

Supplementary Material

Table A1: CIR-TOF-MS calibration details. The measured compound is given along with the method employed for calibration, the relative humidity of the sample matrix during calibration and, where appropriate the surrogate compound employed. The instrument sensitivity to each given compound is provided along with an uncertainty/error estimate for the measurement.

Target	Method	Relative Humidity / %	Calibration Compound	Sensitivity¹ / ncps ppbV⁻¹	Calibration Error² / %
2,4,6-trimethyl phenol	Gas Standard ³	0	phenol	226.35 – 372.54	11.04 – 21.78
3,5-dimethyl benzaldehyde	Gas Standard	0	m-tolualdehyde	98.65 – 145.35	9.35 – 17.20
O ₂ -bridged nitrate (TM135BPNO ₃) ⁴	Gas Standard	0	m-tolualdehyde	98.65 – 145.35	9.35 – 17.20
O ₂ -bridged diol (TM135BP2OH) ⁴	Gas Standard	0	m-tolualdehyde	98.65 – 145.35	9.35 – 17.20
O ₂ -bridged ketone (TM135OBPOH) ⁴	Gas Standard	0	m-tolualdehyde	98.65 – 145.35	9.35 – 17.20
bicyclic marker ⁴	Gas Standard	0	m-tolualdehyde	98.65 – 145.35	9.35 – 17.20
<i>m/z</i> 129	Permeation Tube	50	methacrolein	9.46 – 19.27	3.95 – 4.20
furanones (<i>m/z</i> 111 & 113)	Teflon Bag ⁵	50	citraconic anhydride	32.53 – 119.90	27.60 – 27.63
hydroxy acetic acid	Permeation Tube ⁶	50	acetic acid	17.43 – 45.93	2.93 – 5.96

Target	Method	Relative Humidity / %	Calibration Compound	Sensitivity ¹ / ncps ppbV ⁻¹	Calibration Error ² / %
hydroxy acetone	Permeation Tube	50	acetone	55.60 – 104.04	3.25 – 4.87
methyl glyoxal	Permeation Tube	50	isoprene	9.46 – 19.27	6.53 – 11.56
acetic acid	Permeation Tube	50	acetic acid	17.43 – 45.93	2.93 – 5.96
acetone	Permeation Tube	50	acetone	55.60 – 104.04	3.25 – 4.87
formic acid	Permeation Tube	50	formic Acid	5.14 – 9.52	3.77 – 6.78
acetaldehyde	Permeation Tube	50	acetaldehyde	57.01 – 107.33	3.17 – 3.31
carbonyl marker	Permeation Tube	50	acetone	55.60 – 104.04	3.25 – 4.87
methanol	Permeation Tube	50	methanol	22.25 – 46.06	3/94 – 6.76

¹ Instrument sensitivity is given as a range covering all drift cell conditions employed during the study (see **Table 1** for further information).

² Measurement uncertainty/error is given as a range covering all drift cell conditions employed during the study (see **Table 1** for further information).

³ Gas standards provided by Air Environmental Inc. (US) and courtesy of PSI. Compound mixing ratio accuracy: 5 %.

⁴ Calibrated values used only to calculate 'pseudo' VOC yields

⁵ Calibration conducted by injecting liquid citraconic anhydride (Sigma Aldrich, 99%) into an 80 L Teflon sample bag (SKC, Ltd). Sticking factors employed to adjust for deposition/wall loss.

⁶ Permeation tubes supplied by Ecoscientific (UK) and Vici Inc. (US). Compound emission rate accuracy: 2.02 – 11.24 %

Table A2: VOC yields for various compounds measured by CIR-TOF-MS during experiments 1 - 7

Volatile Organic Compound Product Yield / %							
Experiment	1	2	3	4	5	6	7
Compound							
O ₂ -bridged nitrate (TM135BPNO3)	1.8	2.8	2.7	2.9	4.3	3.7	5.1
O ₂ -bridged ketone (TM135OBPOH)	0.7	0.6	1.0	1.1	3.0	0.8	2.3
O ₂ -bridged diol (TM13BP2OH)	0.2	0.3	n/m	0.4	0.8	0.2	0.9
2,4,6-trimethylphenol	0.9	2.5	1.6	2.7	n/m	3.8	2.4
3,5-dimethyl benzaldehyde	1.3	2.5	1.6	2.6	1.9	2.7	2.2
<i>m/z</i> 129	5.0	4.4	11.8	18.6	29.5	8.4	12.9
<i>m/z</i> 113	15.6	46.6	37.2	38.4	33.3	39.6	26.5
3 me. 5-methyl-5-(2H) furanone	5.7	10.3	8.8	7.9	3.6	8.1	8.9
hydroxy-acetone	0.6	0.5	1.1	1.0	1.5	0.6	1.2
hydroxy acetic acid	3.1	n/m	2.0	3.1	18.6	5.9	8.3
methyl glyoxal	13.5	24.3	31.1	28.8	21.3	22.5	21.0
acetic acid	19.5	14.7	11.9	10.0	33.1	16.0	32.2
acetone	n/m	0.4	3.3	1.4	3.1	1.3	1.5
formic acid	11.51	13.1	32.5	15.3	48.5	10.9	n/m
carbonyls	32.1	44.7	51.2	26.2	17.8	24.9	41.2
methanol	1.7	1.0	1.0	0.7	2.8	1.4	2.6

n/m: Not measured