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Real-time measurement of phase partitioning of organic compounds using a proton-transfer-reaction time-of-flight mass spectrometer coupled to a CHARON inlet

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Table S1. The information of pure analytes, their molecular formula, density, molecular weight and vapor pressure.

Compound	Molecular Formula	Density (ρ, g cm^{-3})	Molecular weight (Mw, g mol^{-1})	Vapor pressure [a] (p, Pa, 25 °C)
Ammonium nitrate	NH_4NO_3	1.7	80.043	
2,7-dihydroxynaphthalene	$C_{10}H_8O_2$	1.3	160.170	1.10×10^{-4}
Levoglucosan	$C_6H_{10}O_5$	1.7	162.140	9.98×10^{-6}
Phthalic acid	$C_8H_6O_4$	1.6	166.130	1.02×10^{-4}
Vanillic acid	$C_8H_8O_4$	1.4	168.150	1.97×10^{-4}
Cis-pinonic acid	$C_{10}H_{16}O_3$	1.2	184.230	8.26×10^{-2}
3-methylbutane-1,2,3-tricarboxylic acid	$C_8H_{12}O_6$	1.4	204.180	8.22×10^{-5}
2-pentadecanone	$C_{15}H_{30}O$	0.8	226.400	4.77×10^{-1}
1-pentadecanol	$C_{15}H_{32}O$	0.8	228.410	3.78×10^{-3}
Sucrose	$C_{12}H_{22}O_{11}$	1.6	342.300	4.69×10^{-14}

[a] Taken from Estimation Program Interface (EPI) Suite (Version v4.11), US EPA

Table S2. Measured unitless enrichment factor (*EF*) of ammonium nitrate particles as a function of particle size in the 100–450 nm range and the corresponding relative standard deviation (RSD) from all replicating measurements.

Size (nm)	Mean *EF* for each size bin (number of tests)	RSD
100	6 (11)	11%
150	13 (11)	8%
200	16 (11)	10%
250	17 (4)	10%
300	17 (11)	7%
350	18 (11)	8%
400	18 (4)	8%
450	18 (3)	9%

Table S3. Measured unitless enrichment factor (*EF*) and corresponding relative standard deviation (RSD) of the selected organic standards under different temperatures. Overall RSD $=\sqrt{RSD_{tem}{}^2+RSD_{each}{}^2}$.

Standards	Molecular Formula	Mean signal in the 70–140 °C range (ncps ppb^{-1})	RSD_{tem} in the 70–140 °C range	*EF*	RSD_{each} at each temperature	Overall RSD
2,7-dihydroxynaphthalene	$C_{10}H_8O_2$	5551.44	3%	10	11%	12%
Levoglucosan	$C_6H_{10}O_5$	6687.43	3%	14	13%	13%
Phthalic acid	$C_8H_6O_4$	10611.46	5%	13	11%	12%
Vanillic acid	$C_8H_8O_4$	9694.58	1%	16	7%	7%
Cis-pinonic acid	$C_{10}H_{16}O_3$	5381.82	6%	16	15%	16%
3-methylbutane-1,2,3-tricarboxylic acid	$C_8H_{12}O_6$	6916.67	6%	13	21%	22%
2-pentadecanone	$C_{15}H_{30}O$	9370.66	3%	13	19%	19%
1-pentadecanol	$C_{15}H_{32}O$	12810.38	4%	20	10%	10%
Sucrose	$C_{12}H_{22}O_{11}$	6924.86	14%	10	20%	25%

Table S4. Relative abundance of all product ions observed from nine organic standards tested under different desorption temperatures (70–140 °C). The protonated parent molecule, $[M+H]^+$, is highlighted in bold. RSD: relative standard deviation. NA: Not Available. ND: Not Detected.

Standards	Molecular Formula	Detected ion mass (*m/z*)	Ion sum formula	Mean relative abundance	Temperature tests (normalized relative intensity)								RSD
					140 °C	130 °C	120 °C	110 °C	100 °C	90 °C	80 °C	70 °C	
2,7-dihydroxynaphthalene	$C_{10}H_8O_2$	**161.060**	**$C_{10}H_9O_2$**	**100%**	1.000	1.072	1.066	1.069	1.043	1.057	1.086	1.120	3.0%
Levoglucosan	$C_6H_{10}O_5$	69.033	C_4H_5O	13.5%	0.137	0.133	0.141	0.141	0.140	0.141	0.145	0.148	3.1%
		85.028	$C_4H_5O_2$	40.8%	0.406	0.414	0.415	0.420	0.424	0.428	0.439	0.451	3.4%
		87.044	$C_4H_7O_2$	3.8%	0.039	0.040	0.039	0.040	0.039	0.038	0.040	0.042	2.7%
		97.028	$C_5H_5O_2$	11.8%	0.118	0.120	0.117	0.120	0.123	0.125	0.130	0.133	4.5%
		127.039	$C_6H_7O_3$	15.4%	0.152	0.161	0.154	0.160	0.158	0.162	0.166	0.172	4.0%
		145.050	$C_6H_9O_4$	14.2%	0.143	0.148	0.142	0.143	0.146	0.149	0.154	0.160	4.3%
		163.060	**$C_6H_{11}O_5$**	**0.5%**	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	4.7%
Phthalic acid	$C_8H_6O_4$	149.023	$C_8H_5O_3$	89.2%	0.899	0.914	0.875	0.844	0.816	0.810	0.798	0.805	5.4%
		167.034	**$C_8H_7O_4$**	**10.8%**	0.101	0.106	0.108	0.102	0.102	0.100	0.100	0.101	3.0%
Vanillic acid	$C_8H_8O_4$	151.039	$C_8H_7O_3$	10.5%	0.107	0.108	0.107	0.105	0.106	0.104	0.105	0.106	1.2%
		169.050	**$C_8H_9O_4$**	**89.5%**	0.893	0.921	0.901	0.902	0.904	0.890	0.901	0.912	1.1%
Cis-pinonic acid	$C_{10}H_{16}O_3$	71.049	C_4H_7O	27.9%	0.279	0.262	0.260	0.260	0.298	0.277	0.267	NA	6.6%
		115.075	$C_6H_{11}O_2$	36.0%	0.364	0.326	0.345	0.334	0.385	0.361	0.342	NA	7.2%
		139.112	$C_9H_{14}O$	6.1%	0.062	0.059	0.057	0.057	0.065	0.061	0.058	NA	6.4%

		167.107	$C_{10}H_{15}O_2$	18.5%	0.185	0.172	0.177	0.167	0.199	0.185	0.177	NA	7.1%
		185.117	**$C_{10}H_{17}O_3$**	**11.4%**	0.111	0.106	0.112	0.104	0.120	0.116	0.111	NA	6.4%
3-methylbutane-1,2,3-tricarboxylic acid	$C_8H_{12}O_6$	141.055	$C_7H_9O_3$	20.2%	0.180	0.206	0.201	0.181	0.205	0.230	0.182	0.181	9.3%
		187.060	$C_8H_{11}O_5$	79.8%	0.820	0.836	0.857	0.872	0.889	0.959	0.946	0.808	6.3%
		205.071	**$C_8H_{13}O_6$**	**0**	ND	ND	ND	ND	ND	ND	ND	ND	
2-pentadecanone	$C_{15}H_{30}O$	211.206	$C_{14}H_{27}O$	32.6%	0.305	0.314	0.301	0.294	0.308	0.322	0.328	NA	3.9%
		227.237	**$C_{15}H_{31}O$**	**19.8%**	0.237	0.194	0.204	0.158	0.180	0.171	0.182	NA	13.7%
		229.216	$C_{14}H_{29}O_2$	47.6%	0.458	0.447	0.437	0.441	0.453	0.460	0.478	NA	3.0%
1-pentadecanol	$C_{15}H_{32}O$	41.039	C_3H_5	1.0%	0.011	0.011	0.011	0.011	0.011	0.011	0.012	NA	2.7%
		43.054	C_3H_7	3.1%	0.032	0.034	0.033	0.033	0.035	0.036	0.037	NA	6.7%
		57.070	C_4H_9	28.5%	0.284	0.313	0.309	0.311	0.316	0.323	0.331	NA	6.6%
		71.086	C_5H_{11}	32.2%	*0.322*	0.347	0.346	0.352	0.354	0.368	0.375	NA	7.4%
		85.101	C_6H_{13}	26.6%	0.265	0.285	0.286	0.294	0.294	0.303	0.310	NA	7.4%
		99.117	C_7H_{15}	1.8%	0.017	0.018	0.019	0.019	0.019	0.020	0.021	NA	12.3%
		113.132	C_8H_{17}	0.9%	0.009	0.010	0.009	0.010	0.010	0.010	0.011	NA	13.4%
		127.148	C_9H_{19}	0.9%	0.009	0.010	0.010	0.010	0.010	0.011	0.011	NA	12.6%
		141.164	$C_{10}H_{21}$	0.9%	0.009	0.009	0.009	0.010	0.010	0.011	0.011	NA	12.4%
		155.179	$C_{11}H_{23}$	0.5%	0.005	0.005	0.005	0.006	0.006	0.006	0.006	NA	15.2%
		169.195	$C_{12}H_{25}$	0.2%	0.002	0.002	0.002	0.002	0.002	0.002	0.002	NA	7.5%
		211.242	$C_{15}H_{31}$	2.9%	0.029	0.031	0.030	0.032	0.032	0.034	0.035	NA	10.9%

		227.237	$C_{15}H_{31}O$	0.4%	0.005	0.005	0.005	0.005	0.005	0.005	0.005	NA	8.0%
		229.253	**$C_{15}H_{33}O$**	**0**	ND	ND	ND	ND	ND	ND	ND	NA	
		69.033	C_4H_5O	8.8%	0.079	0.083	0.077	0.067	0.066	0.073	0.091	0.075	10.7%
		85.028	$C_4H_5O_2$	23.9%	0.206	0.235	0.211	0.191	0.180	0.204	0.254	0.203	11.3%
		97.028	$C_5H_5O_2$	19.2%	0.218	0.229	0.197	0.175	0.164	0.177	0.218	0.177	12.6%
Sucrose	$C_{12}H_{22}O_{11}$	109.028	$C_6H_5O_2$	4.6%	0.056	0.052	0.047	0.039	0.037	0.041	0.048	0.040	15.1%
		127.039	$C_6H_7O_3$	35.0%	0.369	0.385	0.325	0.289	0.266	0.293	0.351	0.290	13.4%
		145.050	$C_6H_9O_4$	8.5%	0.071	0.083	0.076	0.068	0.064	0.071	0.091	0.071	11.7%
		343.123	**$C_{12}H_{23}O_{11}$**	**0**	ND	ND	ND	ND	ND	ND	ND	ND	

Table S5. Campaign average fraction of measured ($F_{p,m}$) and predicted ($F_{p,p}$) organic species in the particle phase grouped by the oxygen number, and predicted F_p was also corrected assuming the identified species are fragments of corresponding parent compounds through neutral losses of H_2O, CO, CO_2, and C_2H_6O, respectively.

Detected ion	Mass	Class	$F_{p,m}$	$F_{p,p}$	$F_{p,p}$ (+H_2O)	$F_{p,p}$ (+CO)	$F_{p,p}$ (+CO_2)	$F_{p,p}$ (+C_2H_6O)
$C_3H_4H^+$	41.039	C_xH_y	5.08×10^{-3}	2.59×10^{-10}	1.83×10^{-8}	5.11×10^{-8}	4.88×10^{-6}	1.46×10^{-7}
$C_2H_2OH^+$	43.018	C_xH_yO	6.30×10^{-3}	6.88×10^{-9}	8.68×10^{-7}	1.96×10^{-6}	2.59×10^{-4}	4.88×10^{-6}
$C_3H_6H^+$	43.054	C_xH_y	4.64×10^{-3}	2.59×10^{-10}	1.83×10^{-8}	5.11×10^{-8}	4.88×10^{-6}	1.46×10^{-7}
$C_2H_4OH^+$	45.033	C_xH_yO	3.34×10^{-2}	6.88×10^{-9}	8.68×10^{-7}	1.96×10^{-6}	2.59×10^{-4}	4.88×10^{-6}
$C_2H_6OH^+$	47.049	C_xH_yO	1.62×10^{-2}	6.88×10^{-9}	8.68×10^{-7}	1.96×10^{-6}	2.59×10^{-4}	4.88×10^{-6}
$C_3H_4OH^+$	57.033	C_xH_yO	7.75×10^{-3}	1.83×10^{-8}	1.96×10^{-6}	4.88×10^{-6}	5.75×10^{-4}	1.28×10^{-5}
$C_3H_6OH^+$	59.049	C_xH_yO	5.87×10^{-3}	1.83×10^{-8}	1.96×10^{-6}	4.88×10^{-6}	5.75×10^{-4}	1.28×10^{-5}
$C_2H_4O_2H^+$	61.028	$C_xH_yO_2$	2.97×10^{-3}	8.66×10^{-7}	1.31×10^{-4}	2.59×10^{-4}	3.70×10^{-2}	5.75×10^{-4}
$C_2H_6O_2H^+$	63.044	$C_xH_yO_2$	3.62×10^{-2}	8.66×10^{-7}	1.31×10^{-4}	2.59×10^{-4}	3.70×10^{-2}	5.75×10^{-4}
$C_2H_8O_2H^+$	65.060	$C_xH_yO_2$	3.26×10^{-2}	8.66×10^{-7}	1.31×10^{-4}	2.59×10^{-4}	3.70×10^{-2}	5.75×10^{-4}
$C_5H_6H^+$	67.054	C_xH_y	1.46×10^{-2}	2.31×10^{-9}	1.46×10^{-7}	4.21×10^{-7}	3.45×10^{-5}	1.23×10^{-6}
$C_4H_4OH^+$	69.033	C_xH_yO	7.75×10^{-2}	5.10×10^{-8}	4.88×10^{-6}	1.28×10^{-5}	1.37×10^{-3}	3.45×10^{-5}
$C_5H_8H^+$	69.070	C_xH_y	5.73×10^{-3}	2.31×10^{-9}	1.46×10^{-7}	4.21×10^{-7}	3.45×10^{-5}	1.23×10^{-6}
$C_3H_2O_2H^+$	71.013	$C_xH_yO_2$	7.81×10^{-2}	1.96×10^{-6}	2.59×10^{-4}	5.75×10^{-4}	7.18×10^{-2}	1.37×10^{-3}
$C_4H_6OH^+$	71.049	C_xH_yO	8.01×10^{-3}	5.10×10^{-8}	4.88×10^{-6}	1.28×10^{-5}	1.37×10^{-3}	3.45×10^{-5}
$C_5H_{10}H^+$	71.086	C_xH_y	6.52×10^{-3}	2.31×10^{-9}	1.46×10^{-7}	4.21×10^{-7}	3.45×10^{-5}	1.23×10^{-6}
$C_3H_4O_2H^+$	73.028	$C_xH_yO_2$	1.82×10^{-2}	1.96×10^{-6}	2.59×10^{-4}	5.75×10^{-4}	7.18×10^{-2}	1.37×10^{-3}
$C_3H_6O_2H^+$	75.044	$C_xH_yO_2$	5.28×10^{-3}	1.96×10^{-6}	2.59×10^{-4}	5.75×10^{-4}	7.18×10^{-2}	1.37×10^{-3}
$C_2H_4O_3H^+$	77.023	$C_xH_yO_3$	2.33×10^{-3}	1.31×10^{-4}	2.13×10^{-2}	3.70×10^{-2}	8.60×10^{-1}	7.18×10^{-2}
$C_5H_4OH^+$	81.033	C_xH_yO	5.53×10^{-2}	1.45×10^{-7}	1.28×10^{-5}	3.45×10^{-5}	3.44×10^{-3}	9.55×10^{-5}
$C_6H_8H^+$	81.070	C_xH_y	1.24×10^{-2}	6.88×10^{-9}	4.21×10^{-7}	1.23×10^{-6}	9.55×10^{-5}	3.59×10^{-6}
$C_4H_2O_2H^+$	83.013	$C_xH_yO_2$	4.21×10^{-2}	4.87×10^{-6}	5.75×10^{-4}	1.37×10^{-3}	1.45×10^{-1}	3.44×10^{-3}
$C_5H_6OH^+$	83.049	C_xH_yO	2.59×10^{-2}	1.45×10^{-7}	1.28×10^{-5}	3.45×10^{-5}	3.44×10^{-3}	9.55×10^{-5}
$C_6H_{10}H^+$	83.086	C_xH_y	7.98×10^{-3}	6.88×10^{-9}	4.21×10^{-7}	1.23×10^{-6}	9.55×10^{-5}	3.59×10^{-6}
$C_4H_4O_2H^+$	85.028	$C_xH_yO_2$	1.03×10^{-1}	4.87×10^{-6}	5.75×10^{-4}	1.37×10^{-3}	1.45×10^{-1}	3.44×10^{-3}
$C_5H_8OH^+$	85.065	C_xH_yO	1.02×10^{-2}	1.45×10^{-7}	1.28×10^{-5}	3.45×10^{-5}	3.44×10^{-3}	9.55×10^{-5}
$C_6H_{12}H^+$	85.101	C_xH_y	5.96×10^{-3}	6.88×10^{-9}	4.21×10^{-7}	1.23×10^{-6}	9.55×10^{-5}	3.59×10^{-6}
$C_3H_2O_3H^+$	87.008	$C_xH_yO_3$	1.66×10^{-1}	2.59×10^{-4}	3.70×10^{-2}	7.18×10^{-2}	9.19×10^{-1}	1.45×10^{-1}
$C_4H_6O_2H^+$	87.044	$C_xH_yO_2$	1.51×10^{-2}	4.87×10^{-6}	5.75×10^{-4}	1.37×10^{-3}	1.45×10^{-1}	3.44×10^{-3}
$C_3H_4O_3H^+$	89.023	$C_xH_yO_3$	1.20×10^{-1}	2.59×10^{-4}	3.70×10^{-2}	7.18×10^{-2}	9.19×10^{-1}	1.45×10^{-1}
$C_2H_2O_4H^+$	91.003	$C_xH_yO_4$	5.99×10^{-2}	2.10×10^{-2}	7.92×10^{-1}	8.60×10^{-1}	9.99×10^{-1}	9.19×10^{-1}
$C_3H_6O_3H^+$	91.039	$C_xH_yO_3$	5.58×10^{-3}	2.59×10^{-4}	3.70×10^{-2}	7.18×10^{-2}	9.19×10^{-1}	1.45×10^{-1}
$C_7H_{10}H^+$	95.086	C_xH_y	1.71×10^{-2}	2.05×10^{-8}	1.23×10^{-6}	3.59×10^{-6}	2.68×10^{-4}	1.06×10^{-5}
$C_5H_4O_2H^+$	97.028	$C_xH_yO_2$	5.11×10^{-2}	1.28×10^{-5}	1.37×10^{-3}	3.44×10^{-3}	2.84×10^{-1}	8.90×10^{-3}
$C_6H_8OH^+$	97.065	C_xH_yO	2.47×10^{-2}	4.20×10^{-7}	3.45×10^{-5}	9.55×10^{-5}	8.90×10^{-3}	2.68×10^{-4}
$C_7H_{12}H^+$	97.101	C_xH_y	1.40×10^{-2}	2.05×10^{-8}	1.23×10^{-6}	3.59×10^{-6}	2.68×10^{-4}	1.06×10^{-5}

$C_4H_2O_3H^+$	99.008	$C_xH_yO_3$	2.85×10^{-2}	5.74×10^{-4}	7.18×10^{-2}	1.45×10^{-1}	9.58×10^{-1}	2.84×10^{-1}
$C_5H_6O_2H^+$	99.044	$C_xH_yO_2$	3.67×10^{-2}	1.28×10^{-5}	1.37×10^{-3}	3.44×10^{-3}	2.84×10^{-1}	8.90×10^{-3}
$C_6H_{10}OH^+$	99.080	C_xH_yO	5.13×10^{-3}	4.20×10^{-7}	3.45×10^{-5}	9.55×10^{-5}	8.90×10^{-3}	2.68×10^{-4}
$C_4H_4O_3H^+$	101.023	$C_xH_yO_3$	1.02×10^{-1}	5.74×10^{-4}	7.18×10^{-2}	1.45×10^{-1}	9.58×10^{-1}	2.84×10^{-1}
$C_5H_8O_2H^+$	101.060	$C_xH_yO_2$	8.67×10^{-3}	1.28×10^{-5}	1.37×10^{-3}	3.44×10^{-3}	2.84×10^{-1}	8.90×10^{-3}
$C_4H_6O_3H^+$	103.039	$C_xH_yO_3$	5.49×10^{-2}	5.74×10^{-4}	7.18×10^{-2}	1.45×10^{-1}	9.58×10^{-1}	2.84×10^{-1}
$C_3H_4O_4H^+$	105.018	$C_xH_yO_4$	3.48×10^{-1}	3.62×10^{-2}	8.60×10^{-1}	9.19×10^{-1}	9.99×10^{-1}	9.58×10^{-1}
$C_7H_8OH^+$	109.065	C_xH_yO	4.26×10^{-2}	1.22×10^{-6}	9.55×10^{-5}	2.68×10^{-4}	2.34×10^{-2}	7.61×10^{-4}
$C_8H_{12}H^+$	109.101	C_xH_y	1.84×10^{-2}	6.13×10^{-8}	3.59×10^{-6}	1.06×10^{-5}	7.61×10^{-4}	3.11×10^{-5}
$C_6H_6O_2H^+$	111.044	$C_xH_yO_2$	9.37×10^{-2}	3.45×10^{-5}	3.44×10^{-3}	8.90×10^{-3}	4.92×10^{-1}	2.34×10^{-2}
$C_7H_{10}OH^+$	111.080	C_xH_yO	2.49×10^{-2}	1.22×10^{-6}	9.55×10^{-5}	2.68×10^{-4}	2.34×10^{-2}	7.61×10^{-4}
$C_8H_{14}H^+$	111.117	C_xH_y	8.78×10^{-3}	6.13×10^{-8}	3.59×10^{-6}	1.06×10^{-5}	7.61×10^{-4}	3.11×10^{-5}
$C_5H_4O_3H^+$	113.023	$C_xH_yO_3$	1.01×10^{-1}	1.37×10^{-3}	1.45×10^{-1}	2.84×10^{-1}	9.81×10^{-1}	4.92×10^{-1}
$C_6H_8O_2H^+$	113.060	$C_xH_yO_2$	3.02×10^{-2}	3.45×10^{-5}	3.44×10^{-3}	8.90×10^{-3}	4.92×10^{-1}	2.34×10^{-2}
$C_7H_{12}OH^+$	113.096	C_xH_yO	1.07×10^{-2}	1.22×10^{-6}	9.55×10^{-5}	2.68×10^{-4}	2.34×10^{-2}	7.61×10^{-4}
$C_4H_2O_4H^+$	115.003	$C_xH_yO_4$	2.13×10^{-1}	6.90×10^{-2}	9.19×10^{-1}	9.58×10^{-1}	1.00	9.81×10^{-1}
$C_5H_6O_3H^+$	115.039	$C_xH_yO_3$	7.16×10^{-2}	1.37×10^{-3}	1.45×10^{-1}	2.84×10^{-1}	9.81×10^{-1}	4.92×10^{-1}
$C_6H_{10}O_2H^+$	115.075	$C_xH_yO_2$	1.34×10^{-2}	3.45×10^{-5}	3.44×10^{-3}	8.90×10^{-3}	4.92×10^{-1}	2.34×10^{-2}
$C_4H_4O_4H^+$	117.018	$C_xH_yO_4$	6.98×10^{-2}	6.90×10^{-2}	9.19×10^{-1}	9.58×10^{-1}	1.00	9.81×10^{-1}
$C_5H_8O_3H^+$	117.055	$C_xH_yO_3$	4.48×10^{-2}	1.37×10^{-3}	1.45×10^{-1}	2.84×10^{-1}	9.81×10^{-1}	4.92×10^{-1}
$C_4H_6O_4H^+$	119.034	$C_xH_yO_4$	1.17×10^{-1}	6.90×10^{-2}	9.19×10^{-1}	9.58×10^{-1}	1.00	9.81×10^{-1}
$C_9H_{10}H^+$	119.086	C_xH_y	6.79×10^{-3}	1.83×10^{-7}	1.06×10^{-5}	3.11×10^{-5}	2.17×10^{-3}	9.19×10^{-5}
$C_9H_{12}H^+$	121.101	C_xH_y	1.72×10^{-3}	1.83×10^{-7}	1.06×10^{-5}	3.11×10^{-5}	2.17×10^{-3}	9.19×10^{-5}
$C_7H_6O_2H^+$	123.044	$C_xH_yO_2$	2.03×10^{-2}	9.53×10^{-5}	8.90×10^{-3}	2.34×10^{-2}	7.10×10^{-1}	6.11×10^{-2}
$C_8H_{10}OH^+$	123.080	C_xH_yO	4.38×10^{-2}	3.58×10^{-6}	2.68×10^{-4}	7.61×10^{-4}	6.11×10^{-2}	2.17×10^{-3}
$C_9H_{14}H^+$	123.117	C_xH_y	1.88×10^{-2}	1.83×10^{-7}	1.06×10^{-5}	3.11×10^{-5}	2.17×10^{-3}	9.19×10^{-5}
$C_6H_4O_3H^+$	125.023	$C_xH_yO_3$	4.61×10^{-2}	3.43×10^{-3}	2.84×10^{-1}	4.92×10^{-1}	9.91×10^{-1}	7.10×10^{-1}
$C_7H_8O_2H^+$	125.060	$C_xH_yO_2$	6.95×10^{-2}	9.53×10^{-5}	8.90×10^{-3}	2.34×10^{-2}	7.10×10^{-1}	6.11×10^{-2}
$C_8H_{12}OH^+$	125.096	C_xH_yO	2.55×10^{-2}	3.58×10^{-6}	2.68×10^{-4}	7.61×10^{-4}	6.11×10^{-2}	2.17×10^{-3}
$C_9H_{16}H^+$	125.132	C_xH_y	1.99×10^{-2}	1.83×10^{-7}	1.06×10^{-5}	3.11×10^{-5}	2.17×10^{-3}	9.19×10^{-5}
$C_6H_6O_3H^+$	127.039	$C_xH_yO_3$	1.81×10^{-1}	3.43×10^{-3}	2.84×10^{-1}	4.92×10^{-1}	9.91×10^{-1}	7.10×10^{-1}
$C_7H_{10}O_2H^+$	127.075	$C_xH_yO_2$	3.87×10^{-2}	9.53×10^{-5}	8.90×10^{-3}	2.34×10^{-2}	7.10×10^{-1}	6.11×10^{-2}
$C_8H_{14}OH^+$	127.112	C_xH_yO	1.17×10^{-2}	3.58×10^{-6}	2.68×10^{-4}	7.61×10^{-4}	6.11×10^{-2}	2.17×10^{-3}
$C_5H_4O_4H^+$	129.018	$C_xH_yO_4$	1.86×10^{-1}	1.36×10^{-1}	9.58×10^{-1}	9.81×10^{-1}	1.00	9.91×10^{-1}
$C_6H_8O_3H^+$	129.055	$C_xH_yO_3$	7.18×10^{-2}	3.43×10^{-3}	2.84×10^{-1}	4.92×10^{-1}	9.91×10^{-1}	7.10×10^{-1}
$C_7H_{12}O_2H^+$	129.091	$C_xH_yO_2$	1.36×10^{-2}	9.53×10^{-5}	8.90×10^{-3}	2.34×10^{-2}	7.10×10^{-1}	6.11×10^{-2}
$C_5H_6O_4H^+$	131.034	$C_xH_yO_4$	2.38×10^{-1}	1.36×10^{-1}	9.58×10^{-1}	9.81×10^{-1}	1.00	9.91×10^{-1}
$C_6H_{10}O_3H^+$	131.070	$C_xH_yO_3$	3.49×10^{-2}	3.43×10^{-3}	2.84×10^{-1}	4.92×10^{-1}	9.91×10^{-1}	7.10×10^{-1}
$C_5H_8O_4H^+$	133.050	$C_xH_yO_4$	1.17×10^{-1}	1.36×10^{-1}	9.58×10^{-1}	9.81×10^{-1}	1.00	9.91×10^{-1}
$C_9H_8OH^+$	133.065	C_xH_yO	4.52×10^{-2}	1.05×10^{-5}	7.61×10^{-4}	2.17×10^{-3}	1.52×10^{-1}	6.24×10^{-3}
$C_{10}H_{12}H^+$	133.101	C_xH_y	7.02×10^{-3}	5.47×10^{-7}	3.11×10^{-5}	9.19×10^{-5}	6.24×10^{-3}	2.72×10^{-4}
$C_8H_6O_2H^+$	135.044	$C_xH_yO_2$	4.00×10^{-2}	2.68×10^{-4}	2.34×10^{-2}	6.11×10^{-2}	8.64×10^{-1}	1.52×10^{-1}

$C_9H_{10}OH^+$	135.080	C_xH_yO	2.53×10^{-2}	1.05×10^{-5}	7.61×10^{-4}	2.17×10^{-3}	1.52×10^{-1}	6.24×10^{-3}
$C_{10}H_{14}H^+$	135.117	C_xH_y	3.18×10^{-3}	5.47×10^{-7}	3.11×10^{-5}	9.19×10^{-5}	6.24×10^{-3}	2.72×10^{-4}
$C_7H_4O_3H^+$	137.023	$C_xH_yO_3$	6.61×10^{-2}	8.84×10^{-3}	4.92×10^{-1}	7.10×10^{-1}	9.96×10^{-1}	8.64×10^{-1}
$C_8H_8O_2H^+$	137.060	$C_xH_yO_2$	3.00×10^{-2}	2.68×10^{-4}	2.34×10^{-2}	6.11×10^{-2}	8.64×10^{-1}	1.52×10^{-1}
$C_9H_{12}OH^+$	137.096	C_xH_yO	3.99×10^{-2}	1.05×10^{-5}	7.61×10^{-4}	2.17×10^{-3}	1.52×10^{-1}	6.24×10^{-3}
$C_{10}H_{16}H^+$	137.132	C_xH_y	7.83×10^{-3}	5.47×10^{-7}	3.11×10^{-5}	9.19×10^{-5}	6.24×10^{-3}	2.72×10^{-4}
$C_7H_6O_3H^+$	139.039	$C_xH_yO_3$	5.92×10^{-2}	8.84×10^{-3}	4.92×10^{-1}	7.10×10^{-1}	9.96×10^{-1}	8.64×10^{-1}
$C_8H_{10}O_2H^+$	139.075	$C_xH_yO_2$	5.51×10^{-2}	2.68×10^{-4}	2.34×10^{-2}	6.11×10^{-2}	8.64×10^{-1}	1.52×10^{-1}
$C_9H_{14}OH^+$	139.112	C_xH_yO	1.74×10^{-2}	1.05×10^{-5}	7.61×10^{-4}	2.17×10^{-3}	1.52×10^{-1}	6.24×10^{-3}
$C_6H_4O_4H^+$	141.018	$C_xH_yO_4$	9.21×10^{-2}	2.57×10^{-1}	9.81×10^{-1}	9.91×10^{-1}	1.00	9.96×10^{-1}
$C_7H_8O_3H^+$	141.055	$C_xH_yO_3$	1.62×10^{-1}	8.84×10^{-3}	4.92×10^{-1}	7.10×10^{-1}	9.96×10^{-1}	8.64×10^{-1}
$C_8H_{12}O_2H^+$	141.091	$C_xH_yO_2$	3.99×10^{-2}	2.68×10^{-4}	2.34×10^{-2}	6.11×10^{-2}	8.64×10^{-1}	1.52×10^{-1}
$C_9H_{16}OH^+$	141.127	C_xH_yO	1.84×10^{-2}	1.05×10^{-5}	7.61×10^{-4}	2.17×10^{-3}	1.52×10^{-1}	6.24×10^{-3}
$C_6H_6O_4H^+$	143.034	$C_xH_yO_4$	2.81×10^{-1}	2.57×10^{-1}	9.81×10^{-1}	9.91×10^{-1}	1.00	9.96×10^{-1}
$C_7H_{10}O_3H^+$	143.070	$C_xH_yO_3$	8.03×10^{-2}	8.84×10^{-3}	4.92×10^{-1}	7.10×10^{-1}	9.96×10^{-1}	8.64×10^{-1}
$C_8H_{14}O_2H^+$	143.107	$C_xH_yO_2$	1.76×10^{-2}	2.68×10^{-4}	2.34×10^{-2}	6.11×10^{-2}	8.64×10^{-1}	1.52×10^{-1}
$C_6H_8O_4H^+$	145.050	$C_xH_yO_4$	2.86×10^{-1}	2.57×10^{-1}	9.81×10^{-1}	9.91×10^{-1}	1.00	9.96×10^{-1}
$C_9H_6O_2H^+$	147.044	$C_xH_yO_2$	8.89×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_6H_{10}O_4H^+$	147.065	$C_xH_yO_4$	7.55×10^{-2}	2.57×10^{-1}	9.81×10^{-1}	9.91×10^{-1}	1.00	9.96×10^{-1}
$C_8H_4O_3H^+$	149.023	$C_xH_yO_3$	8.18×10^{-2}	2.30×10^{-2}	7.10×10^{-1}	8.64×10^{-1}	9.99×10^{-1}	9.44×10^{-1}
$C_9H_8O_2H^+$	149.060	$C_xH_yO_2$	5.26×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_{10}H_{12}OH^+$	149.096	C_xH_yO	3.10×10^{-2}	3.11×10^{-5}	2.17×10^{-3}	6.24×10^{-3}	3.33×10^{-1}	1.79×10^{-2}
$C_{11}H_{16}H^+$	149.132	C_xH_y	7.56×10^{-3}	1.63×10^{-6}	9.19×10^{-5}	2.72×10^{-4}	1.79×10^{-2}	8.05×10^{-4}
$C_8H_6O_3H^+$	151.039	$C_xH_yO_3$	1.03×10^{-1}	2.30×10^{-2}	7.10×10^{-1}	8.64×10^{-1}	9.99×10^{-1}	9.44×10^{-1}
$C_9H_{10}O_2H^+$	151.075	$C_xH_yO_2$	8.29×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_{10}H_{14}OH^+$	151.112	C_xH_yO	1.65×10^{-2}	3.11×10^{-5}	2.17×10^{-3}	6.24×10^{-3}	3.33×10^{-1}	1.79×10^{-2}
$C_{11}H_{18}H^+$	151.148	C_xH_y	2.68×10^{-2}	1.63×10^{-6}	9.19×10^{-5}	2.72×10^{-4}	1.79×10^{-2}	8.05×10^{-4}
$C_8H_8O_3H^+$	153.055	$C_xH_yO_3$	7.72×10^{-2}	2.30×10^{-2}	7.10×10^{-1}	8.64×10^{-1}	9.99×10^{-1}	9.44×10^{-1}
$C_9H_{12}O_2H^+$	153.091	$C_xH_yO_2$	6.97×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_{10}H_{16}OH^+$	153.127	C_xH_yO	7.90×10^{-3}	3.11×10^{-5}	2.17×10^{-3}	6.24×10^{-3}	3.33×10^{-1}	1.79×10^{-2}
$C_7H_6O_4H^+$	155.034	$C_xH_yO_4$	1.79×10^{-1}	4.38×10^{-1}	9.91×10^{-1}	9.96×10^{-1}	1.00	9.99×10^{-1}
$C_8H_{10}O_3H^+$	155.070	$C_xH_yO_3$	1.36×10^{-1}	2.30×10^{-2}	7.10×10^{-1}	8.64×10^{-1}	9.99×10^{-1}	9.44×10^{-1}
$C_9H_{14}O_2H^+$	155.107	$C_xH_yO_2$	3.82×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_7H_8O_4H^+$	157.050	$C_xH_yO_4$	2.20×10^{-1}	4.38×10^{-1}	9.91×10^{-1}	9.96×10^{-1}	1.00	9.99×10^{-1}
$C_8H_{12}O_3H^+$	157.086	$C_xH_yO_3$	6.79×10^{-2}	2.30×10^{-2}	7.10×10^{-1}	8.64×10^{-1}	9.99×10^{-1}	9.44×10^{-1}
$C_9H_{16}O_2H^+$	157.122	$C_xH_yO_2$	2.49×10^{-2}	7.59×10^{-4}	6.11×10^{-2}	1.52×10^{-1}	9.44×10^{-1}	3.33×10^{-1}
$C_7H_{10}O_4H^+$	159.065	$C_xH_yO_4$	1.31×10^{-1}	4.38×10^{-1}	9.91×10^{-1}	9.96×10^{-1}	1.00	9.99×10^{-1}
$C_{10}H_8O_2H^+$	161.060	$C_xH_yO_2$	7.07×10^{-2}	2.17×10^{-3}	1.52×10^{-1}	3.33×10^{-1}	9.78×10^{-1}	5.85×10^{-1}
$C_9H_6O_3H^+$	163.039	$C_xH_yO_3$	6.36×10^{-2}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_{10}H_{10}O_2H^+$	163.075	$C_xH_yO_2$	7.99×10^{-2}	2.17×10^{-3}	1.52×10^{-1}	3.33×10^{-1}	9.78×10^{-1}	5.85×10^{-1}
$C_{12}H_{18}H^+$	163.148	C_xH_y	1.61×10^{-2}	4.87×10^{-6}	2.72×10^{-4}	8.05×10^{-4}	5.02×10^{-2}	2.38×10^{-3}
$C_8H_4O_4H^+$	165.018	$C_xH_yO_4$	1.12×10^{-1}	6.43×10^{-1}	9.96×10^{-1}	9.99×10^{-1}	1.00	9.99×10^{-1}

$C_9H_8O_3H^+$	165.055	$C_xH_yO_3$	1.31×10^{-1}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_{10}H_{12}O_2H^+$	165.091	$C_xH_yO_2$	7.85×10^{-2}	2.17×10^{-3}	1.52×10^{-1}	3.33×10^{-1}	9.78×10^{-1}	5.85×10^{-1}
$C_{11}H_{16}OH^+$	165.127	C_xH_yO	5.81×10^{-2}	9.18×10^{-5}	6.24×10^{-3}	1.79×10^{-2}	5.85×10^{-1}	5.02×10^{-2}
$C_{12}H_{20}H^+$	165.164	C_xH_y	2.77×10^{-2}	4.87×10^{-6}	2.72×10^{-4}	8.05×10^{-4}	5.02×10^{-2}	2.38×10^{-3}
$C_8H_6O_4H^+$	167.034	$C_xH_yO_4$	2.50×10^{-1}	6.43×10^{-1}	9.96×10^{-1}	9.99×10^{-1}	1.00	9.99×10^{-1}
$C_9H_{10}O_3H^+$	167.070	$C_xH_yO_3$	2.14×10^{-1}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_{10}H_{14}O_2H^+$	167.107	$C_xH_yO_2$	5.21×10^{-2}	2.17×10^{-3}	1.52×10^{-1}	3.33×10^{-1}	9.78×10^{-1}	5.85×10^{-1}
$C_{11}H_{18}OH^+$	167.143	C_xH_yO	4.79×10^{-2}	9.18×10^{-5}	6.24×10^{-3}	1.79×10^{-2}	5.85×10^{-1}	5.02×10^{-2}
$C_8H_8O_4H^+$	169.050	$C_xH_yO_4$	2.43×10^{-1}	6.43×10^{-1}	9.96×10^{-1}	9.99×10^{-1}	1.00	9.99×10^{-1}
$C_9H_{12}O_3H^+$	169.086	$C_xH_yO_3$	1.14×10^{-1}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_{10}H_{16}O_2H^+$	169.122	$C_xH_yO_2$	2.64×10^{-2}	2.17×10^{-3}	1.52×10^{-1}	3.33×10^{-1}	9.78×10^{-1}	5.85×10^{-1}
$C_8H_{10}O_4H^+$	171.065	$C_xH_yO_4$	2.32×10^{-1}	6.43×10^{-1}	9.96×10^{-1}	9.99×10^{-1}	1.00	9.99×10^{-1}
$C_9H_{14}O_3H^+$	171.102	$C_xH_yO_3$	7.56×10^{-2}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_8H_{12}O_4H^+$	173.081	$C_xH_yO_4$	1.49×10^{-1}	6.43×10^{-1}	9.96×10^{-1}	9.99×10^{-1}	1.00	9.99×10^{-1}
$C_9H_{16}O_3H^+$	173.117	$C_xH_yO_3$	1.16×10^{-1}	5.90×10^{-2}	8.64×10^{-1}	9.44×10^{-1}	9.99×10^{-1}	9.78×10^{-1}
$C_{10}H_8O_3H^+$	177.055	$C_xH_yO_3$	1.08×10^{-1}	1.42×10^{-1}	9.44×10^{-1}	9.78×10^{-1}	1.00	9.92×10^{-1}
$C_{11}H_{12}O_2H^+$	177.091	$C_xH_yO_2$	8.45×10^{-2}	6.21×10^{-3}	3.33×10^{-1}	5.85×10^{-1}	9.92×10^{-1}	8.00×10^{-1}
$C_{13}H_{20}H^+$	177.164	C_xH_y	2.07×10^{-2}	1.45×10^{-5}	8.05×10^{-4}	2.38×10^{-3}	1.34×10^{-1}	7.04×10^{-3}
$C_{10}H_{10}O_3H^+$	179.070	$C_xH_yO_3$	1.35×10^{-1}	1.42×10^{-1}	9.44×10^{-1}	9.78×10^{-1}	1.00	9.92×10^{-1}
$C_{11}H_{14}O_2H^+$	179.107	$C_xH_yO_2$	8.47×10^{-2}	6.21×10^{-3}	3.33×10^{-1}	5.85×10^{-1}	9.92×10^{-1}	8.00×10^{-1}
$C_{12}H_{18}OH^+$	179.143	C_xH_yO	7.47×10^{-2}	2.71×10^{-4}	1.79×10^{-2}	5.02×10^{-2}	8.00×10^{-1}	1.34×10^{-1}
$C_{13}H_{22}H^+$	179.179	C_xH_y	2.40×10^{-2}	1.45×10^{-5}	8.05×10^{-4}	2.38×10^{-3}	1.34×10^{-1}	7.04×10^{-3}
$C_{10}H_{12}O_3H^+$	181.086	$C_xH_yO_3$	1.53×10^{-1}	1.42×10^{-1}	9.44×10^{-1}	9.78×10^{-1}	1.00	9.92×10^{-1}
$C_{11}H_{16}O_2H^+$	181.122	$C_xH_yO_2$	8.12×10^{-2}	6.21×10^{-3}	3.33×10^{-1}	5.85×10^{-1}	9.92×10^{-1}	8.00×10^{-1}
$C_9H_{10}O_4H^+$	183.065	$C_xH_yO_4$	1.73×10^{-1}	8.12×10^{-1}	9.99×10^{-1}	9.99×10^{-1}	1.00	1.00
$C_{10}H_{14}O_3H^+$	183.102	$C_xH_yO_3$	1.44×10^{-1}	1.42×10^{-1}	9.44×10^{-1}	9.78×10^{-1}	1.00	9.92×10^{-1}
$C_{11}H_{18}O_2H^+$	183.138	$C_xH_yO_2$	6.64×10^{-2}	6.21×10^{-3}	3.33×10^{-1}	5.85×10^{-1}	9.92×10^{-1}	8.00×10^{-1}
$C_{10}H_{16}O_3H^+$	185.117	$C_xH_yO_3$	7.71×10^{-2}	1.42×10^{-1}	9.44×10^{-1}	9.78×10^{-1}	1.00	9.92×10^{-1}
$C_{10}H_{10}O_4H^+$	195.065	$C_xH_yO_4$	1.21×10^{-1}	9.15×10^{-1}	9.99×10^{-1}	1.00	1.00	1.00
$C_{12}H_{18}O_2H^+$	195.138	$C_xH_yO_2$	1.09×10^{-1}	1.76×10^{-2}	5.85×10^{-1}	8.00×10^{-1}	9.97×10^{-1}	9.19×10^{-1}
$C_{12}H_{20}O_2H^+$	197.154	$C_xH_yO_2$	7.00×10^{-2}	1.76×10^{-2}	5.85×10^{-1}	8.00×10^{-1}	9.97×10^{-1}	9.19×10^{-1}
$C_{13}H_{20}O_2H^+$	209.154	$C_xH_yO_2$	9.76×10^{-2}	4.88×10^{-2}	8.00×10^{-1}	9.19×10^{-1}	9.99×10^{-1}	9.70×10^{-1}

Table S6. Numerical values approximately extracted from the Figure in Donahue et al. (2011).

Y = aX+b	a	b	Averaged relative error			Overall
C_xH_y	-0.4708	11.755	34% (Alkanes)			34%
$C_xH_yO_1$	-0.4712	10.104	22% (Aldehydes)	9% (Ketones)	16% (Alcohols)	16%
$C_xH_yO_2$	-0.4572	8.0405	39% (Acids)	12% (Diols)		25%
$C_xH_yO_4$	-0.4218	3.743	54% (DiAcids)			54%

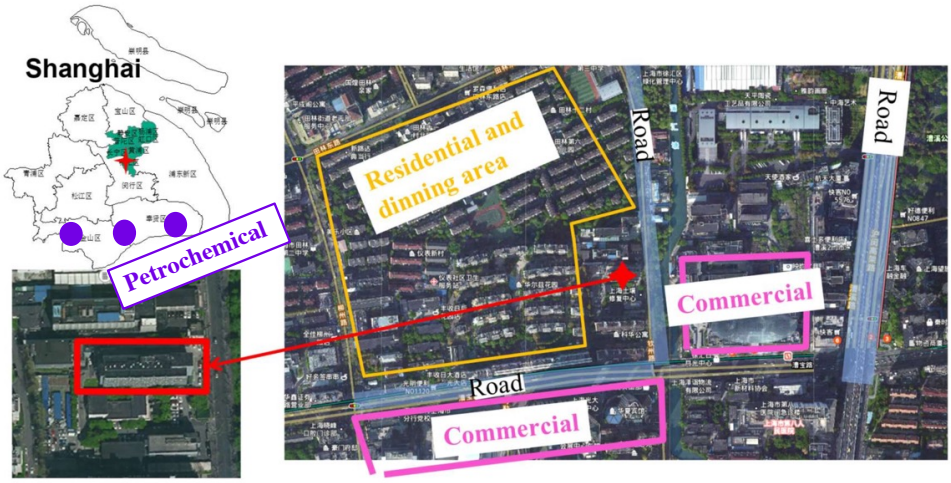


Figure S1. Location of the sampling site based on Huang et al. (2021). The base map was from © Google Maps.

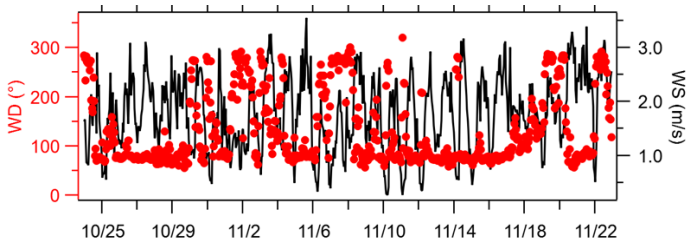
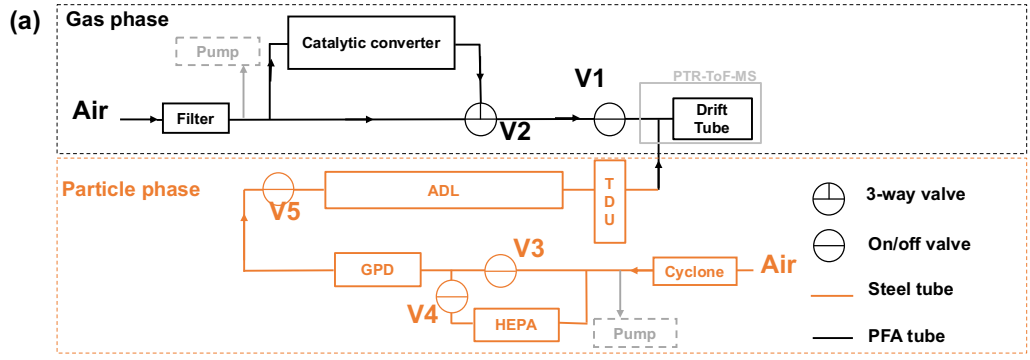


Figure S2. Wind direction and speed at the site during the observation period.



Valve settings	V1	V2	V3	V4	V5
Particle phase	close	close	open	close	open
Particle phase (zero)	close	close	close	open	open
Gas phase	open	close	close	close	close
Gas phase (zero)	open	open	close	close	close

HEPA: a High-Efficiency Particulate Air filter
GPD: a Gas-Phase Denuder
ADL: an Aero-Dynamic Lens
TDU: a Thermo-Desorption Unit

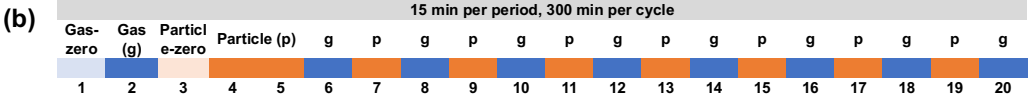


Figure S3. (a) Schematic diagram of the inlet system for the CHARON–PTR-ToF-MS in this study. The open of 3-way valve (V2) means switching to direct the zero air into the drift tube. (b) Measurement cycle setting during the campaign. One color block represents 15 min for gas- or particle- phase measurement.

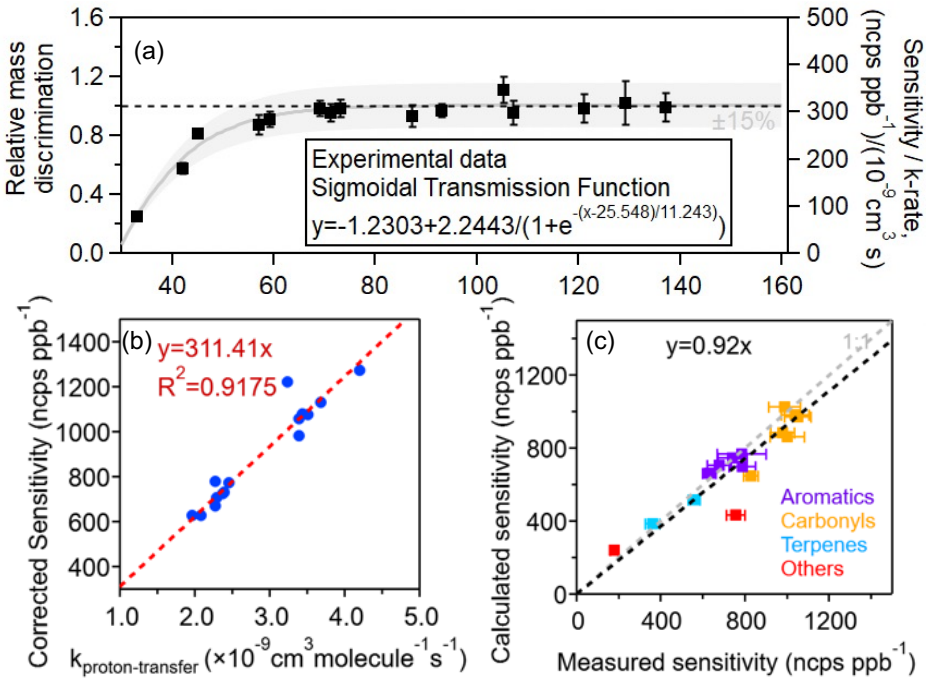


Figure S4. (a) Relative mass discrimination (±1σ) of selected chemical standards by PTR-ToF-MS. Here the transmission efficiency of 1,3,5-Trimethylbenzene (*m/z* = 121) is used as the reference, i.e., 100%, as shown by the dash line. The grey shade represents ±15% deviation in the measurements. The grey solid line represents a sigmoidal fit to the measurements. (b) Corrected sensitivities as a function of kinetic rate constants for proton transfer reactions of H_3O^+ with species. The dashed red line means the fitted line for blue points. (c) Comparison of the theoretical calculated and measured sensitivity (±1σ) for different calibrants.

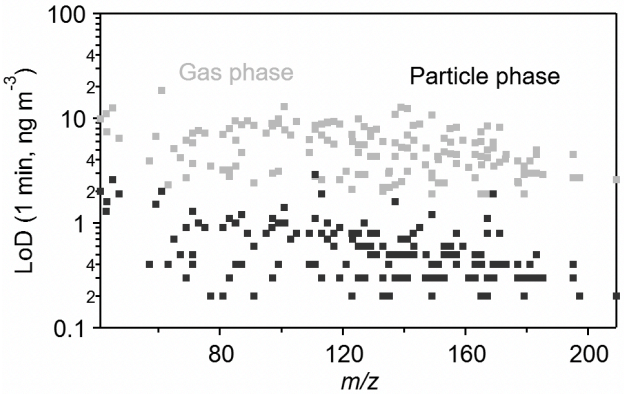


Figure S5. The concentration of 1 min limit of detection (LoD, ng m^{-3}) of organic compounds detected in the gas and particle phase.

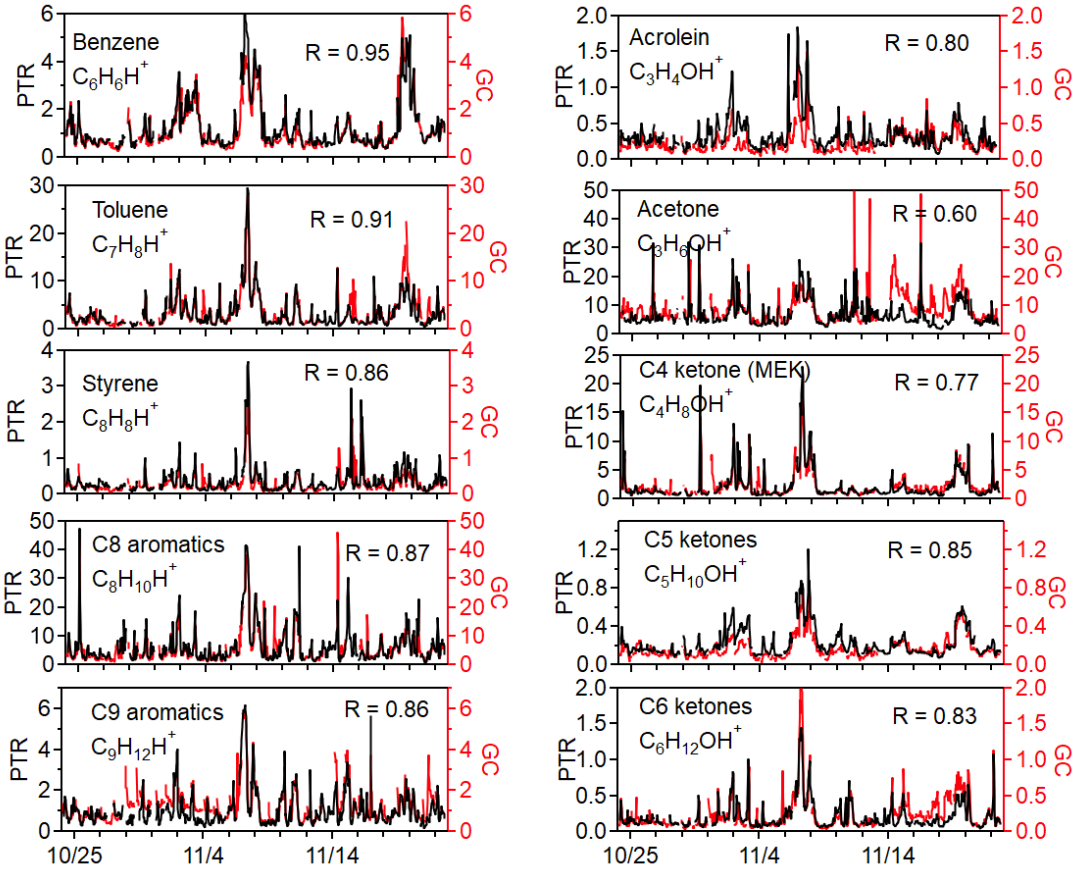


Figure S6. Comparison of month-long mass concentrations (μg m^{-3}) of gaseous organic compounds measured by PTR-ToF-MS (PTR) and GC-MS/FID (GC).

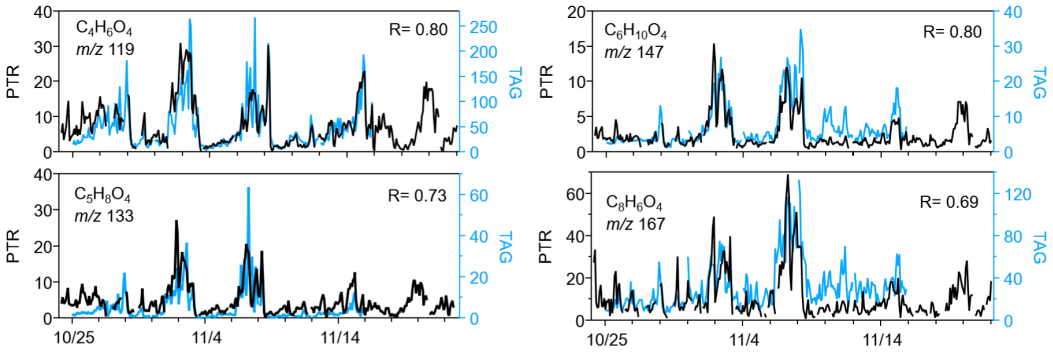


Figure S7. Comparison of aerosol mass concentrations (ng m^{-3}) of selected $C_xH_yO_4$ species measured by CHARON–PTR-ToF-MS (PTR) and a thermal desorption aerosol gas chromatograph (TAG).

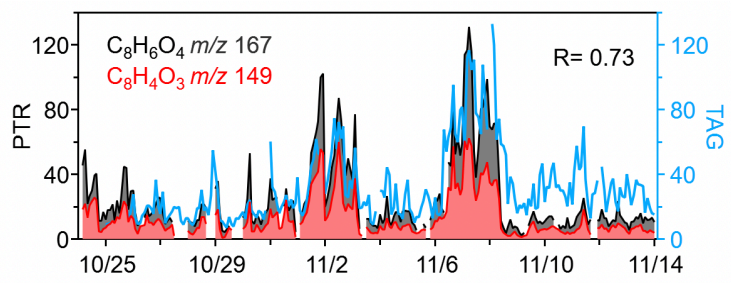


Figure S8. Comparison of $C_8H_6O_4$ (ng m^{-3}) and its fragment, $C_8H_4O_3$ in CHARON–PTR-ToF-MS (PTR), with phthalic acid (and iso/terephthalic acid) in TAG.

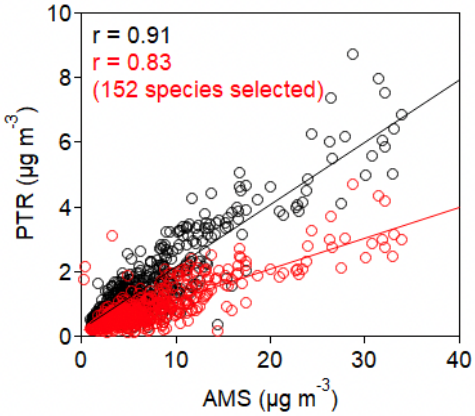


Figure S9. Scatter plot of organic aerosol masses measured by CHARON–PTR-ToF-MS vs. AMS. Black markers represent the total mass concentration of all nominal masses below 300 Th and red markers represent the total mass concentrations of the identified 152 species in the particle phase.

Figure S10 gives the comparison of the observed vs. modeled particle-phase fractions ($F_{p,\,obs}$ vs. $F_{p,\,mod}$) of all species investigated here. Uncertainties associated with the predictions of $F_{p,\,mod}$ were given as error bars. For species of high volatility (i.e., $C^{*}>10^{4}$ μg m^{-3}), the modeled particle-phase fraction ($F_{p,\,mod}$) is several orders of magnitude higher than the corresponding observations ($F_{p,\,obs}$), and the uncertainties associated with the modeling have a minimal impact on the discrepancies between measurements and model predictions. For $C_xH_yO_2$ and $C_xH_yO_3$ groups, such impact was still low, within 10%. For species with relatively low volatilities, the uncertainties in the model predictions could have appreciable impact (~ 62% on average) on the comparison between $F_{p,\,obs}$ and $F_{p,\,mod}$.

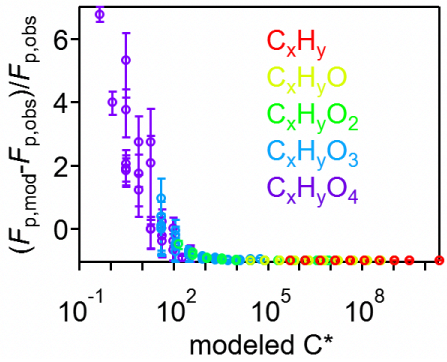


Figure S10. Discrepancy between modeled F_p ($F_{p,mod}$) and observed F_p ($F_{p,obs}$) as a function of the modeled C^{*}(μg m^{-3}) of detected species.

S1. We did not include the higher mass here because we only considered masses below 200 amu from the field measurement for the study of gas–particle partitioning. One of previous studies (Wu et al., 2020) have used the gas standard of decamethylcyclopentasiloxane (D5, *m/z* 371) to calibrate the same type of PTR-ToF-MS instrument, and the obtained transmission efficiency agree well with the present study. While we tested a higher mass (e.g., sucrose, M_w=342 g mol^{-1}) in the particle collection efficiency experiment, we aim to examine whether labile high-molecular-weight compounds can be evaporated effectively while maintaining an intact molecular structure under the evaporation temperature range used.

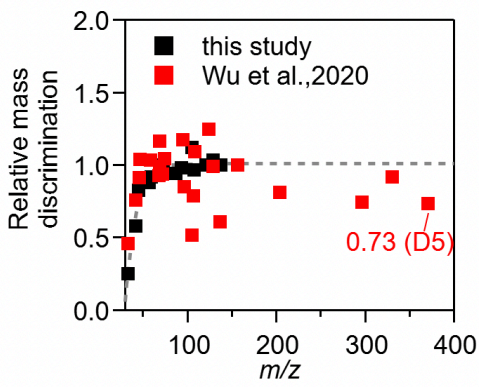


Figure S11. The relative transmission efficiency of various masses. Black markers were experimental data from this study, and red markers were taken from Wu et al. (2020). The relative transmission of decamethylcyclopentasiloxane (D5, *m/z* 371) was ~27% lower than the fitted curve (gray dashed line) used in this study.

S2. The most common fragmentation mechanism during the PTR ionization process includes the neutral losses of a carboxyl group (–CO_2), a carbonyl group (–CO), a hydroxyl group (–H_2O), or an alcohol group (–C_2H_6O), with predicted volatilities (C^*) of 1.58×10^7, 2.51×10^9, 3.76×10^9 and 1.06×10^9 (μg m^{-3}), respectively. If a species $C_xH_yO_z$ losses a H_2O group, for example, and becomes $C_xH_yO_z$-H_2O, then its saturation mass concentration (C^*) will increase by around 100 times accordingly. For example, for the species detected as $C_6H_6O_3$ in the PTR-MS mass spectra, it is unknown whether this species is a real compound present in the air or a fragment of its parent compound $C_6H_6O_3$+H_2O. If it is the latter, then the model predicted C^* based on the derived formula of $C_6H_6O_3$ would be 99 times higher than its actual C^*, and as a result, the model predicted particle-phase fraction ($F_{p,mod}$ of $C_6H_6O_3$ = 0.003) would be significantly lower than its actual particle-phase fraction ($F_{p,mod}$ of $C_6H_8O_4$ = 0.284).

Our calculations show that neutral losses of H_2O and CO_2 give the lower and upper limit, respectively, of the predicted fraction of all compounds investigated in this study. Specifically, for $C_{3\text{-}13}H_{4\text{-}22}$, $C_{2\text{-}12}H_{2\text{-}18}O$, $C_{2\text{-}11}H_{4\text{-}14}O_2$, $C_{2\text{-}10}H_{4\text{-}16}O_3$ and $C_{2\text{-}10}H_{2\text{-}10}O_4$, the predicted F_p values increase by around 5.85×10^1~1.27×10^4, 8.33×10^1~1.97×10^4, 9.57×10^1~1.33×10^4, 61.2~774 and 6.03~6.87, respectively. It is no surprise that lower masses with higher volatilities are subject to significant changes in the particle-phase fraction as a result of neutral losses during the PTR ionization process.

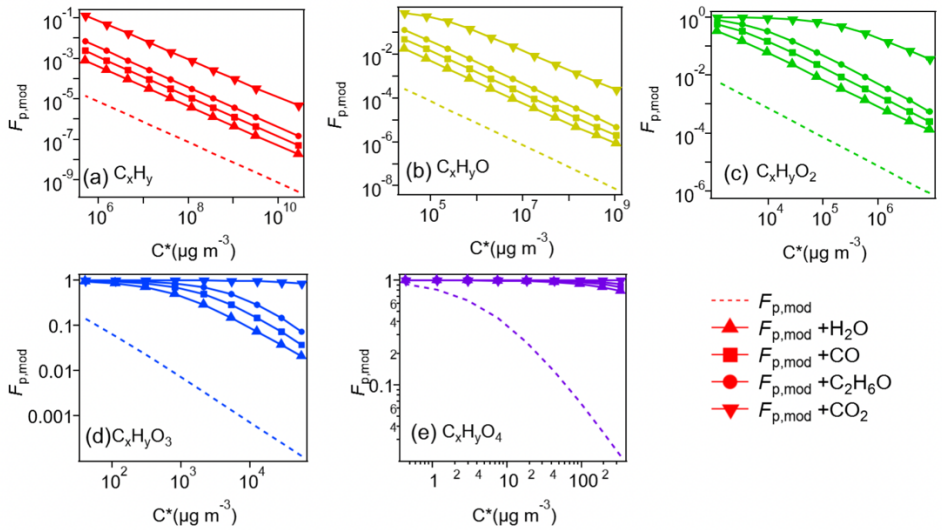


Figure S12. Predicted F_p as a function of C^* of (a–e) different groups on a log scale assuming the identified species are fragments of corresponding parent compounds through neutral losses of H_2O, CO, CO_2, and C_2H_6O.

S3. Take the C_2H_4O (acetaldehyde) as an example, the PTR measured fraction in the particle phase was around 0.19, when its gas and particle phase concentrations were 979 and 234 ng m^{-3}, respectively, at 4:00 pm local time on Oct 29th. The predicted F_p was only ~10^{-9} (C_{OA}=2.92 μg m^{-3}). The fraction of C_2H_4O in the aerosol aqueous phase (F_{aq}) is estimated assuming equilibrium partitioning between the gas phase and the aerosol liquid water content. The modeled mass in aerosol aqueous phase C_p (μg m^{-3}) is calculated by (Shen et al., 2018; Gkatzelis et al., 2021):

$$C_p = K_H M_w \frac{ALWC}{\rho_{water}} C_g$$

Where C_g (ppb) is the gas-phase concentration; K_H is the Henry's law coefficient (M atm^{-1}); M_w (g mol^{-1}) is the molecular weight; ρ_{water} (g cm^{-3}) is the density of water; ALWC is the aerosol liquid water content, typically 9.3 ± 8.3 μg m^{-3} in Shanghai (Cai et al., 2022). K_H of acetaldehyde was 3.76×10^1 M atm^{-1}, obtained from the Henry's Law Database tool (version 4.0, http://www.henrys-law.org) developed by Sander (2015). The estimated aqueous-phase concentration of acetaldehyde is 7.67×10^{-6} ng m^{-3} on average. The estimated F_{aq} is 1.54×10^{-8}, which is far below the measured F_p (0.19). Even if we used the field derived K_H value in Beijing by Gkatzelis et al. (2021), the estimated C_p was ~40.4 ng m^{-3} on average, still much lower than the measurements . Therefore, we think dissolution of water-soluble species in the aerosol water does not contribute significantly to their overall particle phase partitioning.

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