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Development of an International System of Units (SI)-traceable transmission curve reference material to improve the quantitation and comparability of proton-transfer-reaction mass-spectrometry measurements

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Preparation of D3-siloxane reference materials

Hexamethylcyclotrisiloxane (D3-siloxane) is a solid at room temperature and pressure because of its unique phase transition properties. To enable it to be added to the gas cylinder it was dissolved in a solvent (*n*-hexane). *N*-hexane was selected because previous work (Kierkegaard and Mclachlan, 2013) has demonstrated it to be effective for dissolving D3-siloxane.

A ratio of nominally 0.05 mol mol^{-1} of D3-siloxane to *n*-hexane was empirically determined to avoid any precipitation of D3-siloxane from solution and to ensure the homogeneity of the mixture prior to injection into the cylinder. This was determined by preparing different solutions of D3-siloxane in *n*-hexane in 10 mL vials, splitting the content into multiple 2 mL prior to analysis on a GC-MS/FID (Agilent 6890/5973) equipped with a liquid autosampler. The GC-MS/FID was fitted with a capillary column (HP-5MS 30 m x 250 µm x 1 µm), the carrier gas was helium with a constant head pressure of 15 psi and a temperature program started at 30 °C hold for 5 minutes and then ramped up at 10 °C min^{-1} to 140 °C; the total time was 16 minutes.

Table S1. Measured and predicted reaction rate constants for all 20 compounds present in the PRMs and CRMs taken from Zhao and Zhang (2004) and references therein, from Holzinger et al., (2019) and those recommended in this work for those components not reported in Holzinger et al., (2019).

Compound	**Proton reaction rate coefficients (10^{-9} cm^3 s^{-1})**			
	Measured	**Predicted**	**Holzinger et al., (2019)**	**This work**
methanol	2.1 – 3.8	2.33	2.20	-
acetonitrile	4.5	4.74	3.10	-
acetaldehyde	3.55 – 3.7	3.36	3.03	-
propane	-	-	-	-
ethanol	2.7 – 3.8	2.26	-	-
acetone	3.9 – 4.1	3.0	3.25	-
DMS	1.7 – 2.5	2.53	-	2.30
isoprene	2.0, 1.3	1.94	1.85	-
MVK	-	-	2.72	-
MEK	-	-	3.25	-
benzene	1.3 – 2.1	1.97	1.97	-
toluene	1.3 – 2.3	2.12	-	2.15
m-xylene	2.3	2.26	2.31	-
1,2,4-TMB	2.4	2.4	2.40	-
1,2,4-TFB	-	-	2.46	-
3-carene	2.2	2.44	2.04	-
1,2,4-TCB	-	-	2.40	-
D3-siloxane	-	-	2.16	-
D4-siloxane	-	-	2.99	-
D5-siloxane	-	-	3.39	-
PFTBA	-	-	-	3.50

Table S2. Physical properties (boiling point and vapour pressure), purity (%) and sources (chemical manufacturer) of the pure chemicals.

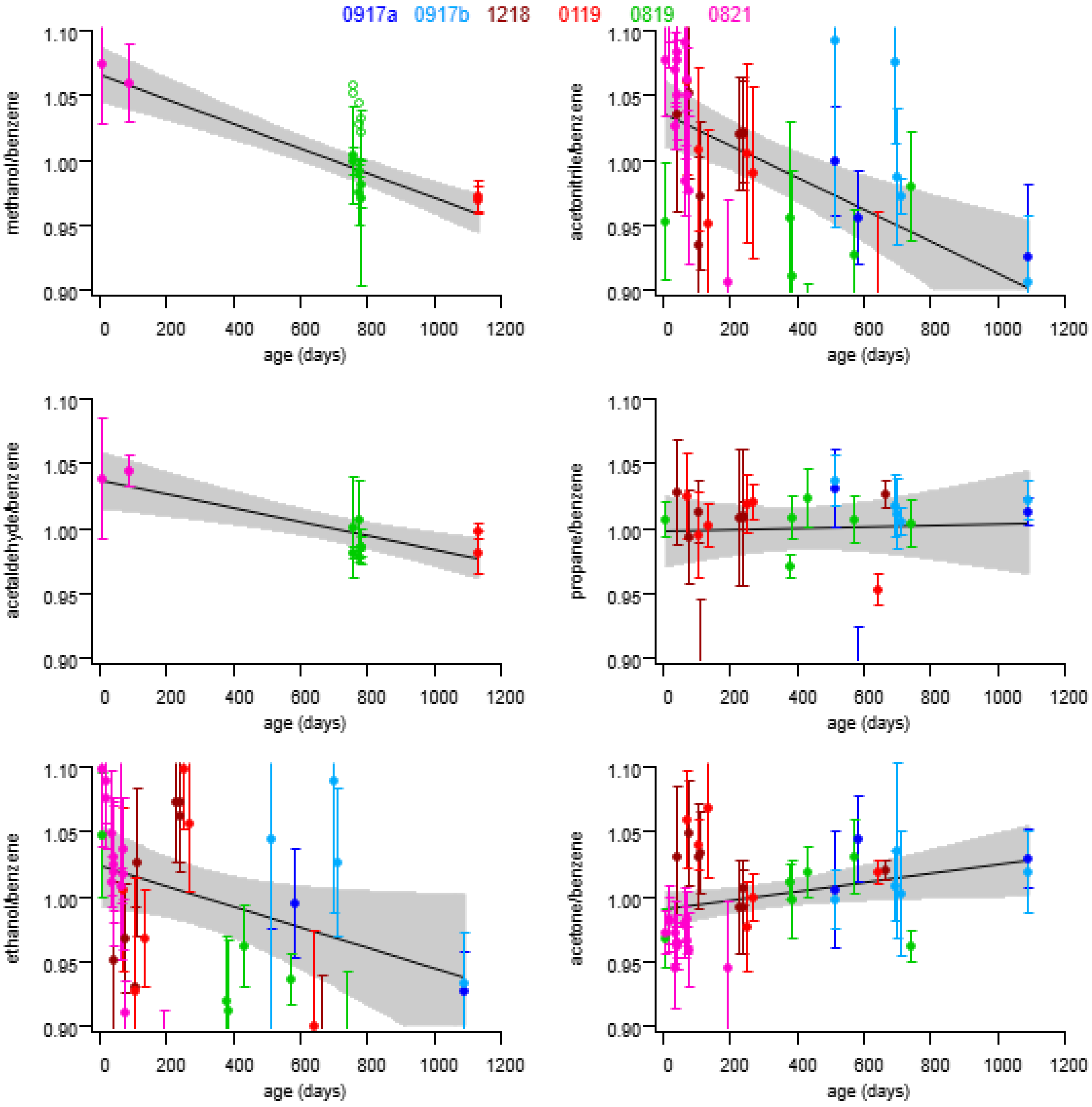
Compound	boiling point (K)		vapour pressure (Pa)		Purity (%)	Source
	NIST[a]	USEPA[b]	Experimental[b]	Estimated[c]		
methanol	337.8 ± 0.3	337.9	1.69×10^{4}	1.58×10^{4}	>99.9	Alfa Aesar
acetonitrile	354.8 ± 0.4	354.8	1.18×10^{4}	2.67×10^{4}	>99.9	Sigma Aldrich
acetaldehyde	294.0 ± 0.8	293.3	1.20×10^{5}	1.21×10^{5}	>99.9	Fluka
propane	231.1 ± 0.2	231.1	9.53×10^{5}	8.19×10^{5}	>99.9	Air Liquide
ethanol	351.5 ± 0.2	351.4	7.91×10^{3}	8.12×10^{3}	>99.9	Fisher Chemical
acetone	329.5 ± 0.9	329.2	3.09×10^{4}	3.32×10^{4}	>99.9	Alfa Aesar
DMS	311 ± 3	310.5	6.69×10^{4}	6.38×10^{4}	99.9	Alfa Aesar
isoprene	307 ± 2	307.2	7.33×10^{4}	7.35×10^{4}	>99.9	Aldrich
MVK	354 ± 4	354.6	nd[e]	1.22×10^{4}	98.0	Alfa Aesar
MEK	353 ± 1	352.7	1.21×10^{4}	1.31×10^{4}	>99.9	Sigma Aldrich
benzene	353.3 ± 0.1	353.2	1.26×10^{4}	1.16×10^{4}	>99.9	Sigma Aldrich
toluene	383.8 ± 0.2	383.8	3.79×10^{3}	3.16×10^{3}	>99.9	Sigma Aldrich
m-xylene	412.3 ± 0.3	412.3	1.11×10^{3}	0.88×10^{3}	99.9	Alfa Aesar
1,2,4-TMB	442.4 ± 0.8	442.5	2.80×10^{2}	2.15×10^{2}	99.6	Fluka
1,2,4-TFB	362 - 364	363.2	nd	7.65×10^{3}	99.9	Alfa Aesar
3-carene	444 ± 5[f]	443.2	Nd	2.79×10^{2}	98.0	Fluka
1,2,4-TCB	486.7	486.7	6.13×10^{1}	2.44×10^{1}	99.5	Sigma Aldrich
D3-siloxane	407	407.2	4.71×10^{2}	1.16×10^{3}	99.9	Aldrich
D4-siloxane	446 - 449	449.0	1.40×10^{2}	1.58×10^{2}	99.7	Aldrich
D5-siloxane	483[g]	483.2	2.67×10^{1}	29.1	99.5	Alfa Aesar
PFTBA	452 ± 1	nd	nd	nd	87.6	Alfa Aesar

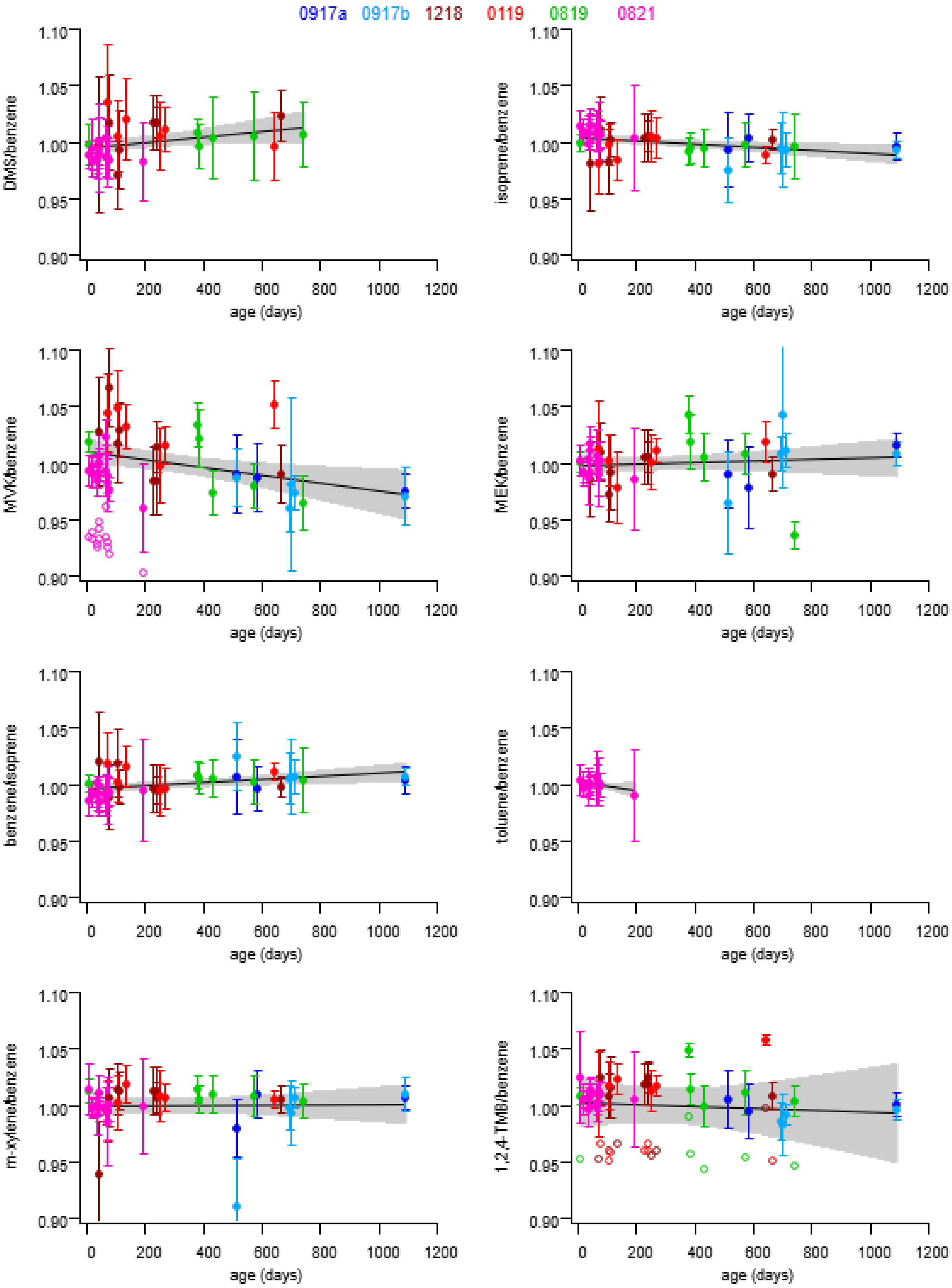
[a] Retrieved from https://webbook.nist.gov on January 11th 2023. [b] Experimental vapiur pressure data at 298 K retrieved from the United States Environmental Protection Agency EPI Suite v4.11, downloaded from https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411 on January 11th 2023. [c] Calculated vapour pressure at 298 K determined as an average of the Antoine and Grain methods determined using the United States Environmental Protection Agency EPI Suite v4.11, downloaded from https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411 on January 11th 2023. [d] Only non-critical impurities are included here as critical impurities, namely any of the 20 components listed in this table, are already included in the final amount fraction of any resultant mixture. [e] no experimental data available. [f] Calculated as the average of 3 results and the uncertainty was determined by combining the reported uncertainties in quadrature. [g] National Center for Biotechnology Information (2023). PubChem Compound Summary for CID 10913, Decamethylcyclopentasiloxane. Retrieved January 11, 2023 from https://pubchem.ncbi.nlm.nih.gov/compound/Decamethylcyclopentasiloxane.

Table S3. Dates for all the comparisons conducted as part of the validation process.

Date of comparison	Instrument	Reference PRM	Unknown PRM	|Age difference| (days)
29 August 2019	GC-FID/MS	0819	1218	262
4 September 2020	GC-FID/MS	0819	1218	262
10 September 2020	GC-FID/MS	0819	0917a	704
11 September 2020	GC-FID/MS	0819	0917b	704
27 October 2020	GC-FID/MS	0819	0119	233
2 December 2020	Cryo-GC-FID	0819	1218	262
10 December 2020	Cryo-GC-FID	0819	0917b	704
11 December 2020	Cryo-GC-FID	0819	0119	233
14 December 2020	Cryo-GC-FID	0819	0917a	704
1 September 2021	GC-FID/MS	0819	0821	709
8 June 2022	GC-FID/MS	0821 (toluene)	D711534	255
16 September 2021	GC-FID/MS	0821 (PFTBA)	D961399	46
17 September 2021	GC-FID/MS	0821 (PFTBA)	D961410	47

Figure S1. Stability plots of all components present in the PTR-MS transmission curve reference material. The open symbols show the original data before being corrected for biases in the parent mixtures (for methanol, MVK and 1,2,4-TMB) or which has been excluded from the regression analysis (for D4-siloxane and D5-siloxane) as discussed in the text. The best fit curves from least squares straight line regression analyses are shown (solid black line) along with the 95 % confidence interval of the fits (shaded area). The slope, intercept and F-statistic data from the regression analyses are shown in Table 3.




0917a
0917b
1218
0119
0819
0821
DMS/benzene
isoprene/benzene
MVK/benzene
MEK/benzene
benzene/isoprene
toluene/benzene
m-xylene/benzene
1,2,4-TMB/benzene
1.10
1.05
1.00
0.95
0.90
0
200
400
600
800
1000
1200
age (days)

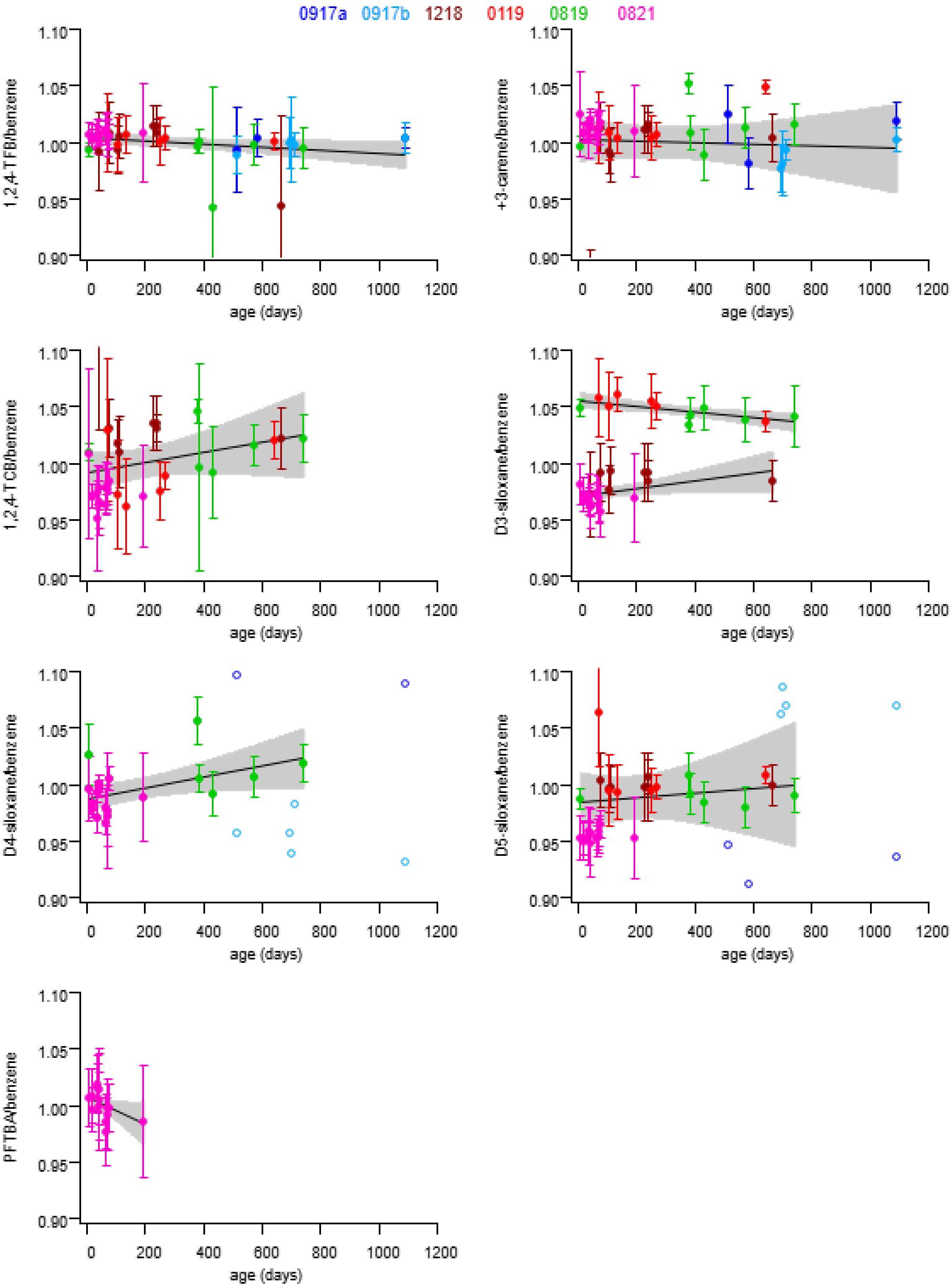
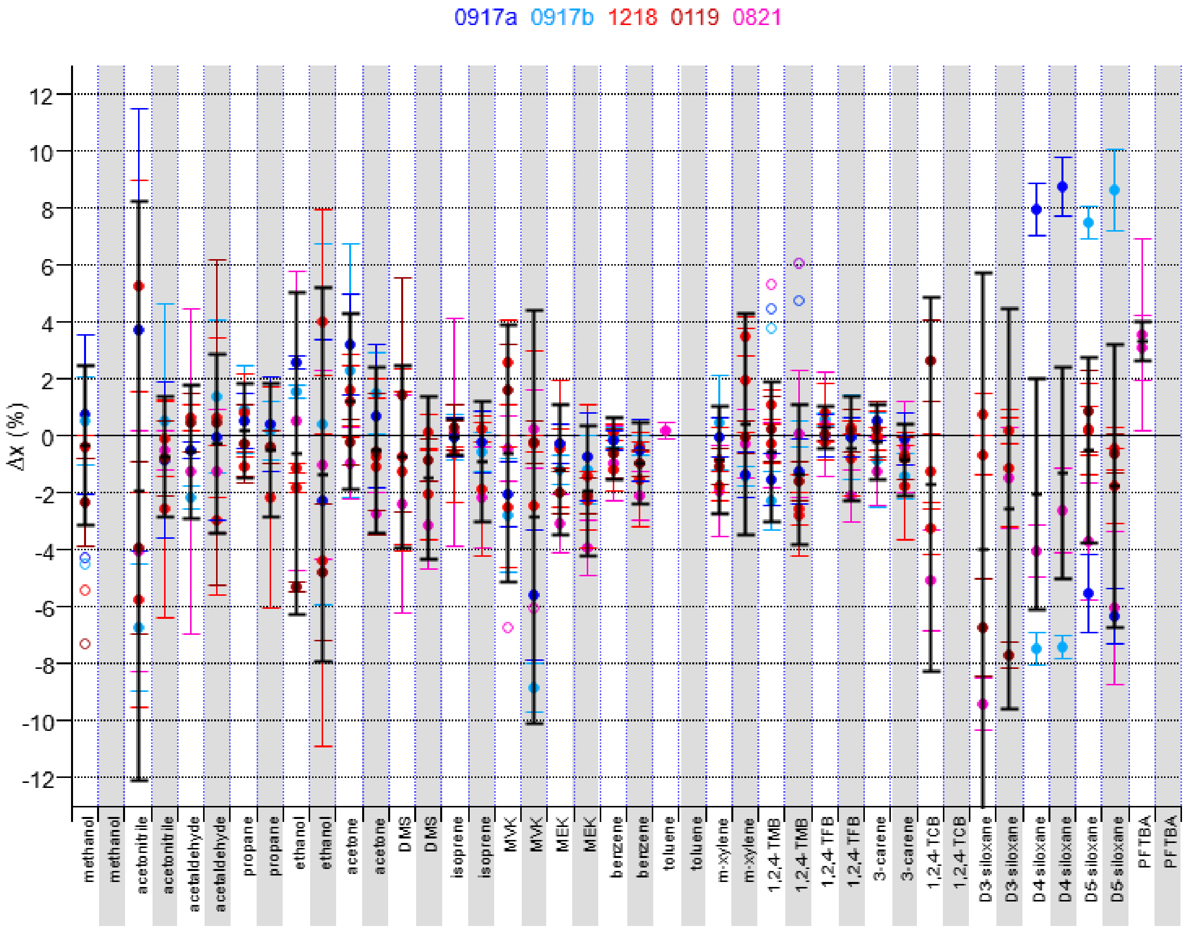

0917a 0917b 1218 0119 0819 0821
1,2,4-TFB/benzene
+3-carene/benzene
1,2,4-TCB/benzene
D3-siloxane/benzene
D4-siloxane/benzene
D5-siloxane/benzene
PFTBA/benzene
0.90
0.95
1.00
1.05
1.10
0
200
400
600
800
1000
1200
age (days)

Figure S2. Supporting validation data showing all the relative difference (Δx) data for MS (shaded boxes) and FID validation data or all components in the different primary reference materials (PRMs; 0917a, 0917b, 1218, 0119, 0819, 0821) relative to NPL PRM 0819 (solid symbols). The solid black line represents the average of these validations with the error bar representing the associated expanded uncertainty (2σ). For D4- and D5-siloxane the averages do not include the validations from NPL PRMs 0917a or 0917b. Methanol and acetaldehyde FID data are from the cryo-GC-FID instrument while all others are from the GC-FID/MS instrument, including the MS data for acetaldehyde. Open symbols represent the original data before correcting for biases observed in three of the parent mixtures (A410, 5 % low for methanol; 3070, 6.3 % low for MVK and D711530 6 % low for 1,2,4-TMB). PFTBA and toluene were only included in the most recently prepared NPL PRM (0821) and are not present in NPL PRM 0819. Their validation is described in the text. No MS data was available for toluene, 1,2,4-TCB or PFTBA because the specific m/Q ions had not been included in the GC-MS method at the time of data acquisition.



Preparation and validation of certified reference materials

In order to meet the requirements of end users an NPL certified reference material (CRM) has been developed and is also described. Its purpose is to facilitate wider uptake and implementation to improve the comparability of PTR-MS measurements in a cost-effective and timely manner for end users. While the proton affinity of *n*-hexane is less than water and therefore does not undergo proton transfer it is still detectable depending on amount fraction because of the presence of minor impurities of O_2^+ and NO^+ typically 1 – 3 % (Amador-Muñoz et al., 2016), which could cause interferences from signals resulting from the charge transfer and hydride abstract ions. Therefore, an additional advantage of the CRMs is that because the solid D3-siloxane is dissolved in the other components no *n*-hexane is used any potential interferences from the presence of n-hexane are avoided.

To prepare the CRMs, the pure components were mixed in vials and an aliquot added to the evacuated gas cylinder, minimising the weighing and liquid addition steps, thus reducing the preparation time and effort considerably. The differences in vapour pressure between compounds, e.g., D5 siloxane (0.0003 bar), acetaldehyde (1.2 bar), could have compromised the blending tolerances of the final CRM, because the more volatile compounds fraction in the liquid mixtures may have been reduced. To minimise this, four vials were prepared, one containing the most volatile compounds (acetaldehyde, DMS, isoprene, methanol, acetone, ethanol, MVK, MEK and acetonitrile), a second containing the less volatile non-polar components (benzene, toluene, 1,2,4-TFB, *m*-xylene, 1,2,4-TMB and 3-carene), a third mixture containing the least volatile components (1,2,4-TCB, D3-siloxane, D4-siloxane and D5-siloxane). Finally, the PFTBA was added separately as it was immiscible in the other three liquid mixtures listed above. The four groups of pure chemicals were added to the vials in order from lower vapour pressure to higher vapour pressure, so the more volatile compounds remained the shortest time in the vials to minimise any evaporative losses. The amount fractions for each compound in each CRM were assigned as the analytical values determined from comparison to PRM (0821), which was used as it contained all the components of interest. The repeatability (blend tolerance) in the preparation of the CRMs was about 20 – 30 % as shown in Figure S3 though this is just indicative of the repeatability of the preparation method and does not have any effect on the assigned amount fractions as these were derived from comparison to the PRM.

Figure S3. Certified amount fractions of 12 CRMs illustrating the preparation repeatability (blend tolerance) at 1 µmol mol^{-1} of approximately 20 - 30 %.

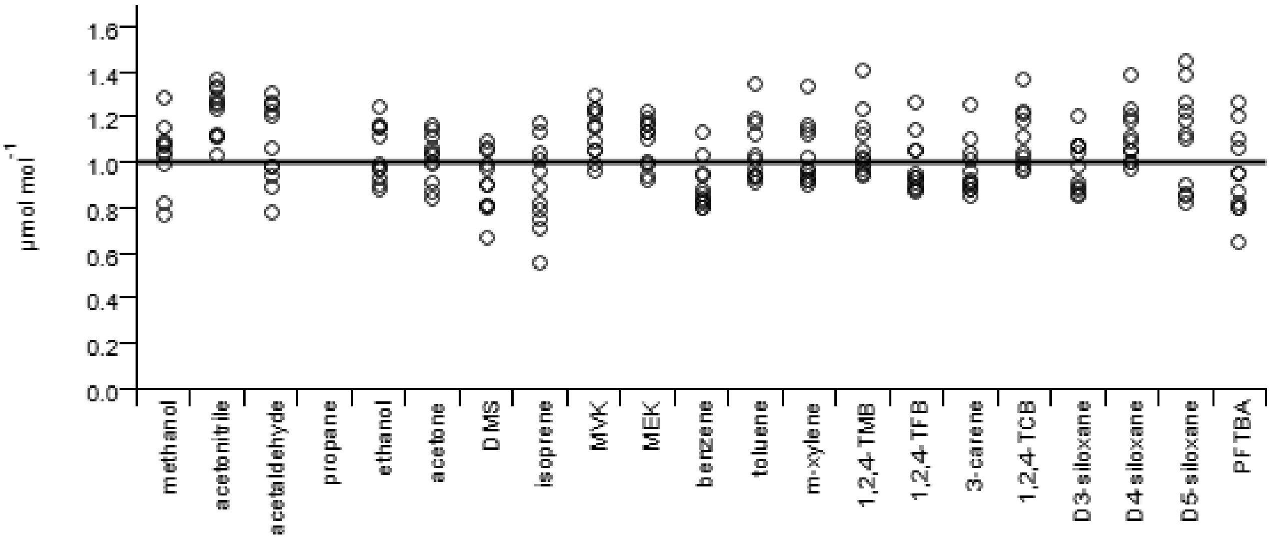
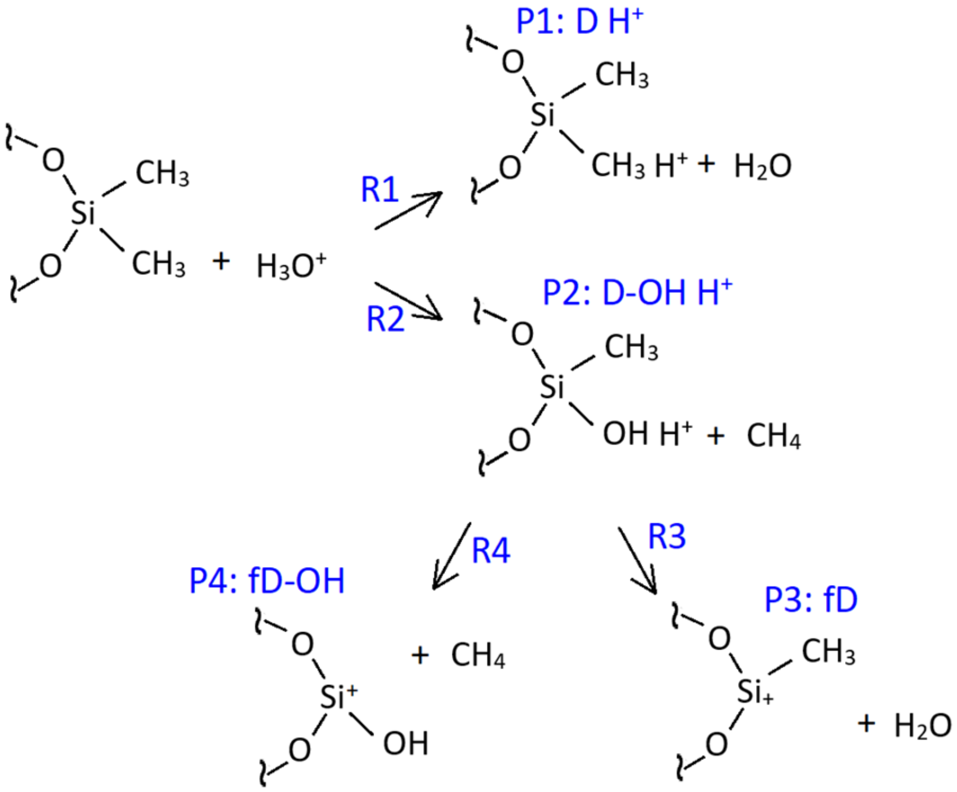


Figure S4. Fragmentation of cyclic siloxanes in PTR-MS



Calculation of product ion abundances from the outlined reaction mechansim:

Compound	**Product ions**			
	P1[a]	**P2**	**P3**	**P4**
D3-siloxane	m223.064*1.37	(m225.044– m223.064*0.13) *1.36	m207.033 * 1.36	(m209.012 – m207.033 * 0.12) *1.35
D4-siloxane	m297.083*1.52	(m299.062– m297.083*0.18) *1.51	m281.052 * 1.50	(m283.031 – m281.052 * 0.18) *1.49
D5-siloxane	m371.101 *1.69	(m373.081 – m371.101 *0.24) *1.68	m355.071 * 1.67	(m357.050 – m355.071 * 0.23) *1.66

[a] Correction for stable isotopes.

These assume that for D3-siloxane (209.012 / 209.030 and 225.044 / 225.061 Th are unresolved), D4-siloxane (299.062 / 299.080 and 283.031 / 283.049 Th are unresolved) and D5-siloxane (373.081 / 373.099 and 357.050 / 357.067 Th are unresolved). Note, that P4 is typically not detected for D3 and D5.

Additional References

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