Supplemental Material to: Deployment and evaluation of an NH_4^+/H_3O^+ reagent-ion switching chemical ionization mass spectrometer for the detection of reduced and oxygenated gas-phase organic compounds

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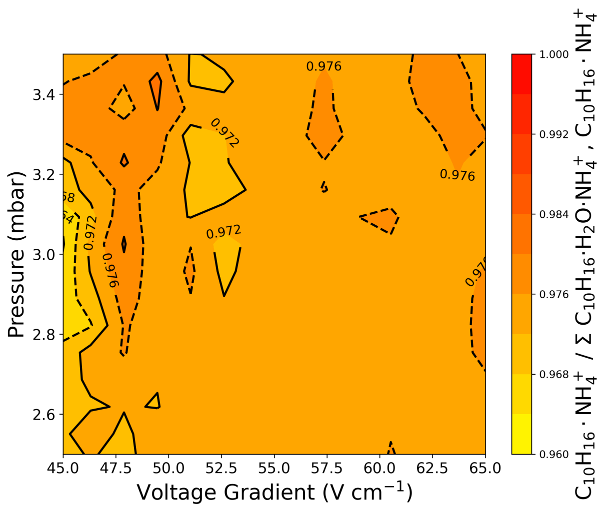

Figure S1. Contribution of the α-pinene water cluster ($\mathrm{C_{10}H_{16} \cdot H_2O \cdot NH_4^+}$) to the sum of the water cluster and molecular ion with $\mathrm{NH_4^+}$.

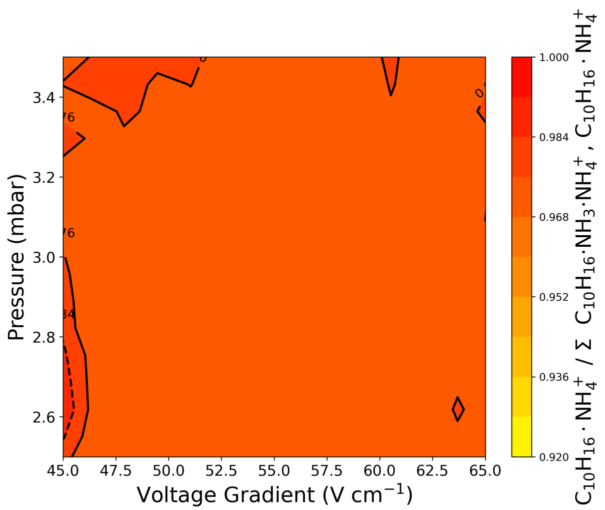

Figure S2. Contribution of the α-pinene ammonia cluster $(C_{10}H_{16} \cdot NH_3 \cdot NH_4^+)$ to the sum of the ammonia cluster and molecular ion with NH_4^+.

Table S1. Table of NH_4^+ and H^+ affinities obtained from the NIST Chemistry WebBook (Edward P. Hunter and Sharon G. Lias; Michael M. Meot-Ner (Mautner) and Sharon G. Lias).

Compound	NH_4^+ Affinity [kJ mol^{-1}]	H^+ Affinity [kJ mol^{-1}]
Ethylene	42	681
Acetone	118	812
Methylal	122	*no data*
2-Methyl-propene	146	802
1,2-Dimethoxy-ethane	160	858
Benzene	81	750
Cyclohexane	40	687
1,3,5-Trimethylbenzene	91	836
Hydrogen sulfide	48	705
Water	86	691
Ammonia	107	854

Table S2. Vapor pressure estimates of certified gas standard analytes at 25°C.[a]

Analyte	Formula	Vapor Pressure μg m^{-3}	Vapor Pressure Pa	Method
dimethyl sulfide	C_2H_6S	1.60E+9	6.38E+4	Mean VP of Antoine & Grain methods
methane thiol	CH_4S	3.92E+9	2.02E+5	Mean VP of Antoine & Grain methods
dimethyl sulfoxide	C_2H_6SO	2.61E+6	82.9	Mean VP of Antoine & Grain methods
benzene	C_6H_6	3.66E+8	1.16E+4	Mean VP of Antoine & Grain methods
toluene	C_7H_8	1.17E+8	3.16E+3	Mean VP of Antoine & Grain methods
1,3,5-trimethylbenzene	C_9H_{12}	1.30E+7	268	Mean VP of Antoine & Grain methods
phenol	C_6H_6O	1.63E+6	43	Modified Grain method
isoprene	C_5H_8	2.02E+9	7.35E+4	Mean VP of Antoine & Grain methods
limonene	$C_{10}H_{16}$	1.06E+7	193	Mean VP of Antoine & Grain methods
acetone	C_3H_6O	7.78E+8	3.32E+4	Mean VP of Antoine & Grain methods
hydroxyacetone	$C_3H_6O_2$	6.93E+6	232	Mean VP of Antoine & Grain methods
methyl ethyl ketone	C_4H_8O	3.81E+8	1.31E+4	Mean VP of Antoine & Grain methods
methyl vinyl ketone	C_4H_6O	3.45E+8	1.22E+4	Mean VP of Antoine & Grain methods
3-hexanone	$C_6H_{12}O$	8.73E+7	2.16E+3	Mean VP of Antoine & Grain methods
2-octanone	$C_8H_{16}O$	1.27E+7	246	Mean VP of Antoine & Grain methods
camphor	$C_{10}H_{16}O$	8.72E+4	1.42	Modified Grain method
acetaldehyde	C_2H_4O	2.15E+9	1.21E+5	Mean VP of Antoine & Grain methods
trans-2-hexenal	$C_6H_{10}O$	2.49E+7	629	Mean VP of Antoine & Grain methods
beta-cyclocitral	$C_{10}H_{16}O$	1.48E+6	24.1	Mean VP of Antoine & Grain methods
trans-3-hexenol	$C_6H_{12}O$	5.05E+6	125	Mean VP of Antoine & Grain methods
acetonitrile	C_2H_3N	4.42E+8	2.67E+4	Mean VP of Antoine & Grain methods
propane-1,2-diol	$C_3H_8O_2$	4.54E+5	14.8	Mean VP of Antoine & Grain methods
D5-Siloxane	$C_{10}H_{30}O_5Si_5$	4.35E+6	29.1	Mean VP of Antoine & Grain methods

[a] Estimated using EPI Suite (US EPA).

Table S3. Comparison of sensitivities calculated in this study with those reported by Xu et al. (2022).[a]

Analyte	This Study counts s^{-1} ppt_v^{-1}	Xu et al. (2022) counts s^{-1} ppt_v^{-1}
Acetonitrile	0.85	0.55
Acetaldehyde	<0.1	0.021
Acetone	0.98	1.2
Isoprene	<0.1	0.028
Methyl vinyl ketone	1.5	1.5
Methyl ethyl ketone	1.3	1.6
Hydroxyacetone	1.6	2.1
Benzene	<0.1	<0.001
Phenol	<0.1	0.19
Hexanone[b]	3.4	3.8
Trimethylbenzene[c]	<0.1	<0.001

[a] We are using a Vocus-S and Xu et al. (2022) report using a Vocus-2R which have different time-of-flight region lengths. The instruments also differ in extraction frequency (i.e., 25 kHz here, and 17.5 kHz for Xu et al. (2022)).

[b] This study used 3-Hexanone and Xu et al. (2022) used 2-Hexanone.

[c] This study used 1,2,5-Trimethylbenzene and Xu et al. (2022) used 1,3,5-Trimethylbenzene.

Table S4. Vapor pressure estimates of potential biogenic ROC analytes at 25°C.[a]

Analyte *MCM name*	Formula	Vapor Pressure μg m^{-3}	Vapor Pressure Pa	Method
LIMCOOH	$C_{10}H_{18}O_3$	4.40E+2	0.00586	Modified Grain method
LIMAOH	$C_{10}H_{18}O_2$	3.55E+3	0.0517	Modified Grain method
LIMBCO	$C_{10}H_{16}O_2$	7.47E+3	0.11	Modified Grain method
LIMONONIC	$C_{10}H_{16}O_3$	8.77E+3	0.118	Modified Grain method
APINBCO	$C_{10}H_{16}O_2$	1.76E+4	0.26	Modified Grain method
PINAL	$C_{10}H_{16}O_2$	3.62E+5	5.34	Modified Grain method
PINONIC	$C_{10}H_{16}O_3$	6.15E+3	0.0828	Modified Grain method
C109OH	$C_{10}H_{16}O_3$	4.66E+2	0.00627	Modified Grain method
C107OH	$C_{10}H_{16}O_3$	1.99E+3	0.0268	Modified Grain method
HCOC5	$C_5H_8O_2$	2.07E+6	51.2	Mean VP of Antoine & Grain methods
LIMALNO3	$C_{10}H_{17}NO_6$	1.16E+1	0.000116	Modified Grain method
NLIMALOH	$C_{10}H_{17}NO_6$	2.32E+1	0.000233	Modified Grain method
MBOANO3	$C_5H_{11}NO_5$	7.79E+3	0.117	Modified Grain method

[a] Estimated using EPI Suite (US EPA).

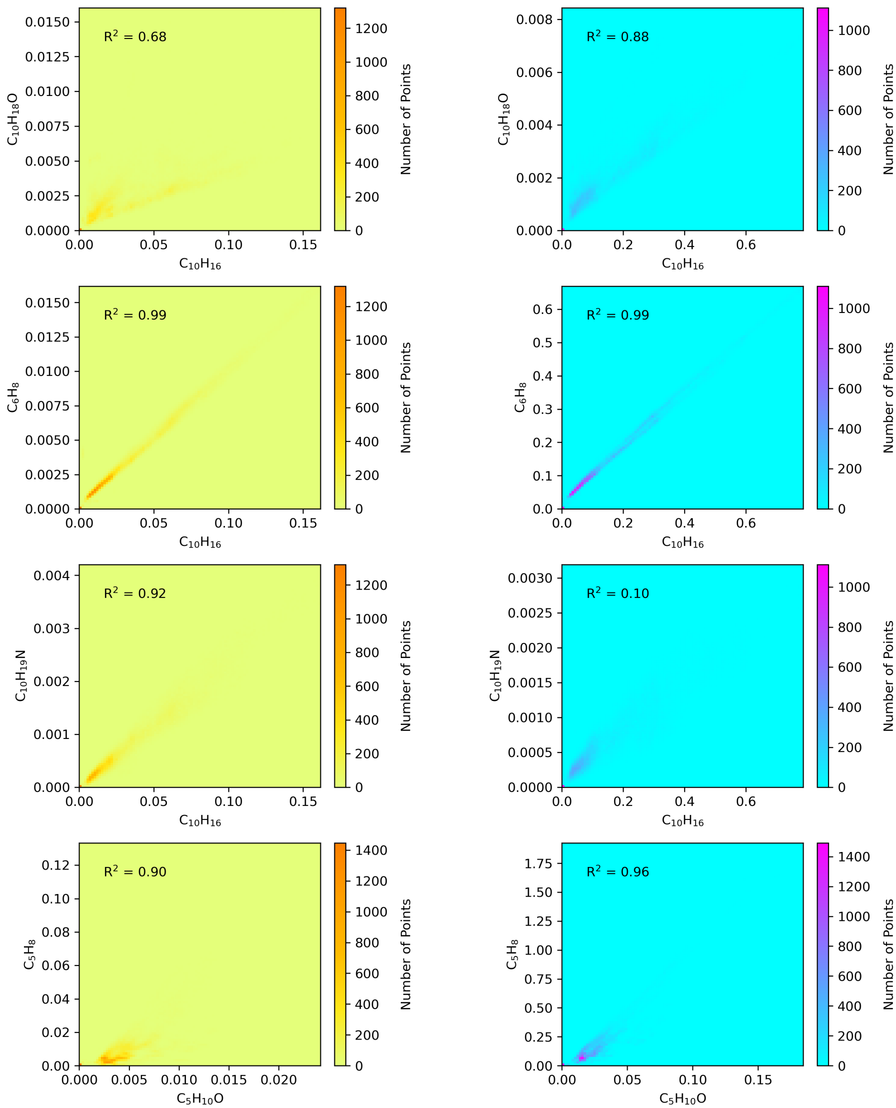

Figure S3. 2D-histograms of ion signals for a selection of ions detected by NH_4^+ (orange/yellow, left) and H_3O^+ (blue/purple, right). Color bars show frequency per bin for the 100 x100 bin grid. Signals for the ions are in counts extraction^{-1} at 25 kHz extraction frequency.

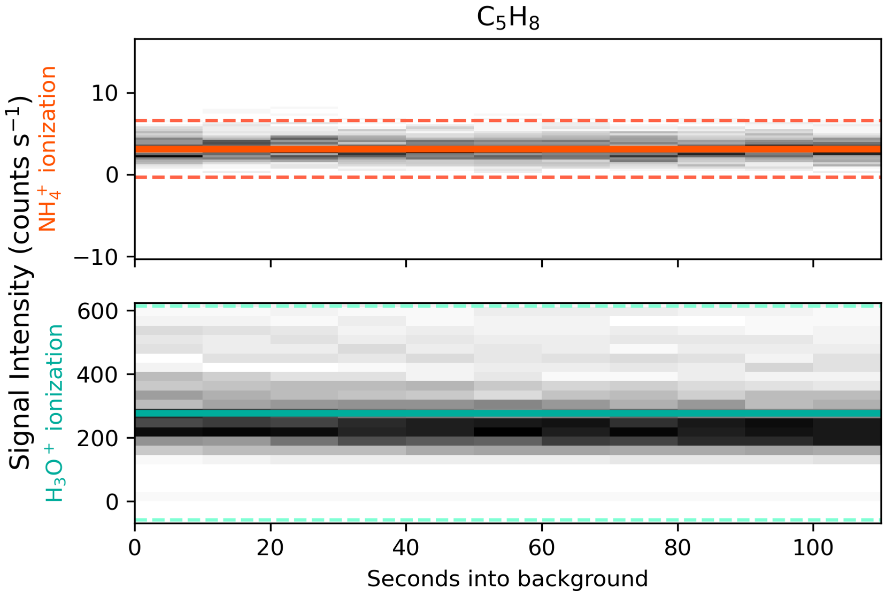

Figure S4. 2D-histograms of campaign zero periods for the C_5H_8 ion detected with NH_4^+ (orange, top) and H_3O^+ (blue, bottom). Solid horizontal lines represent mean signal during zero periods and dashed lines represent 3 σ deviation from the mean.

Table S5. Potential structures and literature precedent for organic nitrate peaks.

Chemical Formula	Name in MCM[a]	Reported in Fry et al. (2013)?	Potential Assignment
$C_5H_9NO_5$	NMBOBCO C4MCONO3OH	no	232-MBO nitrate/ Isoprene nitrate
$C_5H_{11}NO_5$	MBOANO3	no	232-MBO nitrate
$C_{10}H_{15}NO_3$		no	Dehydration fragment of $C_{10}H_{17}NO_4$
$C_{10}H_{15}NO_4$	NC101CO NC91CHO	yes (night)	Terpene nitrate (carbonyl)
$C_{10}H_{15}NO_5$	PINALNO3	no	Fragment from LIMALNO3? Faxon et al. (2018) speculate that is could be a fragment of dimers. Oxidation of primary emissions of terpenoid oxygenates.
$C_{10}H_{15}NO_6$	C10PAN2 C923PAN C918PAN C108NO3	no	Terpene nitrate (PAN/carbonyl nitrate)
$C_{10}H_{17}NO_4$	APINCNO3 BPINBNO3 LIMANO3 LIMCNO3 APINANO3 BPINANO3	yes (day and night)	Terpene nitrate (alcohol)
$C_{10}H_{17}NO_5$	NBPINAOOH NAPINBOOH NLIMOOH	yes (night)	Terpene nitrate (hydroperoxy)
$C_{10}H_{17}NO_6$	LIMALNO3 NLIMALOH	no	Limonene nitrate
$C_{10}H_{16}N_2O_6$		no	Proposed as α-pinene oxidation product (Bates et al., 2022)

[a] Exploration of the MCM is non-exhaustive (Saunders et al., 2003; Jenkin et al., 2015).

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