Supporting Information of

Real time analysis of trace volatile organic compounds in ambient air: a comparison between membrane inlet single photon ionization mass spectrometry and proton transfer reaction mass spectrometry

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Table S1. List of compounds and their certified concentrations in TO15 gas standard (8 L, 6 MPa, Dalian Special Gases Co., Ltd, China).

Mass [amu]	Component	Concentration [ppm]	Relative uncertainty
42	Propene	1.11	10%
46	Ethanol	1.01	10%
50	Chloromethane	0.95	10%
54	1,3-Butadiene	1.02	10%
56	Acrolein	1.02	10%
58	Acetone	0.97	10%
60	2-Propanol	0.81	10%
62	Vinyl chloride	1.01	10%
64	Chloroethane	0.97	10%
72	2-Butanone	0.93	10%
72	Tetrahydrofuran	0.98	10%
76	Carbon disulfide	1.06	10%
78	Benzene	0.99	10%
84	Cyclohexane	0.97	10%
84	Dichloromethane	1.07	10%
86	Vinyl acetate	0.88	10%
86	Hexane	0.94	10%
88	Ethyl acetate	0.92	10%
88	1,4-Dioxane	0.94	10%
88	Methyl tert-butyl ether	0.87	10%
92	Toluene	0.89	10%
94	Bromomethane	1	10%
96	1,1-Dichloroethene	0.97	10%
96	Trans-1,2-Dichloroethene	1.34	10%
96	Cis-1,2-Dichloroethene	1.08	10%
98	1,2-Dichloroethane	0.91	10%
98	1,1-Dichloroethane	0.99	10%
100	Methyl methacrylate	0.93	10%
100	4-Methyl-2-pentanone	0.91	10%
100	2-Hexanone	0.93	10%
100	Heptane	1.02	10%
104	Styrene	0.89	10%
106	Ethylbenzene	1.03	10%
106	*p*-Xylene	0.98	10%
106	*m*-Xylene	0.92	10%
106	*o*-Xylene	0.98	10%
110	Trans-1,3-Dichloropropene	0.96	10%
110	Cis-1,3-Dichloropropene	1.01	10%
112	Chlorobenzene	0.89	10%
112	1,2-Dichloropropane	1.03	10%

118	Chloroform	1.02	10%
120	4-Ethyltoluene	0.93	10%
120	1,3,5-Trimethylbenzene	0.89	10%
120	1,2,4-Trimethylbenzene	0.88	10%
120	Dichlorodifluoromethane	0.92	10%
126	Benzyl chloride	0.89	10%
128	Naphthalene	1.09	10%
131	Trichloroethene	1.02	10%
132	1,1,1-Trichloroethane	0.89	10%
132	1,1,2-Trichloroethane	0.91	10%
137	Trichlorofluoromethane	0.98	10%
146	1,3-Dichlorobenzene	0.98	10%
146	1,4-Dichlorobenzene	0.93	10%
146	1,2-Dichlorobenzene	0.96	10%
153	Carbon tetrachloride	0.98	10%
163	Bromodichloromethane	0.9	10%
164	Perchloroethylene	0.94	10%
166	1,1,2,2-Tetrachloroethane	0.94	10%
170	1,2-Dichlorotetrafluoroethane	0.92	10%
180	124-Trichlorobenzene	0.93	10%
186	1,2-Dibromoethane	1.03	10%
187	112-Trichloro-122-trifluoroethane	0.94	10%
208	Dibromochloromethane	0.94	10%
250	Bromoform	0.86	10%
260	Hexachloro-1,3-butadiene	0.83	10%

Table S2. List of compounds and their certified concentrations in PAMS-DL gas standard (8 L, 6 MPa, Dalian Special Gases Co., Ltd, China).

Mass [amu]	Component	Concentration [ppm]	Relative uncertainty
26	Acetylene	1.01	2%
28	Ethylene	1.02	2%
30	Ethane	1.02	2%
42	Propene	1.01	2%
44	Propane	1.02	2%
56	1-Butene	1.02	2%
56	Trans-2-Butene	1.02	2%
56	Cis-2-Butene	1.05	2%
58	N-Butane	1.07	2%
58	Isobutane	1.02	2%
68	Isoprene	1.04	2%
70	Trans-2-Pentene	1.04	2%
70	Cis-2-Pentene	1.04	2%
70	1-Pentene	1.04	2%
70	Cyclopentane	1	2%
72	*n*-Pentane	1	2%
72	Isopentane	1	2%
78	Benzene	1	2%
84	Methylcyclopentane	1.01	2%
84	Cyclohexane	0.997	2%
84	1-Hexene	1.04	2%
86	N-Hexane	1.02	2%
86	2-Methylpentane	1	2%
86	3-Methylpentane	1	2%
86	2,2-Dimethylbutane	0.993	2%
86	2,3-Dimethylbutane	1.02	2%
92	Toluene	1.03	2%
98	Methylcyclohexane	1.02	2%
100	*n*-Heptane	0.994	2%
100	2-Methylhexane	1	2%
100	3-Methylhexane	0.994	2%
100	2,3-Dimethylpentane	0.993	2%
100	2,4-Dimethylpentane	1	2%
104	Styrene	1	2%
106	Ethylbenzene	1	2%
106	*o*-Xylene	1	2%
106	*m*-Xylene	0.994	2%
106	*p*-Xylene	0.997	2%
114	2-Methylheptane	1	2%
114	3-Methylheptane	1.01	2%

114	*n*-Octane	0.99	2%
114	2,3,4-Trimethylpentane	1.01	2%
114	2,2,4-Trimethylpentane	1.03	2%
120	Isopropylbenzene	1.01	2%
120	*n*-Propylbenzene	0.979	2%
120	*o*-Ethyltoluene	1.01	2%
120	*m*-Ethyltoluene	0.85	2%
120	*p*-Ethyltoluene	1.13	2%
120	1,2,3-Trimethylbenzene	0.93	2%
120	1,2,4-Trimethylbenzene	1	2%
120	1,3,5-Trimethylbenzene	1	2%
128	Nonane	0.997	2%
134	*p*-Diethylbenzene	1.01	2%
134	*m*-Diethylbenzene	1	2%
142	*n*-Decane	0.995	2%
156	Undecane	1	2%
170	Dodecane	1	2%

Table S3. List of compounds and their certified concentrations in PAMS-Linde gas standard (29.5 L, 2000 psig, Linde Gas North America LLC).

Mass [amu]	Component	Concentration [ppb]	Relative uncertainty
26	Acetylene	11	10%
28	Ethylene	11	10%
30	Ethane	11	10%
42	Propene	12	10%
44	Propane	12	10%
56	1-Butene	12	10%
56	Trans-2-Butene	11	10%
56	Cis-2-Butene	12	10%
58	*n*-Butane	12	10%
58	Isobutane	11	10%
68	Isoprene	10	10%
70	Trans-2-Pentene	11	10%
70	Cis-2-Pentene	10	10%
70	1-Pentene	12	10%
70	Cyclopentane	11	10%
72	N-Pentane	12	10%
72	Isopentane	12	10%
78	Benzene	12	10%
84	Methylcyclopentane	11	10%
84	Cyclohexane	12	10%
84	1-Hexene	12	10%
86	N-Hexane	12	10%
86	2-Methylpentane	11	10%
86	3-Methylpentane	12	10%
86	2,2-Dimethylbutane	12	10%
86	2,3-Dimethylbutane	12	10%
92	Toluene	12	10%
98	Methylcyclohexane	12	10%
100	N-Heptane	12	10%
100	2-Methylhexane	11	10%
100	3-Methylhexane	12	10%
100	2,3-Dimethylpentane	12	10%
100	2,4-Dimethylpentane	12	10%
104	Styrene	11	10%
106	Ethylbenzene	12	10%
106	*o*-Xylene	11	10%
106	*m*-Xylene	6	10%
106	*p*-Xylene	6	10%
114	2-Methylheptane	11	10%
114	3-Methylheptane	11	10%

114	n-Octane	12	10%
114	2,3,4-Trimethylpentane	11	10%
114	2,2,4-Trimethylpentane	12	10%
120	Isopropylbenzene	11	10%
120	*n*-Propylbenzene	11	10%
120	*o*-Ethyltoluene	11	10%
120	*m*-Ethyltoluene	12	10%
120	*p*-Ethyltoluene	10	10%
120	1,2,3-Trimethylbenzene	11	10%
120	1,2,4-Trimethylbenzene	12	10%
120	1,3,5-Trimethylbenzene	12	10%
128	Nonane	11	10%
134	*p*-Diethylbenzene	11	10%
134	*m*-Diethylbenzene	11	10%
142	*n*-Decane	11	10%
156	Undecane	11	10%
170	Dodecane	11	10%

Table S4. LODs obtained by using MI-SPI-MS and PTR-MS for the isomeric/isobaric compounds in TO15.

Mass [amu]	Component	Formula	Accuracy [%]		Linearity		LOD [ppt]	
			Accu_SPI	Accu_PTR	R^2_SPI	R^2_PTR	LOD_SPI	LOD_PTR
42	Propene	C3H6	ND*	6.2	ND	1.00	ND	427
46	Ethanol	C2H6O	ND	7.6	ND	0.98	ND	7939
50	Chloromethane	CH3Cl	ND	ND	ND	ND	ND	ND
54	1,3-Butadiene	C4H6	7.1	7.6	1.00	0.98	358	758
56	Acrolein	C3H4O	8.1	6.6	1.00	1.00	2128	285
58	Acetone	C3H6O	6.0	5.9	0.99	1.00	452	145
60	2-Propanol	C3H8O	ND	6.1	ND	1.00	ND	370
62	Vinyl chloride	C2H3Cl	9.7	7.3	0.97	0.99	3439	367
64	Chloroethane	C2H5Cl	ND	ND	ND	ND	ND	ND
72	2-Butanone; Tetrahydrofuran	C4H8O	6.3	5.8	1.00	1.00	223	161
76	Carbon disulfide	CS2	7.0	6.8	1.00	0.99	214	447
78	Benzene	C6H6	5.8	6.0	1.00	1.00	48	119
84	Cyclohexane	C6H12	6.8	ND	1.00	ND	583	ND
	Dichloromethane	CH2Cl2	ND	ND	ND	ND	ND	ND
86	Vinyl acetate	C4H6O2	6.9	ND	1.00	ND	661	ND
	Hexane	C6H14		ND		ND		ND
88	Ethyl acetate; 1,4-Dioxane	C4H8O2	6.5	6.1	1.00	1.00	250	470
	Methyl tert-butyl ether	C5H12O		ND		ND		ND
92	Toluene	C7H8	5.6	6.5	1.00	1.00	14	112
94	Bromomethane	CH3Br	9.1	ND	1.00	ND	1947	ND
96	1,1(trans-1,2; cis-1,2) -Dichloroethene	C2H2Cl2	6.0	6.2	1.00	1.00	214	458
98	1,1 (1,2)-Dichloroethane	C2H4Cl2	6.2	6.3	1.00	1.00	199	372
100	Methyl methacrylate	C5H8O2	5.4	5.7	0.99	0.98	115	58
	4-Methyl-2-pentanone; 2-Hexanone	C6H12O		ND		ND		ND
	Heptane	C7H16		ND		ND		ND
104	Styrene	C8H8	5.5	6.1	0.96	0.96	9	120
106	Ethylbenzene; p (m; o) -Xylene	C8H10	5.2	5.9	0.99	0.98	9	339
110	trans-1,3 (cis-1,3)- Dichloropropene	C3H4Cl2	6.0	ND	0.99	ND	109	ND
112	Chlorobenzene	C6H5Cl	5.5	ND	0.98	ND	36	ND
	1,2-Dichloropropane	C3H6Cl2		6.2		0.98		189
118	Chloroform	CHCl3	ND	6.3	ND	0.98	ND	125
120	4-Ethyltoluene; 1,3,5 (1,2,4) - Trimethylbenzene	C9H12	5.5	6.1	0.96	1.00	28	325
	Dichlorodifluoromethane	CCl2F2		6.3		1.00		1565

126	Benzyl chloride	C10H8	6.3	ND	0.96	ND	33	ND
128	Naphthalene	C7H7Cl	7.2	7.5	0.95	1.00	50	2147
131	Trichloroethene	C2HCl3	6.0	6.2	1.00	1.00	123	712
132	1,1,1 (1,1,2)-Trichloroethane	C2H3Cl3	6.0	6.8	1.00	0.96	144	2066
137	Trichlorofluoromethane	CCl3F	ND	ND	ND	ND	ND	ND
146	1,2 (1,3; 1,4)-Dichlorobenzene	C6H4Cl2	6.2	6.8	0.98	0.96	31	373
153	Carbon tetrachloride	CCl4	ND	ND	ND	ND	ND	ND
163	Bromodichloromethane	CHBrCl2	ND	ND	ND	ND	ND	ND
164	Perchloroethylene	C2Cl4	5.9	ND	0.99	ND	51	ND
166	1,1,2,2-Tetrachloroethane	C2H2Cl4	6.0	ND	0.99	ND	60	ND
170	1,2-Dichlorotetrafluoroethane	C2Cl2F4	7.9	ND	0.99	ND	527	ND
180	124-Trichlorobenzene	C6H3Cl3	7.7	ND	0.95	ND	221	ND
186	1,2-Dibromoethane	C2H4Br2	9.6	ND	0.98	ND	3621	ND
187	112-Trichloro-122-trifluoroethane	C2Cl3F3	ND	ND	ND	ND	ND	ND
208	Dibromochloromethane	CHBr2Cl	ND	ND	ND	ND	ND	ND
250	Bromoform	CHBr3	7.0	ND	0.96	ND	2292	ND
260	Hexachloro-1,3-butadiene	C4Cl6	ND	ND	ND	ND	ND	ND

*ND: the compound is not detectable by MI-SPI-MS or PTR-MS either due to high ionization energy (IE) or due to low proton affinity (PA).

Table S5. LODs obtained by using MI-SPI-MS and PTR-MS for the isomeric compounds in PAMS-DL.

Mass [amu]	Component	Formula	Accuracy [%]		Linearity		LOD [ppt]	
			Accu_SPI	Accu_PTR	R^2_SPI	R^2_PTR	LOD_SPI	LOD_PTR
26	Acetylene	C2H2	ND*	ND	ND	ND	ND	ND
28	Ethylene	C2H4	ND	ND	ND	ND	ND	ND
30	Ethane	C2H6	ND	ND	ND	ND	ND	ND
42	Propene	C3H6	19.9	3.1	0.99	1.00	6075	71
44	Propane	C3H8	ND	ND	ND	ND	ND	ND
56	1 (trans-2; cis-2) -Butene	C4H8	5.9	3.3	1.00	1.00	749	251
58	n (iso)-Butane	C4H10	ND	ND	ND	ND	ND	ND
68	Isoprene	C5H8	5.5	3.4	1.00	1.00	268	210
70	1 (trans-2; cis-2) -Pentene; Cyclopentane	C5H10	5.9	2.9	1.00	1.00	314	754
72	n (iso)-Pentane	C5H12	ND	ND	ND	ND	ND	ND
78	Benzene	C6H6	4.7	2.4	1.00	1.00	143	47
84	Methylcyclopentane; Cyclohexane; 1-Hexene	C6H12	4.8	2.0	1.00	1.00	299	1543
86	n-Hexane; 2 (3)-Methylpentane; 2,2 (2,3)-Dimethylbutane	C6H14	ND	ND	ND	ND	ND	ND
92	Toluene	C7H8	4.1	2.4	1.00	1.00	66	125
98	Methylcyclohexane	C7H14	6.5	ND	1.00	ND	162	ND
100	n-Heptane;2(3)-Methylhexane; 2,3 (2,4)-Dimethylpentane	C7H16	9.5	ND	1.00	ND	2279	ND
104	Styrene	C8H8	2.8	2.7	0.98	0.98	23	172
106	Ethylbenzene; o (m; p)-Xylene	C8H10	2.1	25.3	1.00	1.00	62	158
114	n-Octane; 2 (3)-Methylheptane; 2,2,4 (2,3,4) -Trimethylpentane	C8H18	5.7	ND	1.00	ND	754	ND
120	n (iso) -Propylbenzene; o (m; p)-Ethyltoluene; 123 (124; 135)-Trimethylbenzene	C9H12	1.6	2.3	0.99	0.99	46	200
128	Nonane	C9H20	5.7	ND	0.98	ND	248	ND
134	p (m) -Diethylbenzene	C10H14	2.3	2.5	0.98	0.98	14	91
142	n-Decane	C10H22	5.1	ND	0.99	ND	84	ND
156	Undecane	C11H24	5.5	ND	0.98	ND	76	ND
170	Dodecane	C12H26	5.4	ND	0.96	ND	107	ND

*ND: the compound is not detectable by MI-SPI-MS or PTR-MS either due to high ionization energy (IE) or due to low proton affinity (PA).

Table S6. Ionization energy (IE) and proton affinity (PA) values of haloalkanes in TO15.

Mass [amu]	Compound	IE [eV]	PA [kJ/mol]
50	Chloromethane	11.26	647.3
64	Chloroethane	10.98	693.4
84	Dichloromethane	11.33	628
137	Trichlorofluoromethane	11.68	NA*
153	Carbon tetrachloride	11.47	NA
163	Bromodichloromethane	10.96	NA
187	1,1,2-Trichloro-1,2,2-trifluoroethane	11.99	NA
208	Dibromochloromethane	10.59	NA
260	Hexachloro-1,3-butadiene	NA	NA

*NA, not available.