{SMPS-AS} ^[3] (μg m ⁻³)	SOA thickness ^[4] (nm)	f 44	CE _{AS} ^[5]	CE _{org} ^[6]
	15	20	50 µL	57.5±3.2	66.0±4.9	97.7±21.2	18	0.202±0.018	0.294±0.068	0.338±0.080
α-pinene	16	20	80 ppbv	50.3±5.4	56.2±6.6	83.9±18.4	15	0.193±0.023	0.299 ± 0.074	(0.335±0.085)
	17	60	80 ppbv	43.9±3.0	48.4±4.7	77.1±17.3	47	0.147±0.009	0.284±0.067	0.313±0.076
	18	60	50 µL	40.3±2.2	134.2±8.7	76.0±17.2	73	0.127±0.003	0.265±0.061	0.882±0.207
	19	80	150 μL	51.2±3.4	81.4±7.9	92.3±21.3	23	0.209±0.011	0.277±0.066	0.441±0.110
toluene	20	80	100 µL	55.6±4.5	71.0±6.8	98.2±22.1	12	0.237±0.016	0.283 ± 0.068	(0.362 ± 0.088)
	21	60	200 µL	48.3±4.7	57.5±5.3	85.3±18.8	20	0.210±0.013	0.283 ± 0.068	(0.337 ± 0.080)
	22	80	200 µL	53.2±1.8	84.8±6.0	89.2±20.0	41	0.190 ± 0.003	0.298 ± 0.068	0.475±0.112

602 Table 2. Summary of SOA Chamber Experiments with AS Seed Particles

603 ^[1,2] Average mass concentration of AS seed particles measured by ACSM (using default CE = 0.5, RIE = 1.4) before and after SOA was generated.

604 ^[3] Average mass concentration of AS particles measured by SMPS which was calculated using Eq. 3.

605 ^[4] Coating layer was calculated from geometric mean diameter before and after the coating (Fig. S5).

606 ^[5-6] CE_{AS} and CE_{org} were calculated with Eq. (S7 & 8), uncertainties were evaluated with Eq. (S9 & S10). Wall losses during the SOA coating was ignored. CE_{org} values

607 with brackets were experiments that AS particles were not fully covered with SOA and CE_{org} is actually a combination result of organic shell and AS core.





Figure 1. Schematic of the collapsible atmospheric-pressure fluoropolymer (Teflon) smog
chamber and the instrument setup. AS generation unit was only used in the seed experiments.
During experiments, a total sample flow rate was 1.6 LPM, including 1.0 LPM for ACSM, 0.3 LPM
for DMA-APM-CPC, and 0.3 LPM for SMPS. No zero air was introduced into the chamber during
the experiments.



Figure 2. (a) A typical banana-shaped 3-D plot of the size distribution of aerosols generated from α -pinene oxidation (Exp. 1); (b) Time series of organic mass concentration measured by Q-ACSM (assuming CE_{org} of 0.5 and RIE_{org} of 1.4) and SMPS-APM deduced mass concentration PM_{SMPS} (amended by E_L and E_s). The period between Arrow 1 and Arrow 2 was considered when the organics coated particles reached a "relatively stable state" and was used for data averaging.



Figure 3. (a) Anti-correlation between Q-ACSM RRF and f_{44} . Shadow area represents the unit RRF and the reported ±38% measurement uncertainty (Bahreini et al., 2009) for ambient organic particles. (b) Positive correlation between ρ_{eff} and f_{44} . All the data can be found in Table 1 1 and the

631 default RIE = 1.4 and CE = 0.5 were used in the calculations.



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Figure 4. Time series of a typical experiment with SOA coating on AS (Exp. 19): (a) aerosol size distribution measured by SMPS; (b) Organic, sulfate mass concentrations and f_{44} measured by Q-ACSM (assuming CE = 0.5, RIE_{org} = 1.4, RIE_{SO4} = 1.15). Arrow 1 indicates when the injected AS particles reached stable, Arrow 2 indicates when SOA started to form. The period between Arrows 3 and 4 was when the SOA coated AS particles reached "relative stable state" and was used for data averaging.



Figure 5. CE of SOA coated ammonium sulfate (AS) particles. Gray points represent CE_{AS} before SOA were coated onto AS in experiments with different VOCs. Colored triangles were CEs of AS coated with α-pinene oxidized SOA and colored circles were CEs of AS coated with toluene oxidized SOA. The color scale represents SOA coating thickness; for 80 nm AS particles generated, an SOA coating layer with a thickness of 18-25 nm should be able to fully cover the AS core. All the data can be found in Table 2.