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ABSTRACT

A proton transfer reaction-quadrupole interface time-of-flight mass spectrometer was combined with a hand-made thermal desorption (TD) instrument for real-time analysis of organic aerosol particles. Size-selected single-component organic particles were generated using a nebulizer combined with a differential mobility analyzer. We tested perfluoroalkoxy alkene (PFA) and copper tubing for the TD instrument. Higher signal intensities were observed when using PFA tubing, suggesting that wall deposition loss of vaporized semi-volatile organic compounds was suppressed when PFA tubing was used. Protonated molecules, \([\text{M} + \text{H}]^+\), had the highest intensity in the mass spectrum of dialdehyde particles (i.e., terephthaldialdehyde), whereas ions formed by dehydration from protonated molecules, \([\text{M} + \text{H} - \text{H}_2\text{O}]^+\), had the highest intensities in the mass spectra of carboxylic acid particles (i.e., adipic, phthalic, and cis-pinonic acids) and alcohol particles (i.e., meso-erythritol). The mass spectra obtained for organic aerosol markers will be useful to interpret mass spectra measured for organic aerosol particles by TD-proton transfer reaction-mass spectrometry.

Keywords: Condensable particles, Secondary organic aerosol, Semi-volatile organic compound, Mass spectrometry, Chemical composition analysis
1 INTRODUCTION

Organic aerosols, a major component of atmospheric fine particles, are considered to have an impact on climate and human health (IPCC, 2014; Shiraiwa et al., 2017) and have become a major research target in the field of aerosol and air quality research. Atmospheric organic aerosols include compounds that can be identified by conventional gas chromatography-mass spectrometry such as \( n \)-alkanes and dicarboxylic acids, compounds that have recently been identified by new analytical techniques such as organosulfates and organic peroxides, and compounds still unidentified (Rogge et al., 1993; Nozière et al., 2015).

Conventional off-line analytical techniques have limitations in analyzing highly reactive and semi-volatile components such as organic peroxides, which might decompose or evaporate after collection on a filter (Zhang et al., 2014; Zhao et al., 2018), so the development of online analytical techniques is desirable. The development of online analytical methods for organic aerosol composition has been advanced by combining aerosol pretreatment techniques with mass spectrometry (Fushimi et al., 2018). One of the most successful methods is negative ion chemical ionization mass spectrometry (CIMS). In negative ion CIMS, organic compounds are softly ionized by an addition reaction with nitrate ions and
analyzed by mass spectrometry. This technique has been used to detect highly oxidized molecules that promote particle growth in the atmosphere (Ehn et al., 2014).

In contrast, proton transfer reaction-mass spectrometry (PTR-MS) uses the proton transfer reaction from hydronium ions (H$_3$O$^+$) to ionize organic compounds (Lindinger et al., 1998), and has been mainly used for detection of volatile organic compounds (Inomata et al., 2008). The PTR-MS method can also be used for online analysis of organic aerosol composition by analyzing vaporized organics using the thermal desorption (TD) method (Holzinger et al., 2010a, 2010b). This combined TD-PTR-MS method has an advantage in detecting aldehydes and ketones, and may be complementary to negative ion CI MS, which has an advantage in detecting peroxides and nitrates. The combination of quadrupole interface (Qi) and time-of-flight mass spectrometry (TOFMS) with PTR-MS in the PTR-QiTOF method has been developed for higher sensitivity and resolution (Sulzer et al., 2014). The maximum sensitivity of the PTR-QiTOF method is 0.75 ppt at 1 min integration, and the maximum mass resolution is 10,400.

In this study, single-composition organic aerosols were analyzed online using the TD-PTR-QiTOF method, which combines PTR-QiTOF with a hand-made TD instrument. Single-composition particles of dialdehydes, dicarboxylic acids, and polyols were used in the
study of secondary organic aerosols. The purpose was to investigate the response of the mass spectrometer signal to organic aerosol concentration, TD temperature, and TD tubing material, and to measure the mass spectrum of each single-composition particle as a reference.

2 METHODOLOGY

A schematic diagram of the apparatus used for particle generation and measurement is shown in Fig. 1. Organic aerosol particles were generated using an atomizing aerosol generator (TSI, Model 3076): an aqueous solution of 0.50–2.0 g L\(^{-1}\) of a water-soluble organic compound was sprayed into an airstream of synthetic air to obtain a polydisperse aerosol with a single organic composition. A diffusion dryer (TSI, Model 3062) was used to remove water vapor from the aerosol. The relative humidity at the outlet of the diffusion dryer was 30–40%. A monodisperse aerosol with a geometric mean particle size of 350 nm was obtained from the polydisperse aerosol using a differential mobility analyzer (DMA; TSI, Model 3080). The particle size distribution of the obtained monodisperse aerosol was measured using a scanning mobility particle sizer (SMPS; TSI, Model 3934) and TD-PTR-QiTOF.
A perfluoroalkoxy alkane (PFA) tube or a copper tube was used for the heater of the TD instrument. The heater tube had an outer diameter of 12.7 mm, inner diameter of 9.6 mm, and length of 500 mm. The flow rate in the heater tube was controlled at 0.14–0.30 L min$^{-1}$ by a mass flow controller. A polytetrafluoroethylene (PTFE) membrane filter (Sumitomo Electric Industries Ltd., 47 mm in diameter, 1 μm in pore size) was installed downstream of the heater tubing to remove particles left unvaporized in the heating section. The filter was loaded in a filter holder made of PFA (Savillex, Part Number 401-21-47-10-21-2). The tubing of the heating section and the filter holder were individually heated by ribbon heaters, which were wrapped with glass fiber tape for heat insulation. The heating section of the TD system was defined as the total heated volume present upstream of the filter. The residence time of the heating section was 16 s at 25°C and 0.30 L min$^{-1}$. The temperatures of the tubing and the filter holder were both controlled with an accuracy of ±1°C using thermostats. The response speed of the ribbon heater was adjusted using a slide transformer to minimize overshooting and undershooting of temperature. In order to evaluate whether the residence time of the TD system was sufficient for evaporation of the particles, the time required for evaporation of 350-nm dioctyl phthalate (DOP) particles was calculated (Hinds, 1999; Fujitani et al., 2012) as described in Appendix A. At temperatures of 50°C, 70°C, and 100°C,
it was calculated that it would take 39, 2.7, and 0.084 s, respectively, for the particles to evaporate. Although the calculated results also depended on the particle size, chemical composition, and mixing state, it was shown that the particles would evaporate within the residence time by controlling temperature to 70°C in the case of the DOP particles.

The organic matter vaporized in the TD system was analyzed using PTR-QiTOF (Ionicon, PTR-QiTOF). Of the introduced sample gas, ~0.1 L min\(^{-1}\) was used for analysis. Both inlet and drift tube temperatures were set to 120°C. To suppress fragmentation during ionization, the converted electric field, i.e., the ratio of electric field strength \((E)\) to molecular number density \((N)\) \((E/N)\), was set as low as possible to 53 Td \((1 \text{ Td} = 10^{-21} \text{ V m}^2)\). The typical ionic strength of \(\text{H}_3\text{O}^+\) was \(~4 \times 10^5\) cps. The produced organic ions were introduced into the TOFMS through the Qi. The signals of the mass spectra measured by the mass spectrometer were recorded at intervals of 0.001–0.005 Da. The signals for each mass number were integrated and the integration results recorded every 10 s.

Table 1 shows the organic compound used in the measurement, the TD tube, the temperature of the tube, the flow velocity in the tube, and the mass concentration of the particles in each experimental run. Table 2 shows the densities, vapor pressures at 25°C, evaporation enthalpies, and diffusion coefficients of the vapors of the organic compounds...
used in the measurements; these values were calculated using the SPARC online calculator (Hilal et al., 2003) based on the structure–active phase relationships. The five organic compounds used in the measurements were adipic acid, phthalic acid, meso-erythritol, cis-pinonic acid, and terephthaldialdehyde, which are representative molecular markers or surrogates of primary and secondary organic aerosols in the atmosphere. The vapor pressure, evaporation enthalpy, and diffusion coefficient calculated by SPARC were used to calculate the time required for the evaporation of the single-component particles using the method shown in Appendix A, and the temperature at which the time required for evaporation was equal to the residence time of the TD was determined. The density value calculated by SPARC was also used to calculate the mass concentration from the volume concentration of particles measured by SMPS.

3 RESULTS AND DISCUSSION

3.1 Temperature-Varied Online Measurements

As a typical measurement result, Fig. 2 shows the time-series of total mass peak intensities measured in Run 10 in which meso-erythritol particles were measured in a TD apparatus with PFA tubing at different temperatures in the range of 25–120°C. When meso-erythritol was measured, not only ions of m/z 123, which were protonated molecules
([M + H]^+)\), but also fragment ions of \(m/z\) 105 ([M + H – H2O]^+), 87 ([M + H – 2H2O]^+), and 69 ([M + H – 3H2O]^+) were detected. The signal intensity of each mass peak was obtained by calculating the sum of the signals in the interval of ±0.08 Da from the center of the peak.

The TD temperature was 25°C at the beginning of the measurement. At this time, \textit{meso}-erythritol particles were already being measured by SMPS, but TD-PTR-QiTOF detected almost no signal, except for a background signal at \(m/z\) 105. The \textit{meso}-erythritol was almost entirely present as particles at 25°C, and the particles were removed by the filter, indicated by the lack of detection of a signal of gaseous organic matter. The signal intensity of each peak increased when the TD temperature was increased to 120°C. The particles heated in the TD tube or on the filter were volatilized. The volatilized gas penetrated the filter to be detected by PTR-QiTOF. The signal intensity stabilized in 10 min after the TD temperature reached 120°C.

After the signal intensity became constant and measurement was continued for 10–20 min, the temperature setting was lowered from 120°C to 100°C to start cooling the TD tube. As soon as the temperature was lowered, the signal intensity of each peak decreased. The air cooling was stopped when the TD temperature reached 100°C. The fragmentation pattern of \textit{meso}-erythritol did not change significantly with temperature. This result suggests that the
fragmentation of *meso*-erythritol most likely occurred during the ionization process in the
drift tube of the PTR-MS, rather than during heating by the TD method. The signal intensity
of m/z 105 at 30°C at the end of the measurement was slightly lower than that at 25°C at the
start. Thus, it is likely that there was a change in the background signal before and after the
measurement. To correct for any such change, the background signal values measured before
and after the measurement were used, and the background contribution was subtracted from
the signal during the measurement by linear completion.

3.2 Response to Particle Concentration

The response of the signal intensity to particle concentration was investigated. Fig. 3 plots the response of TD-PTR-QiTOF as a function of SMPS particle concentration using a
TD system with PFA tubing and a TD temperature of 100°C. The particle concentration was
controlled by changing the concentration of the aqueous solution provided to the particle
generator. The mass concentration of the gaseous organic compound (μg m⁻³) was converted
from the concentration of the molecule M ([M] (ppb)), which was calculated from the
PTR-QiTOF measurement results. The [M] was obtained by calculating the concentration
([M_i] (ppb)) from the signal intensity ([f^+]) (cps)) of each peak appearing in the mass
spectrum detected by PTR-QiTOF and summing the [M_i] for n peaks (de Gouw et al., 2003):
where $k$ is the reaction rate constant of H$_3$O$^+$ with molecule M (cm$^3$ molecule$^{-1}$ s$^{-1}$), $t_R$ is the residence time in the drift tube (s), [H$_3$O$^+$] is the signal intensity of H$_3$O$^+$ (cps), [air] is the concentration of air in the drift tube (molecule cm$^{-3}$), $T_{f_i^+}$ is the transmission coefficient of $f_i^+$ ions, and $T_{H_3O^+}$ is the transmission coefficient of H$_3$O$^+$. A value of $2.0 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was used for $k$ for all molecules (Zhao and Zhang, 2004); the $t_R$ value was $2.0 \times 10^{-4}$ s; [H$_3$O$^+$] was calculated by multiplying the signal of the m/z 21 isotope by 488; and the values of $T_{f_i^+}$ and $T_{H_3O^+}$ were calculated by a spline function fitted to the measured transmission efficiency of ions formed from 10 standard gases with molecular weight range of 32–120. The accuracy of the concentration of gaseous organics obtained by the calculation is determined by the accuracy of $k$. Based on the range of $k$ for various organics (Zhao and Zhang, 2004), the accuracy of the calculated gaseous organic concentrations is about a factor of two. Furthermore, under low $E/N$ conditions, as in this study, ionization effects due to water cluster ions, which are not assumed in Eq. (2), may appear. According to the evaluation of the effects of water cluster ions by Cappellin et al. (2012), the effective value
of $k$ under the $E/N$ and relative humidity conditions of this study was estimated to be more than twice that of the case assuming ionization by H$_3$O$^+$ alone. It should be noted that there is uncertainty in the absolute values of the concentrations obtained by applying Eq. 2 to the results of this study. However, the vapor concentration evaluated by PTR-QiTOF signals for adipic acid ($r^2 = 1.00$), phthalic acid ($r^2 = 0.99$), and meso-erythritol ($r^2 = 0.95$) showed linear relationships with the SMPS aerosol concentration in the range below 300 $\mu$g m$^{-3}$.

For terephthaldehyde and cis-pinonic acid, we did not measure the response to particle concentration and TD temperature because we could not obtain monodisperse aerosols with a substantial concentration. In this study, the particle evaporation temperature ($t^*$) is defined as the temperature at which the time it takes for a single-component particle of 350 nm to evaporate is equal to the residence time of the TD. The $t^*$ values for adipic acid, phthalic acid, meso-erythritol, cis-pinonic acid, and terephthalic aldehyde were 58°C, 49°C, 49°C, 28°C, and −19°C, respectively (Table 2). The organic particles of cis-pinonic acid and terephthalic aldehyde may have partially evaporated during their passage through the TD system, even at 25°C.

3.3 Response to TD Temperature, Tubing Material, and Flow Rate
Fig. 4 shows the ratio of PTR-QiTOF gas concentration to TD temperature for adipic acid (Run 2), phthalic acid (Run 7), and meso-erythritol (Run 10). No gas signal was measured at 25°C for any of the three organics. Half of the values for the gas/particle ratio at 120°C were obtained at 50–70°C for adipic acid and phthalic acid, and at 30–50°C for meso-erythritol particles.

Using adipic acid, the TD tube was changed to a copper tube for measurement (Run 4, Table 1). However, significant signals were detected only at 90°C and 120°C. At 120°C, the signal intensity of adipic acid in the copper tube was 3300 times lower than that in the PFA tube. It is likely that the adsorption rate of semi-volatile organic molecules vaporized by heating on the wall of the copper tube was higher than that of the PFA tube, or the desorption rate from the wall was lower than that of the PFA tube.

For particles of adipic acid (Run 5), phthalic acid (Run 8), and meso-erythritol (Run 11), the effect of the filter was confirmed by using a copper tube in the TD heating section but not removing the particles with the filter. When adipic acid, phthalic acid, and meso-erythritol particles were measured, ion signals derived from each compound were observed even at 25°C without the filter. The apparent gas/particle ratios for adipic acid, phthalic acid, and meso-erythritol particles were 1.04, 0.84, and 0.42, respectively, suggesting that the particles
introduced directly into the PTR-QiTOF system were vaporized at the inlet at 120°C and the signal was detected. As the TD temperature increased, the signal decreased for all three organics and became almost zero for 90–120°C. When the copper tube was heated, the organic compounds vaporized in the tube were removed by adsorption to the inner wall of the tube, and their amounts that passed through the TD system decreased.

Holzinger et al. (2010a) and Eichler et al. (2015) used stainless steel for the TD heating section of TD-PTR-MS. Because organic peroxides are easily degraded on metal surfaces, they may be measured using online analysis of organic aerosols (Ehn et al., 2014). The PFA tube used in this study may be superior to stainless steel for measurement of organic peroxides.

The flow velocity in the TD tube was set to 0.14 L min\(^{-1}\) using the PFA tube (Run 3). Adipic acid particles were used for the measurement. When the flow velocity was decreased from 0.3 to 0.14 L min\(^{-1}\), the residence time in the TD tube at 25°C increased from 16 to 35 s. As the residence time increases, the heat transfer time to the particles increases and the gas signal to be vaporized is expected to increase. However, the gas/particle ratio of the particles at 0.14 L min\(^{-1}\) was conversely reduced compared to 0.30 L min\(^{-1}\) (Fig. 4). It is likely that deposition and adsorption on the wall cannot be neglected even when PFA tubing is used.
3.4 Mass Spectrum of Vaporized Oxygenated Organic Compounds

Fig. 5 shows the mass spectrum of adipic acid particles (Run 1, Table 1) when the TD temperature was set at 100°C and PFA was used for the TD tube. The background mass spectrum at the TD temperature of 100°C was subtracted from the mass spectrum measured for adipic acid particles. The mass spectrum showed peaks at \( m/z \) 147, 129, 111, and 101. The signal intensity ratio of \( \frac{m/z 147}{m/z 129}{:}\frac{m/z 111}{m/z 101} \) was 0.21:1.00:0.19:0.10, with the strongest peak at \( m/z 129 \). The signal at \( m/z 147 \) was due to protonated adipic acid ([M + H]\(^+\)). The fragments at \( m/z 129 \) and \( m/z 111 \) represented the ions of [M + H]\(^+\) with one and two water molecules eliminated, respectively ([M + H – H\(_2\)O]\(^+\) and [M + H – 2H\(_2\)O]\(^+\)), respectively, while the fragment at \( m/z 101 \) was from the ion formed by the elimination of CH\(_2\)O\(_2\) from [M + H]\(^+\) ([M + H – CH\(_2\)O\(_2\)]\(^+\)). The signal intensity ratio of \( \frac{m/z 167}{m/z 149} \) was 0.05:1.00 for the mass spectrum of phthalic acid particles, and that of \( \frac{m/z 185}{m/z 169} \) was 0.23:1.00 for the mass spectrum of cis-pinonic acid particles. For the molecules with carboxyl groups, i.e., adipic acid, phthalic acid, and cis-pinonic acid, the largest peak was [M + H – H\(_2\)O]\(^+\), although [M + H]\(^+\) was detected in all cases.

Fig. 6 shows the mass spectrum obtained from measurement of terephthaldehyde particles (Run 6, Table 1) and had a signal intensity ratio of \( \frac{m/z 135}{m/z 79} \) of 1.00:0.11.
The ion represented at $m/z$ 135 was a protonated terephthalaldehyde ([M + H]$^+$). The protonated molecule was the major peak as in the case of the PTR-MS measurement of monoaldehyde and monoketone molecules. The peak at $m/z$ 79 was due to the ion formed by the elimination of C$_3$H$_4$O from [M + H]$^+$ ([M + H – C$_3$H$_4$O]$^+$).

Fig. 7 shows the mass spectrum from the measurement of meso-erythritol particles (Run 9, Table 1), with a signal intensity ratio of ($m/z$ 123):($m/z$ 105):($m/z$ 87):($m/z$ 69) of 0.43:1.00:0.99:0.18. The ion signal of $m/z$ 123 is attributed to protonated meso-erythritol ([M + H]$^+$). The fragment ions at $m/z$ 105, $m/z$ 87, and $m/z$ 69 represented one, two, and three water molecules eliminated from [M + H]$^+$, respectively. The elimination of water molecules from the protonated molecules was similar to that observed in PTR-MS measurements of monoalcohol molecules (Spanel and Smith, 1997). In the case of meso-erythritol, a polyhydric alcohol, multiple water molecules were shown to be desorbed from the protonated molecules.

The organic compounds present in secondary organic aerosol particles include dicarboxylic acids, dialdehydes, diketones, polyols, and organic peroxides. When the secondary organic aerosol particles containing these molecules are measured by
TD-PTR-QiTOF, [M + H]$^+$ and [M + H – H$_2$O]$^+$ are expected to be detected in a mixed state, and care should be taken in interpreting the detected ions.

3.5 Comparison with Previous Studies and Future Work

Here, we discuss the advantages of our results compared with previous studies. Eichler et al. (2015) reported the mass spectra of secondary organic aerosols derived from limonene (C$_{10}$H$_{16}$) measured by TD-PTR-TOFMS instrument. They detected signals such as C$_{10}$H$_{17}$O$^+$, C$_{10}$H$_{17}$O$_2^+$, and C$_{10}$H$_{17}$O$_3^+$ from particles formed by ozone oxidation of C$_{10}$H$_{16}$, but did not interpret the detected ions. The mass spectral data for secondary organic aerosol markers reported in this study may be useful for interpretation of ions detected in the analysis of secondary organic aerosol particles including alcohols, aldehydes, ketones, and carboxylic acids although an ion signal of a specific $m/z$ is assumed to be attributed to a protonated molecule and ion formed by the dehydration of a protonated molecule. For example, the C$_{10}$H$_{17}$O$_3^+$ ion is attributed to both C$_{10}$H$_{16}$O$_3$ products with an aldehyde or ketone functional group and C$_{10}$H$_{18}$O$_4$ products with a carboxylic acid functional group.

Holzinger et al. (2010b) conducted field observations of organic aerosols using TD-PTR-TOFMS and reported a peak at $m/z$ 129.055, similar to the adipic acid peak ($m/z$ 129.052) in our study, in atmospheric aerosols. They also pointed out that fragmentation of
organic compounds may lead to underestimation of the mass concentration of organic matter. It is suggested that the information on the mass spectra of the standard compounds and the optimization of the measurement conditions obtained in this study are necessary to interpret the mass spectra of real atmospheric samples and calculate more accurate quantitative values. However, there are still some issues to be considered for the practical application of TD-PTR-QiTof: (1) evaluating the feasibility of quantifying compound concentrations in real air, (2) acquiring mass spectra of a wider range of reference materials than in this study, (3) understanding the limitations of detectable organics due to the upper limit of TD temperature, and (4) optimizing TD temperature for measurement of aerosol particles in internal mixing.

4 CONCLUSION

In this study, online analysis of organic aerosol particles was performed using a PTR-QiTof instrument in combination with a hand-made TD instrument. We measured the mass spectra of five single-component particles including dicarboxylic acids, dialdehyde, and polyol and investigated the signal response to TD tube material, particle concentration, TD temperature, and flow rate in the TD. The signal intensity of adipic acid measured at 100°C using PFA as the TD tube was 3300 times higher than that for a copper tube. The use of a
PFA tube was effective because gaseous semi-volatile organic compounds volatilized in the TD system were easily lost by wall deposition loss in the copper tube. In the case of the PFA tube, if the residence time in the TD tube was too long, the signal tended to decrease due to wall deposition loss of gaseous semi-volatile organic compounds. Under the optimized conditions, the signal intensity of the mass spectrometer was proportional to the particle concentration when concentration was below ~300 μg m⁻³. Furthermore, the mass spectrometer signal increased with increasing TD temperature. In the case of adipic acid and phthalic acid particles, the signal intensity reached half of the signal at 120°C in the temperature range of 50–70°C, and in the case of meso-erythritol, the signal intensity reached half of the signal at 120°C in the temperature range of 30–50°C. For cis-pinonic acid and terephthaldehyde, it was not possible to generate sufficient amounts of particles for measurement due to their high volatility. For terephthaldehyde, the protonated molecule ([M + H]⁺) was the major ion, whereas for the carboxylic acids (adipic, phthalic, and cis-pinonic acids) and the polyol (meso-erythritol), the ion ([M + H − H₂O]⁺), formed by elimination of one water molecule from the protonated molecule, was the major ion.

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**APPENDIX A**

In the following, we describe the method and results used to estimate the time to volatilization of single-component particles in this paper. The calculation method described below is based on the method of Hinds (1999).

According to Hinds (1999), the evaporation rate of a single component particle of size $D_p$ can be expressed by Eq. A1:

$$\frac{dD_p}{dt} = \frac{4D_v M}{R \rho D_p} \left( \frac{P}{T} - \frac{P_s}{T_s} \right) \phi,$$  \hspace{1cm} (A1)

where $D_v$ is the diffusion coefficient of volatilized molecules in air, $M$ is the mass of molecules per mol, $R$ is the gas constant, $\rho$ is the density of molecules in the liquid, $P$ is the partial pressure of molecules far from the particle in the system, $T$ is the temperature of the system, $P_s$ is the partial pressure of molecules at the particle surface, $T_s$ is the temperature at
the particle surface, and \( \phi \) is Fuch’s correction factor. Assuming \( P = 0 \) and \( T_s = T \), Eq. A1 can be expressed as Eq. A2 (Fujitani et al., 2012):

\[
\frac{dD_p}{dt} = \frac{4D_vM}{R\rho D_pT}(-P_s)\phi .
\]  

(A2)

The \( P_s \) on the surface of the particles in the right-hand side of Eq. A2 is calculated by the equation for vapor pressure at \( T \) obtained from the Clausius–Clapeyron equation multiplied by the Kelvin ratio (\( K_R \)):

\[
P_s = K_R P_v \exp\left[-\Delta H_v \left(\frac{1}{T} - \frac{1}{298}\right)\right],
\]  

(A3)

where \( P_v \) is the saturation vapor pressure at 298 K, \( \Delta H_v \) is the evaporation enthalpy at 298 K, and \( K_R \) is the coefficient of the increase in vapor pressure at the surface of the microparticles due to the Kelvin effect, as shown in Eq. A4:

\[
K_R = \exp\left(\frac{4\gamma M}{R\rho D_v T}\right).
\]  

(A4)

Fuch’s correction factor on the right-hand side of Eq. A2 is expressed as Eq. A5:

\[
\phi = \frac{2\lambda + D_p}{D_p + 5.33(\lambda^2/D_p) + 3.42\lambda},
\]  

(A5)

where \( \lambda \) is the mean free path of a molecule in air at \( T \). In this study, we used the value of the mean free path of nitrogen molecules as an approximation.
The values of $D_v$, $\rho$, $P_v$, and $\Delta H_v$ for five organic compounds (adipic acid, phthalic acid, meso-erythritol, cis-pinonic acid, and terephthaldehlyde) were calculated using the SPARC online calculator (Hilal et al., 2003). The literature value of the surface tension of dioctyl phthalate (0.0311 N m$^{-1}$; Yaws, 2014) was used as a substitute for the surface tension values of the five organics.

As an example, the calculation results for adipic acid particles with a diameter of 350 nm are shown in Fig. A1. The time to evaporation of adipic acid particles was 53 s, 2.6 s, 51 ms, and 5.1 ms at the system temperatures of 50°C, 70°C, 100°C, and 120°C, respectively. At 58°C, the time to evaporation of 350-nm adipic acid particles was the same as the residence time of the TD system. Similar calculations were performed for organic materials other than adipic acid, and the temperature at which the time for evaporation of 350-nm particles was the same as the residence time of the TD system was investigated. The results are shown in Table 2 in the main text.
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Table 1. Compound, thermal desorption (TD) tubing, TD temperature, flow rate, particle diameter ($D_p$), and particle mass concentration ($C$) in present experiments.

<table>
<thead>
<tr>
<th>Run</th>
<th>Compound</th>
<th>TD tubing</th>
<th>TD temp.</th>
<th>Flow rate</th>
<th>$D_p$</th>
<th>$C^{\text{a})}$</th>
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<td></td>
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<td>(°C)</td>
<td>(L min$^{-1}$)</td>
<td>(nm)</td>
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Table 1: Concentration of terephthalaldehyde PFA 100 0.30 polydisperse 33

451 a) Particle mass concentration was calculated from SMPS volume concentration and density listed in Table 2. b) Experiment was conducted without filter.
Table 2. Molecular weight (MW), density (ρ), vapor pressure (Pv), heat of vaporization (ΔHv), and diffusion coefficient of vapor (Dv) calculated by SPARC calculator and particle vaporization temperature (t*) estimated for compounds examined in this study.

<table>
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<tr>
<th>Compound</th>
<th>MW</th>
<th>ρ</th>
<th>Pv</th>
<th>ΔHv</th>
<th>Dv</th>
<th>t*</th>
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<tr>
<td></td>
<td>(g cm⁻³)</td>
<td>(Pa)</td>
<td>(kJ mol⁻¹)</td>
<td>(cm² s⁻¹)</td>
<td>(°C)</td>
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<td>1.16</td>
<td>8.60 x 10⁻¹</td>
<td>75</td>
<td>0.0650</td>
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</table>

a) Results calculated by SPARC online calculations at a temperature of 25°C. b) Temperature at which particle evaporation lifetime, evaluated for 350-nm single component particles by the method of Hinds (1999), becomes the same as TD residence time.
Fig. 1. Schematic experimental setup for thermal desorption-proton transfer reaction-quadrupole interface time-of-flight mass spectrometry (TD-PTR-QiTOF) analysis; DT is drift tube; DMA is differential mobility analyzer; and SMPS is scanning mobility particle sizer.
Fig. 2. Time series of total mass peak intensity of \textit{m/z} 123, 105, 87, and 69 measured for \textit{meso}-erythritol particles using PFA thermal desorption instrument.
Fig. 3. Thermal desorption-proton transfer reaction-quadrupole interface time-of-flight mass spectrometry (TD-PTR-QiTOF) vapor concentration measured as a function of scanning mobility particle sizer (SMPS) particle concentration. Vapor concentrations were measured at a TD temperature of 100°C using PFA TD instrument.
Fig. 4. Ratio of vapor concentration to particle concentration, measured as a function of thermal desorption (TD) temperature. PFA tubing was used for the TD instrument.
Fig. 5. Mass spectrum measured for adipic acid particles at a thermal desorption (TD) temperature of 100°C using PFA TD instrument. Background signals at a TD temperature of 100°C were subtracted.
Fig. 6. Mass spectrum measured for terephthaldehyde at a thermal desorption (TD) temperature of 100°C using PFA TD instrument. Background signals at a TD temperature of 100°C were subtracted.
Fig. 7. Mass spectrum measured for *meso*-erythritol particles at a thermal desorption (TD) temperature of 100°C using PFA TD instrument. Background signals at a TD temperature of 100°C were subtracted.
Fig. A1 Temporal profiles of diameter calculated for 350-nm adipic acid particles at 50°C, 70°C, 100°C, and 120°C.