An intercomparison study of four different techniques for measuring chemical composition of nanoparticles

Supplementary Material

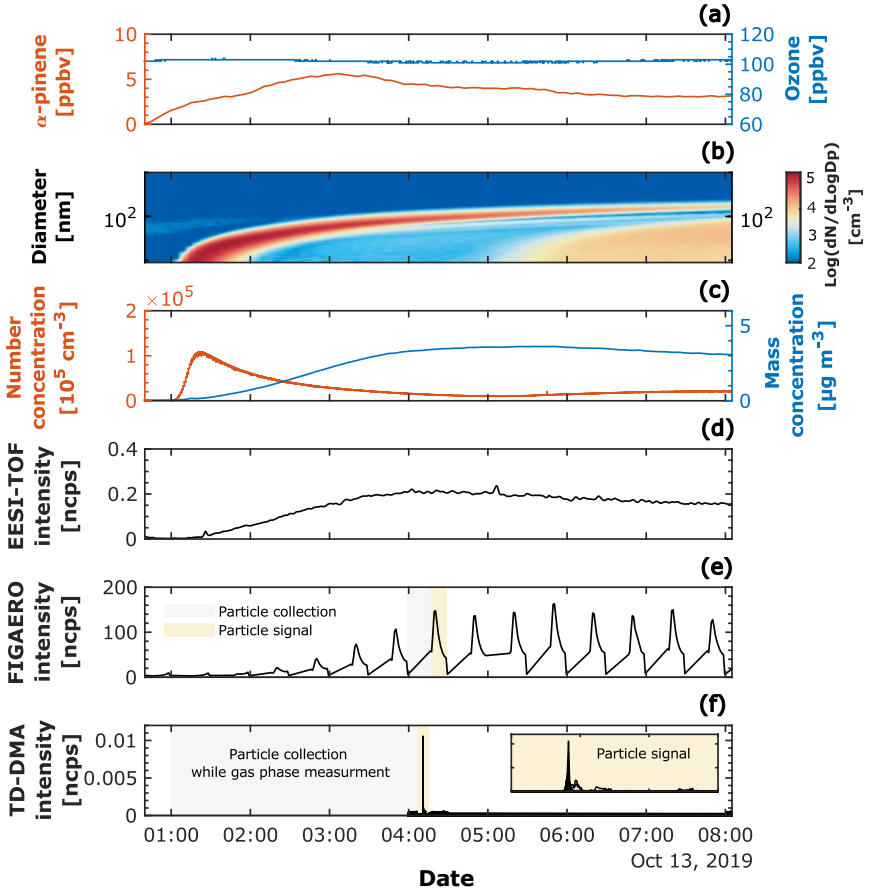

Figure S1. Experimental overview of a representative biogenic new particle formation experiment (α-pinene ozonolysis at -30 °C and 20 % RH), (a) Mixing ratio in ppbv for the precursor gases, α-pinene and ozone. (b) particle size distribution measured by the SMPS, the color scale represents the log 10 of the normalized particle concentration in cubic centimeters (cm^{-3}). (c) Particle number concentration in cm^{-3} measured by the CPC with a cut-off diameter of 2.5 nm and mass concentration in μg m^{-3} (obtained by integrating the normalized mass concentration from the SMPS). (d) particle-phase signal measured continuously by the EESI-TOF. Fifth and sixth panels: Particle-phase measured by FIGAERO and TD-DMA respectively, the gray shaded areas refer to the particle collection period and the yellow shaded areas to the desorption period. FIGAERO measured in a semicontinuous mode in which 15-minute particle collections followed by 15-minute desorption periods were performed during the whole experiment. The TD-DMA collection period was approximately 4 hours while the desorption period lasted around 3 minutes.

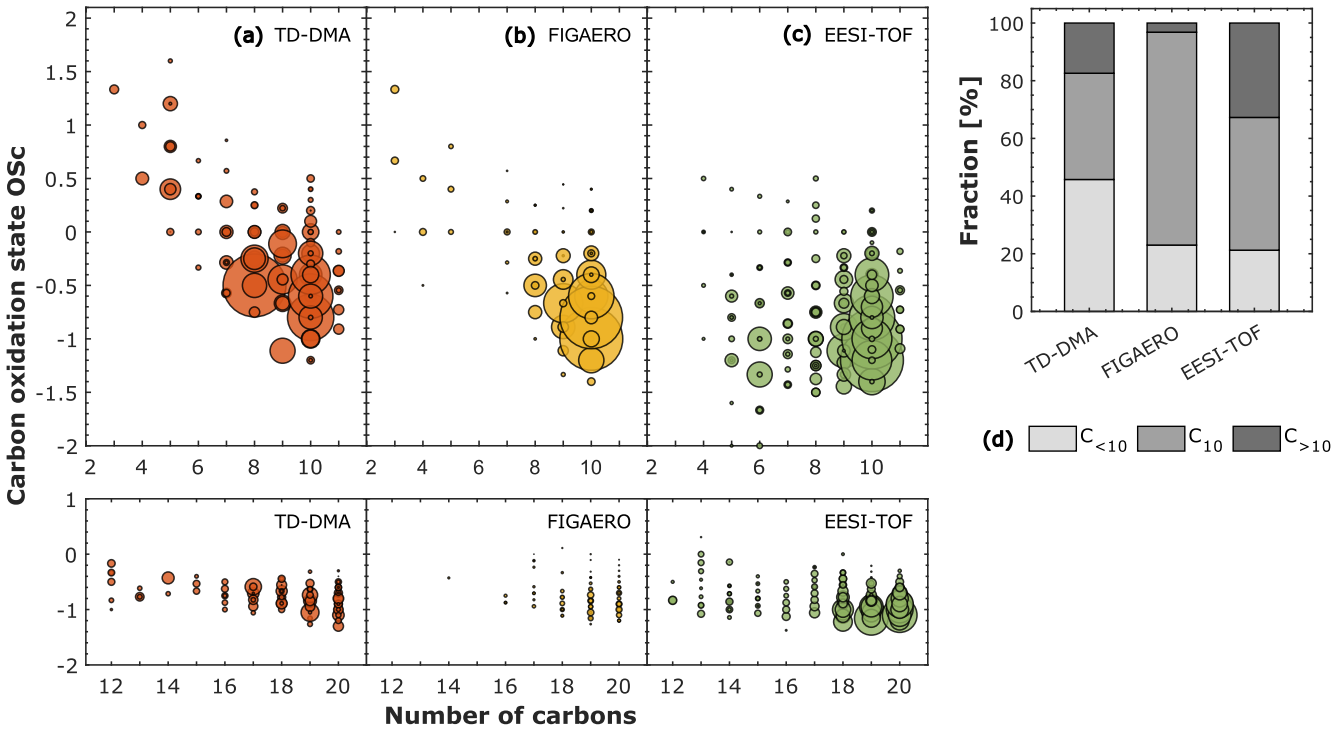

Figure S2. Carbon oxidation state OSc against the number of carbon atoms for α-pinene oxidation products in the particle-phase at -50 ºC and 20 % RH measured by three different techniques. (a) TD-DMA: Thermal Desorption-Differential Mobility Analyzer coupled to a NO_3^- chemical ionization-atmospheric-pressure-interface-time-of-flight mass spectrometer. (b) FIGAERO: Filter Inlet for Gases and AEROsols coupled to an I^- high-resolution time-of-flight chemical-ionization mass spectrometer, and (c) EESI-TOF: Extractive Electrospray Na^+ Ionization time-of-flight mass spectrometer. The level of α-pinene was between 1 and 6 ppbv while the ozone level was ~ 100 ppbv. The carbon oxidation state is calculated as follows: OSc = 2xO:C - H:C. The symbol sizes in (a), (b), and (c) represent the intensities normalized by the total signal in each system. (d) Fraction of species in the particle-phase containing less than 10 carbon atoms ($C_{<10}$), 10 carbon atoms (C_{10}), and more than 10 carbon atoms ($C_{>10}$). The fraction was calculated by normalizing the intensities by the total signal in each system.

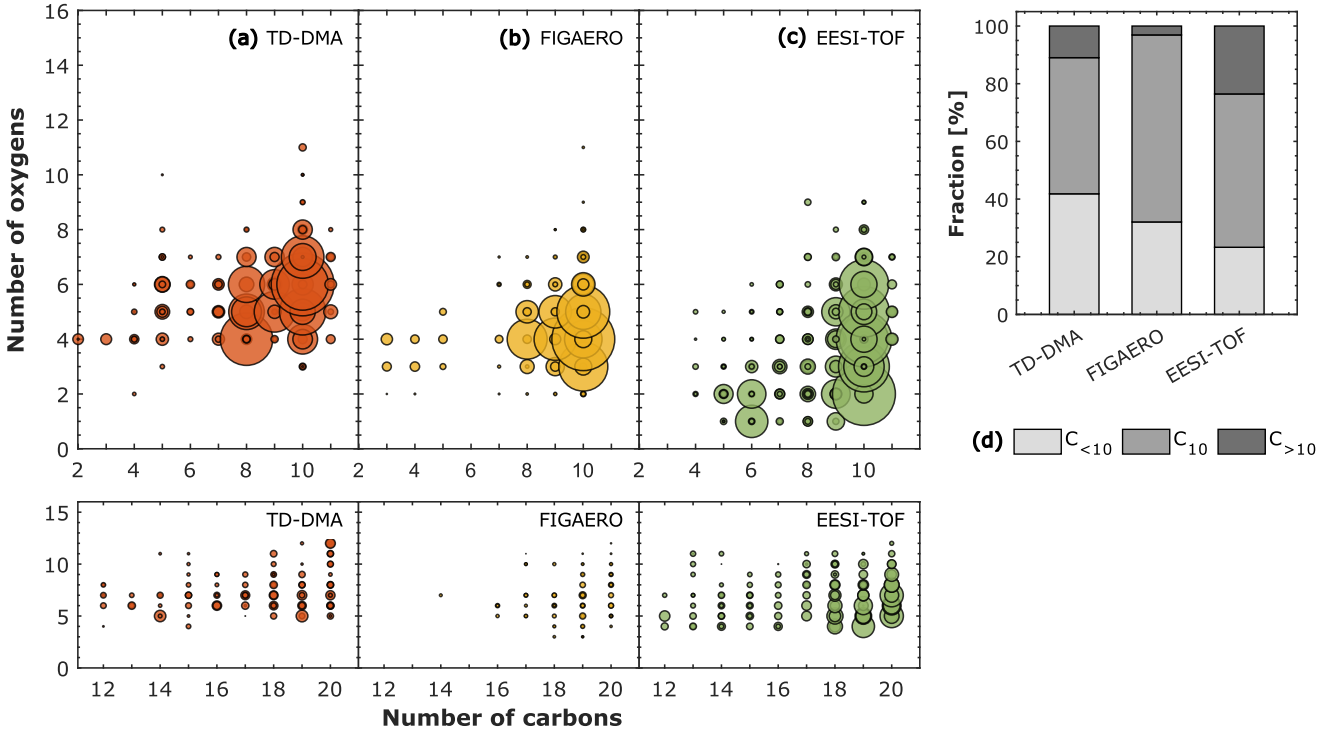

Figure S3. Number of oxygen atoms against the number of carbon atoms for α-pinene oxidation products in the particle-phase at -30 ºC and 20 % RH measured by three different techniques. (a) TD-DMA: Thermal Desorption-Differential Mobility Analyzer coupled to a NO_3^- chemical ionization-atmospheric-pressure-interface-time-of-flight mass spectrometer. (b) FIGAERO: Filter Inlet for Gases and AEROsols coupled to an I^- high-resolution time-of-flight chemical-ionization mass spectrometer, and (c) EESI-TOF: Extractive Electrospray Na^+ Ionization time-of-flight mass spectrometer. The level of α-pinene was between 1 and 6 ppbv while the ozone level was ~ 100 ppbv. The symbol sizes in (a), (b), and (c) represent the intensities normalized by the total signal in each system. (d) Fraction of species in the particle-phase containing less than 10 carbon atoms ($C_{<10}$), 10 carbon atoms (C_{10}), and more than 10 carbon atoms ($C_{>10}$). The fraction was calculated by normalizing the intensities by the total signal in each system.

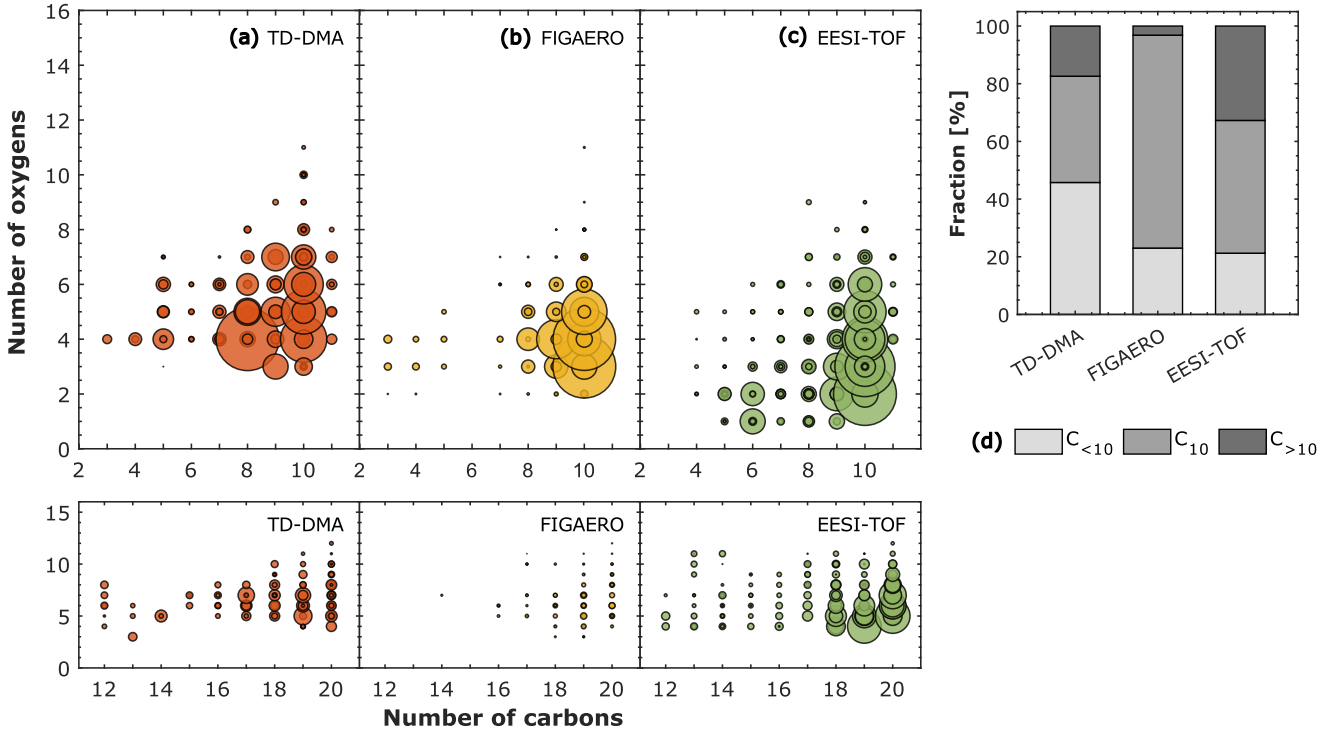

Figure S4. Number of oxygen atoms against the number of carbon atoms for α-pinene oxidation products in the particle-phase at -50 ºC and 20 % RH measured by three different techniques. (a) TD-DMA: Thermal Desorption-Differential Mobility Analyzer coupled to a NO_3^- chemical ionization-atmospheric-pressure-interface-time-of-flight mass spectrometer. (b) FIGAERO: Filter Inlet for Gases and AEROsols coupled to an I^- high-resolution time-of-flight chemical-ionization mass spectrometer, and (c) EESI-TOF: Extractive Electrospray Na^+ Ionization time-of-flight mass spectrometer. The level of α-pinene was between 1 and 6 ppbv while the ozone level was ~ 100 ppbv. The symbol sizes in (a), (b), and (c) represent the intensities normalized by the total signal in each system. (d) Fraction of species in the particle-phase containing less than 10 carbon atoms ($C_{<10}$), 10 carbon atoms (C_{10}), and more than 10 carbon atoms ($C_{>10}$). The fraction was calculated by normalizing the intensities by the total signal in each system.

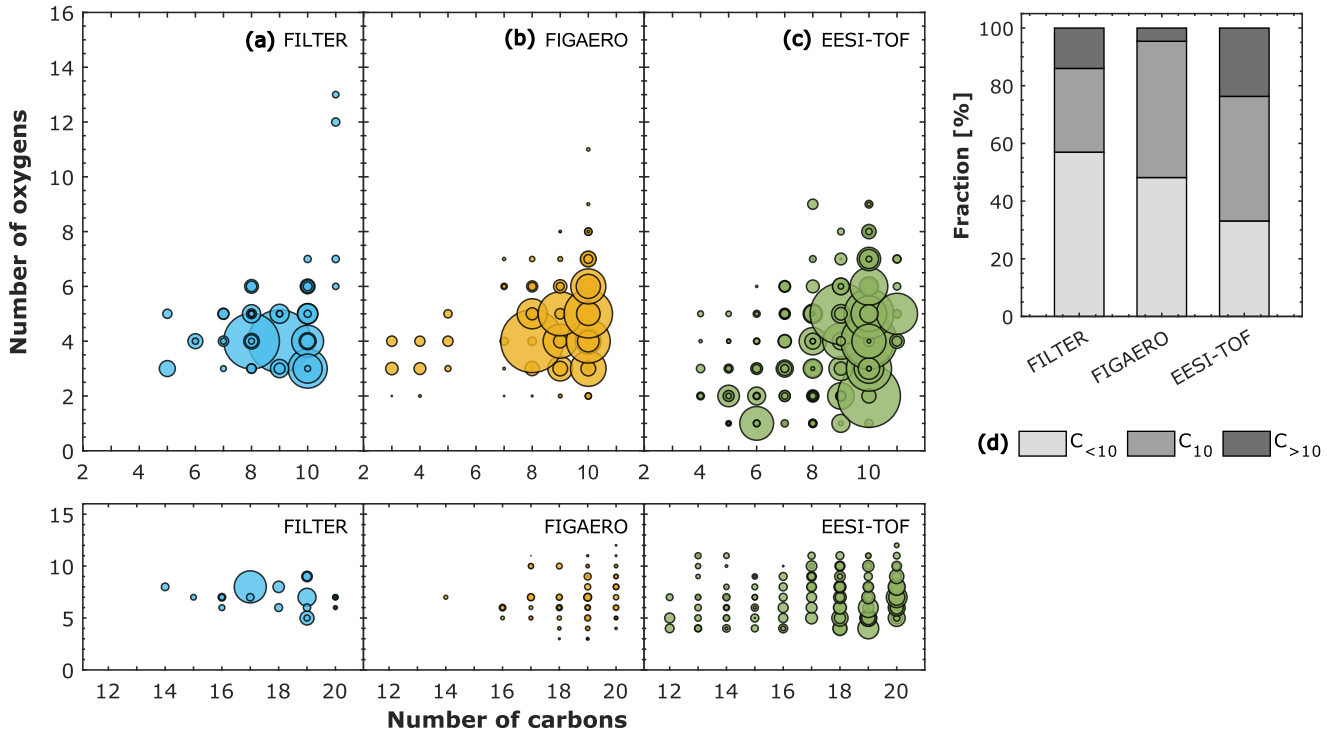

Figure S5. Number of oxygen atoms against the number of carbon atoms for α-pinene oxidation products in the particle-phase at -10 °C and 80 % RH measured by three different techniques. (a) FILTER: Offline analysis of filters using Ultra-high-performance liquid chromatography (UHPLC) and heated electrospray ionization (HESI) coupled to an Orbitrap high-resolution mass spectrometer (HRMS). (b) FIGAERO: Filter Inlet for Gases and AEROsols coupled to an I^- high-resolution time-of-flight chemical-ionization mass spectrometer, and (c) EESI-TOF: Extractive Electrospray Na^+ Ionization time-of-flight mass spectrometer. The level of α-pinene was between 1 and 3 ppbv while the ozone level was ~ 100 ppbv. The symbol sizes in (a), (b), and (c) represent the intensities normalized by the total signal in each system. (d) Fraction of species in the particle-phase containing less than 10 carbon atoms ($C_{<10}$), 10 carbon atoms (C_{10}), and more than 10 carbon atoms ($C_{>10}$). The fraction was calculated by normalizing the intensities by the total signal in each system.

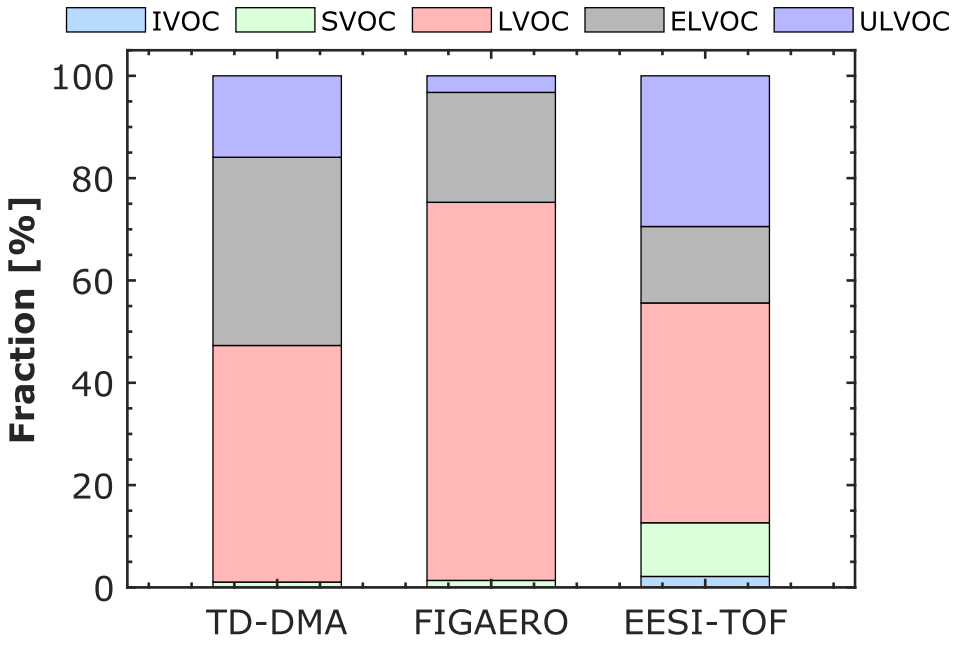

Figure S6. Fraction of volatility regimes for α-pinene oxidation products in the particle-phase at -50 ºC and 20 % RH measured by three different techniques: (TD-DMA) Thermal Desorption-Differential Mobility Analyzer coupled to a NO_3^- chemical ionization-atmospheric-pressure-interface-time-of-flight mass spectrometer, (FIGAERO) Filter Inlet for Gases and AEROsols coupled to an I^- high-resolution time-of-flight chemical-ionization mass spectrometer, and (EESI-TOF) Extractive Electrospray Na^+ Ionization time-of-flight mass spectrometer. The level of α-pinene was between 1 and 6 ppbv while Ozone level was ~ 100 ppbv. The volatility regimes (ULVOC, ELVOC, LVOC, SVOC, IVOC) were defined as in Donahue et al. (2012) and in Schervish and Donahue (2020).

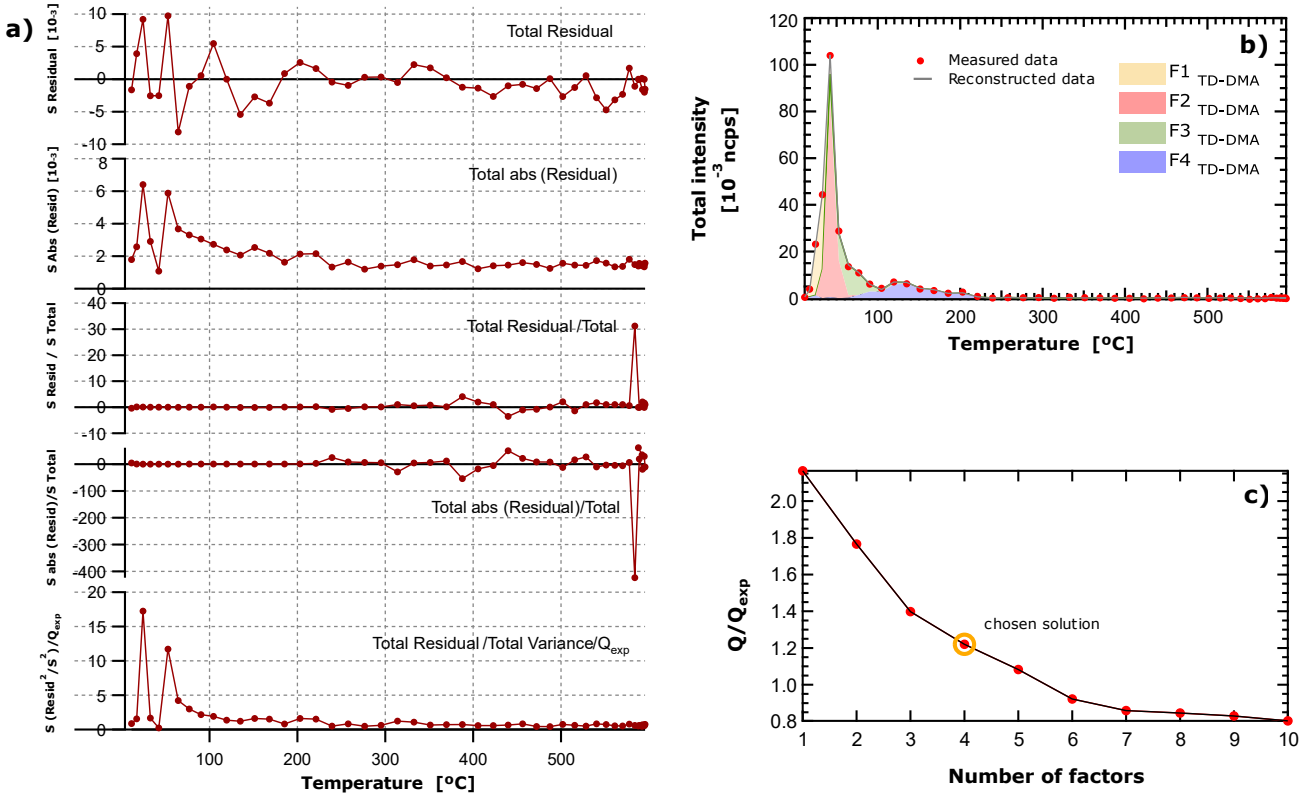

Figure S7. a) Residuals for TD-DMA 4-Factor solution expressed in terms of total residual, absolute residual, variance and Q_{exp} (square of the residual scaled with the error summed over all ions and observations) against the temperature. More details about the calculation and interpretation of these quantities can be found in Buchholz et al. (2020); b) Measured and reconstructed TD-DMA total intensity against the temperature, the contribution of the factors are shown with different colors, and c) Q/Q_{exp} vs Number of factors. Q/Q_{exp} is an optimization parameter based on the residuals and described in Buchholz et al. (2020), in the ideal case Q/Q_{exp} is equal to 1.

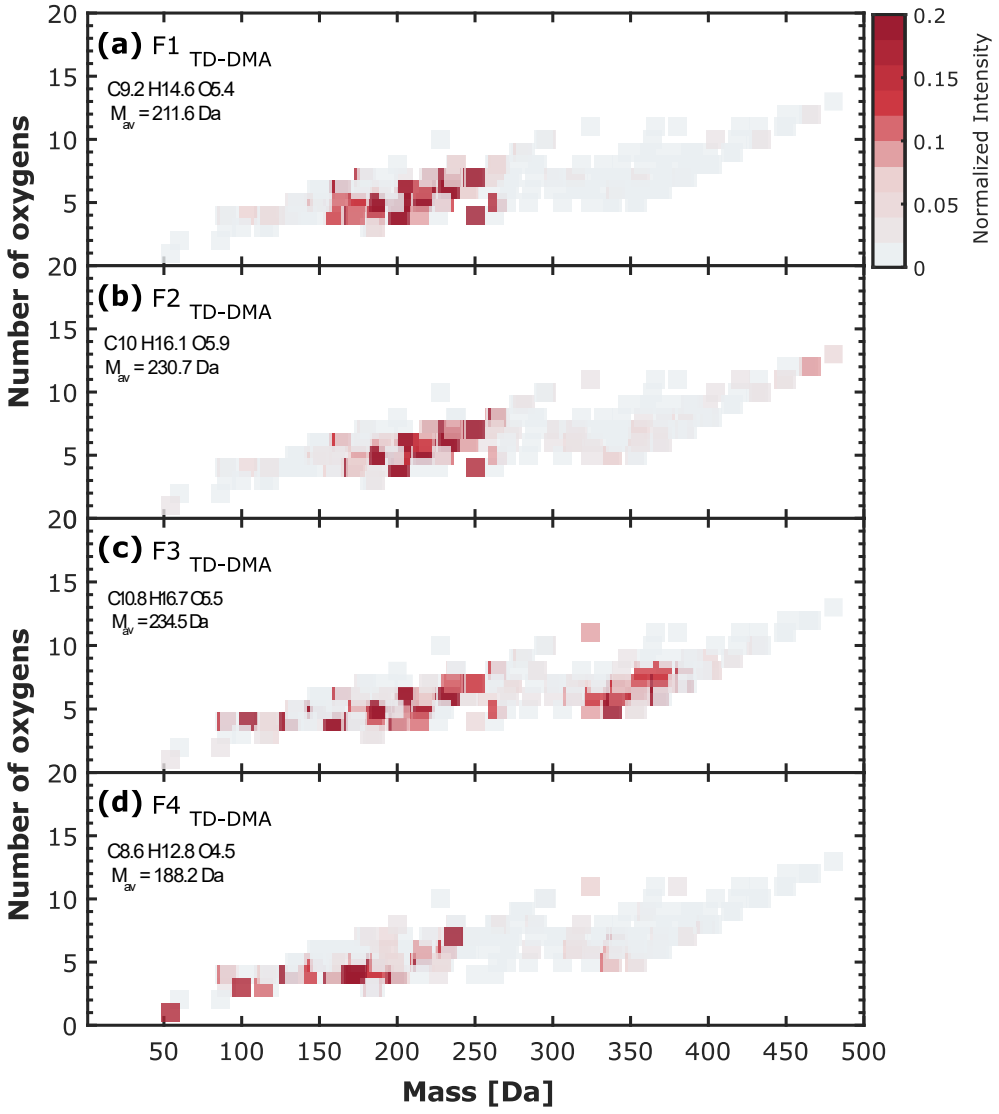

Figure S8. PMF suggested solution on the particle-phase detected by the TD-DMA in α-pinene ozonolysis experiment at -30 ºC and 20 % RH, (a) F1 TD-DMA, (b) F2 TD-DMA, (c) F3 TD-DMA and, (d) F4 TD-DMA are the factors mass spectra expressed in terms of number of oxygens against the neutral ion mass. The colorscale represents the intensity normalized by the total particle signal. The particle-phase signal has been background corrected.

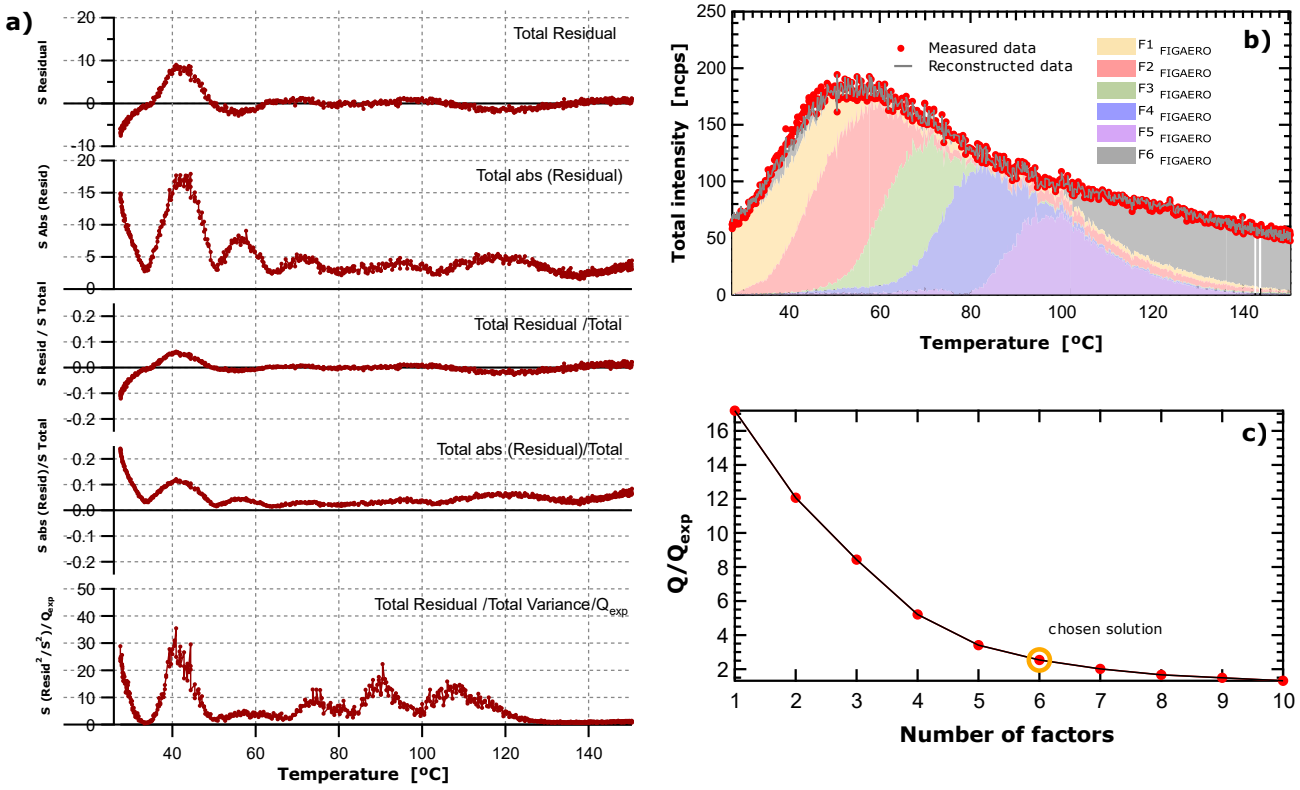

Figure S9. a) Residuals for FIGAERO 6-Factor solution expressed in terms of total residual, absolute residual, variance and Q_{exp} (square of the residual scaled with the error summed over all ions and observations) against the temperature. More details about the calculation and interpretation of these quantities can be found in Buchholz et al. (2020); b) Measured and reconstructed FIGAERO total intensity against the temperature, the contribution of the factors are shown with different colors, and c) Q/Q_{exp} vs Number of factors. Q/Q_{exp} is an optimization parameter based on the residuals and described in Buchholz et al. (2020), in the ideal case Q/Q_{exp} is equal to 1.

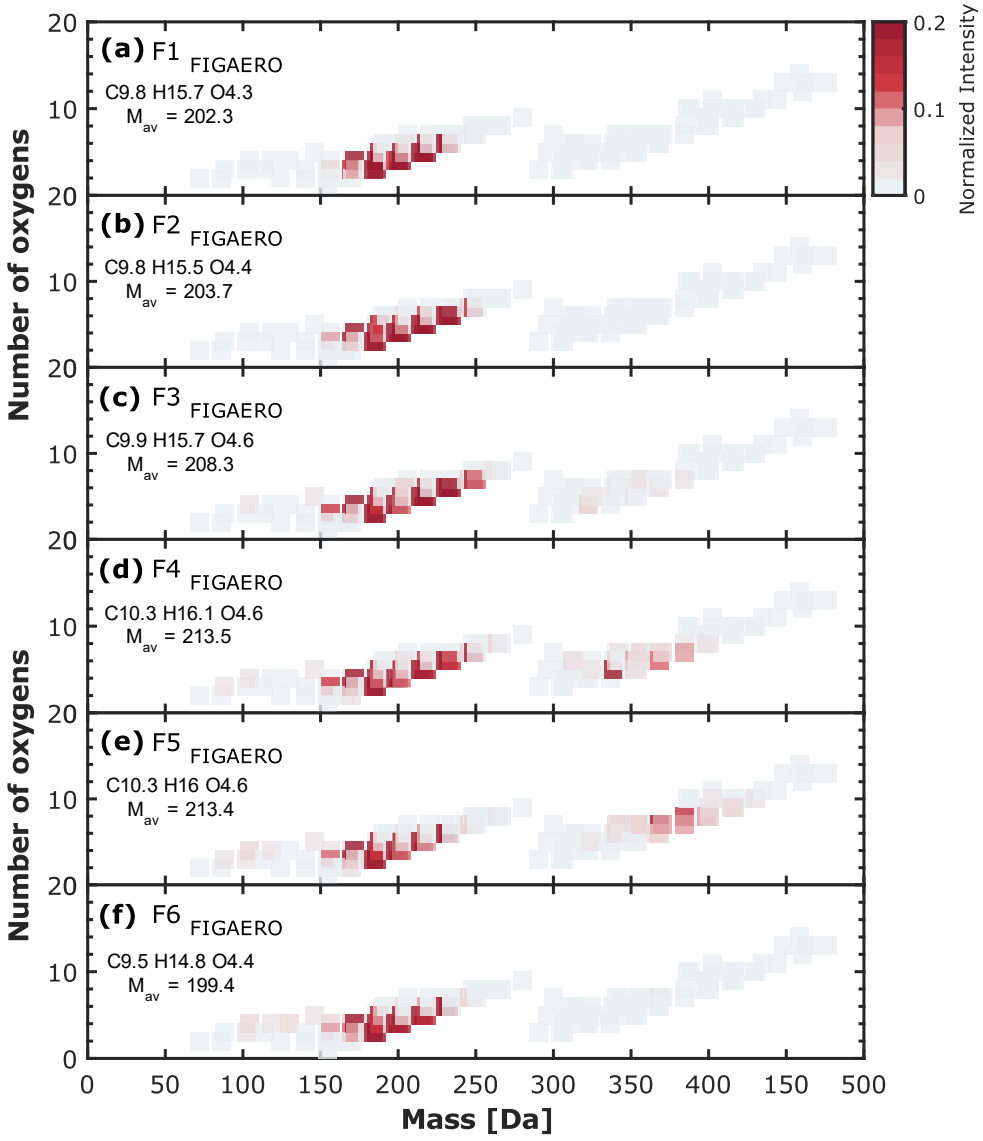

Figure S10. PMF suggested solution on the particle-phase detected by FIGAERO in α-pinene ozonolysis experiment at -30 °C and 20 % RH, (a) F1 FIGAERO, (b) F2 FIGAERO, (c) F3 FIGAERO, (d) F4 FIGAERO, (e) F5 FIGAERO and, (f) F6 FIGAERO are the factors mass spectra expressed in terms of number of oxygens against the neutral ion mass. The colorscale represents the intensity normalized by the total particle signal. The particle-phase signal has been background corrected.

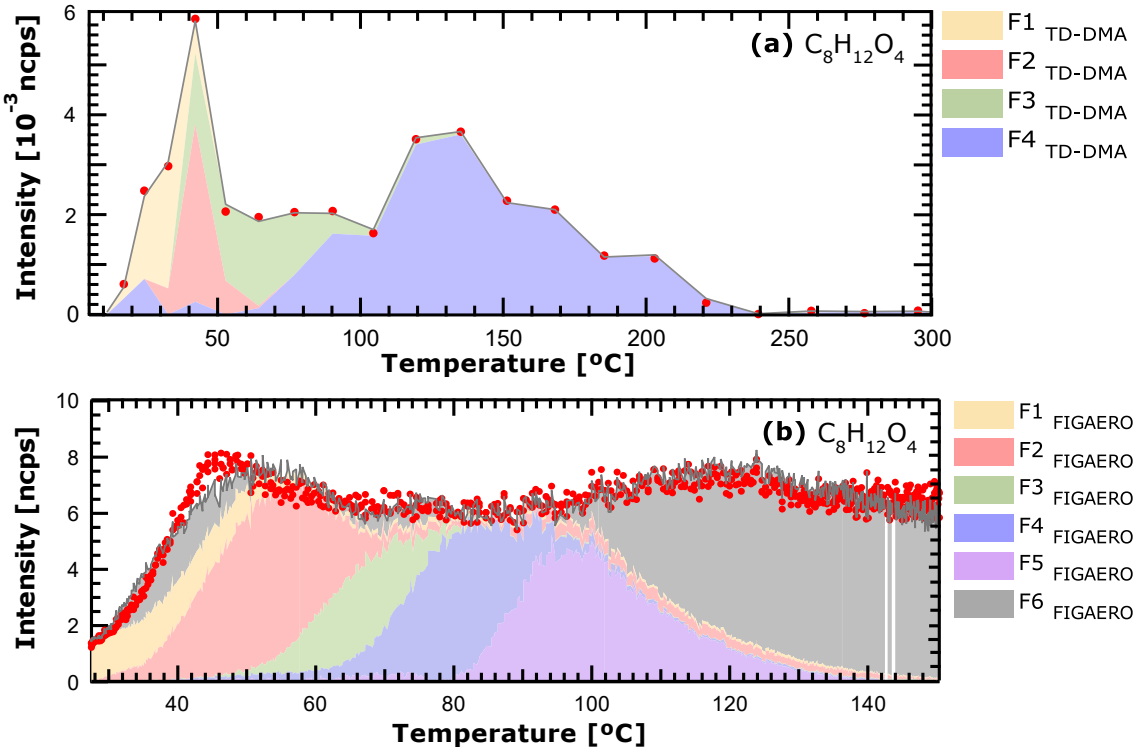

Figure S11. Factor thermograms on the PMF suggested solutions for $C_8H_{12}O_4$ measured by (a) TD-DMA and (b) FIGAERO in the α-pinene ozonolysis experiment at -30 ºC and 20 % RH.

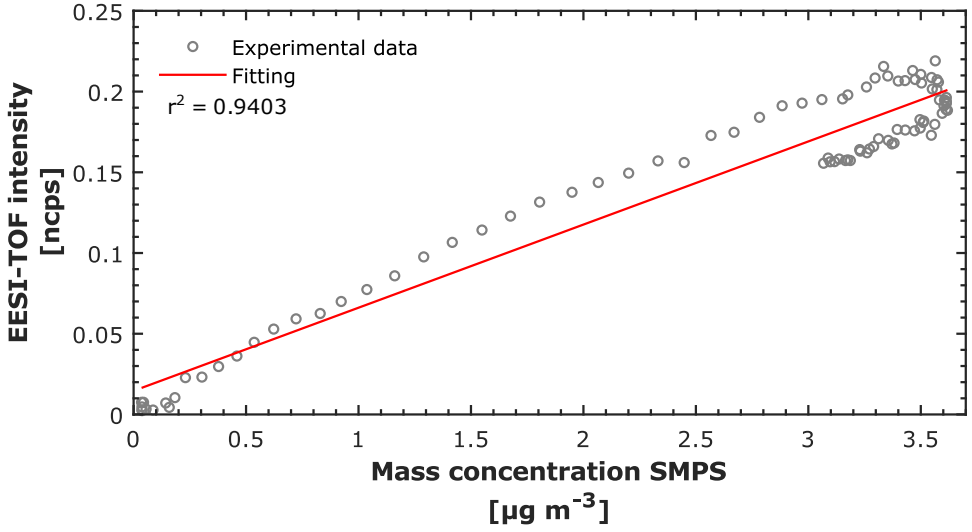

Figure S12. Correlation plot of total EESI intensity in ncps and the mass concentration calculated from the SMPS for the representative experiment shown in Fig. S6. The EESI-TOF particle signal was averaged every 5 minutes for correlation with the SMPS.

Buchholz, A., Ylisirniö, A., Huang, W., Mohr, C., Canagaratna, M., Worsnop, D. R., Schobesberger, S., and Virtanen, A.: Deconvolution of FIGAERO–CIMS thermal desorption profiles using positive matrix factorisation to identify chemical and physical processes during particle evaporation, Atmos. Chem. Phys., 20, 7693-7716, 10.5194/acp-20-7693-2020, 2020.