Supporting Information

Development of an SI-traceable transmission curve reference material to improve comparability of proton transfer reaction mass spectrometry measurements

David R. Worton[1], Sergi Moreno[1,#], Kieran O'Daly[1], Rupert Holzinger[2]

[1] National Physical Laboratory, Hampton Road, Teddington, TW11 0LW

[2] Institute for Marine and Atmospheric Research, IMAU, Utrecht University, Utrecht, the Netherlands

Correspondence to: David R. Worton (dave.worton@npl.co.uk)

[#] Now at World Meteorological Organization (WMO), 7bis Avenue de la Paix, C.P. 2300 CH-1211, Geneva 2, Switzerland

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Preparation of D3-siloxane reference materials

Hexamethylcyclotrisiloxane (D3-siloxane) is a solid at room temperature and pressure. 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 and because the proton affinity of *n*-hexane is less than water and therefore does not undergo proton transfer and is not detectable by PTR-MS when operating in the H_3O^+ mode.

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. 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	2819	A638	262
4 September 2020	GC-FID/MS	2819	A638	262
10 September 2020	GC-FID/MS	2819	A574	704
11 September 2020	GC-FID/MS	2819	A578	704
27 October 2020	GC-FID/MS	2819	A643	233
2 December 2020	Cryo-GC-FID	2819	A638	262
10 December 2020	Cryo-GC-FID	2819	A578	704
11 December 2020	Cryo-GC-FID	2819	A643	233
14 December 2020	Cryo-GC-FID	2819	A574	704
1 September 2021	GC-FID/MS	2819	D961492	709
8 June 2022	GC-FID/MS	D961492 (toluene)	D711534	255
16 September 2021	GC-FID/MS	D961492 (PFTBA)	D961399	46
17 September 2021	GC-FID/MS	D961492 (PFTBA)	D961410	47

Figure S1. 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 (A574, A578, A638, A643 and D961492) relative to primary reference material 2819 (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 A574 or A578. 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 PRM (D961492) and are not present in 2819. 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.

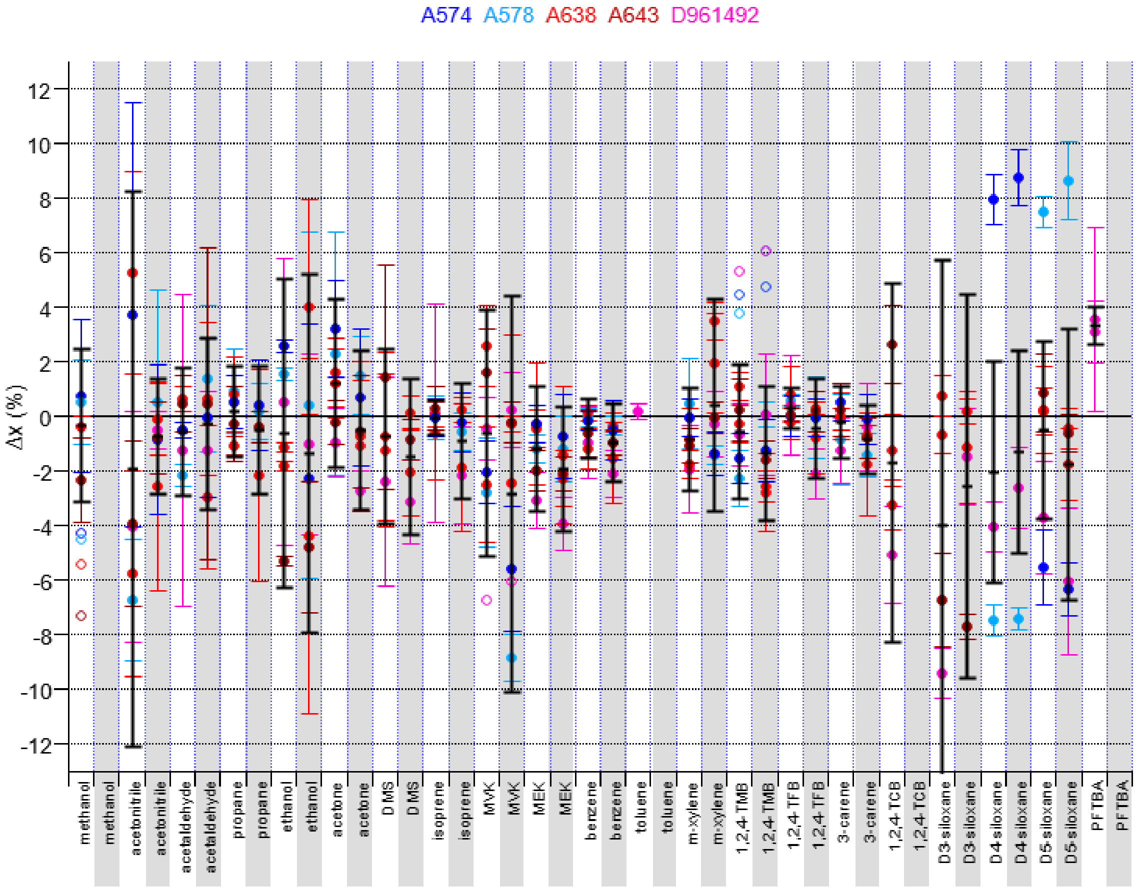
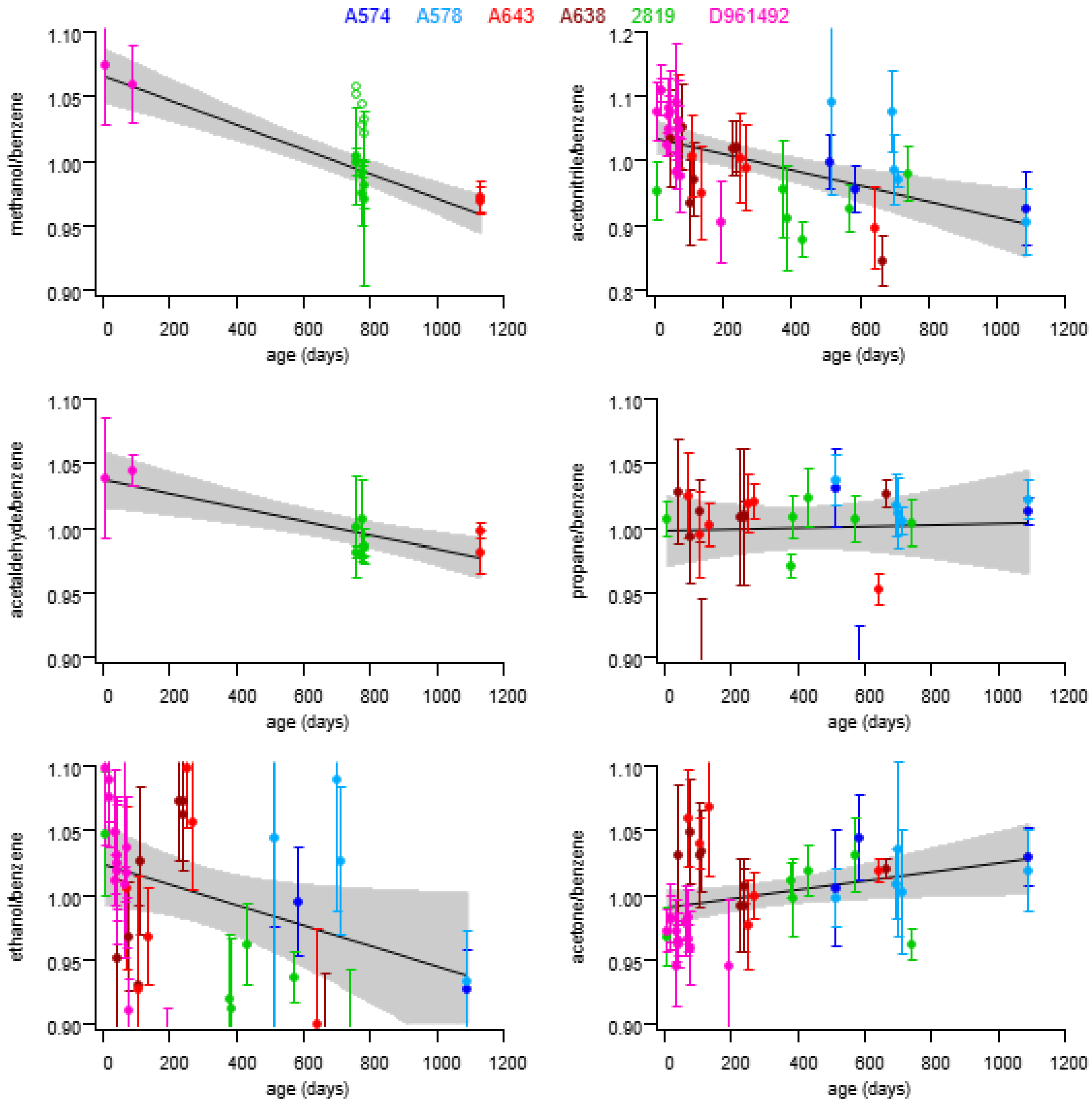
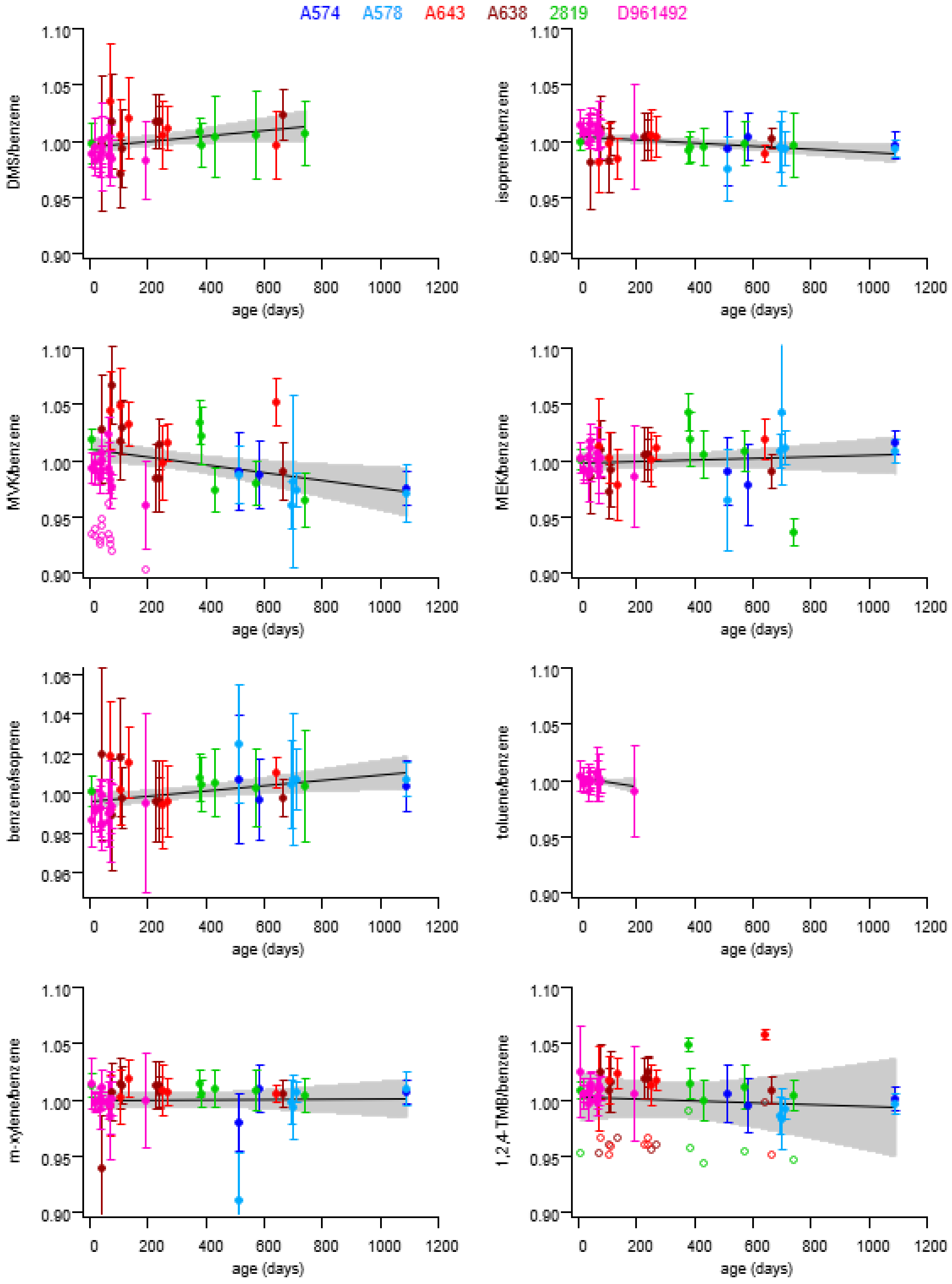
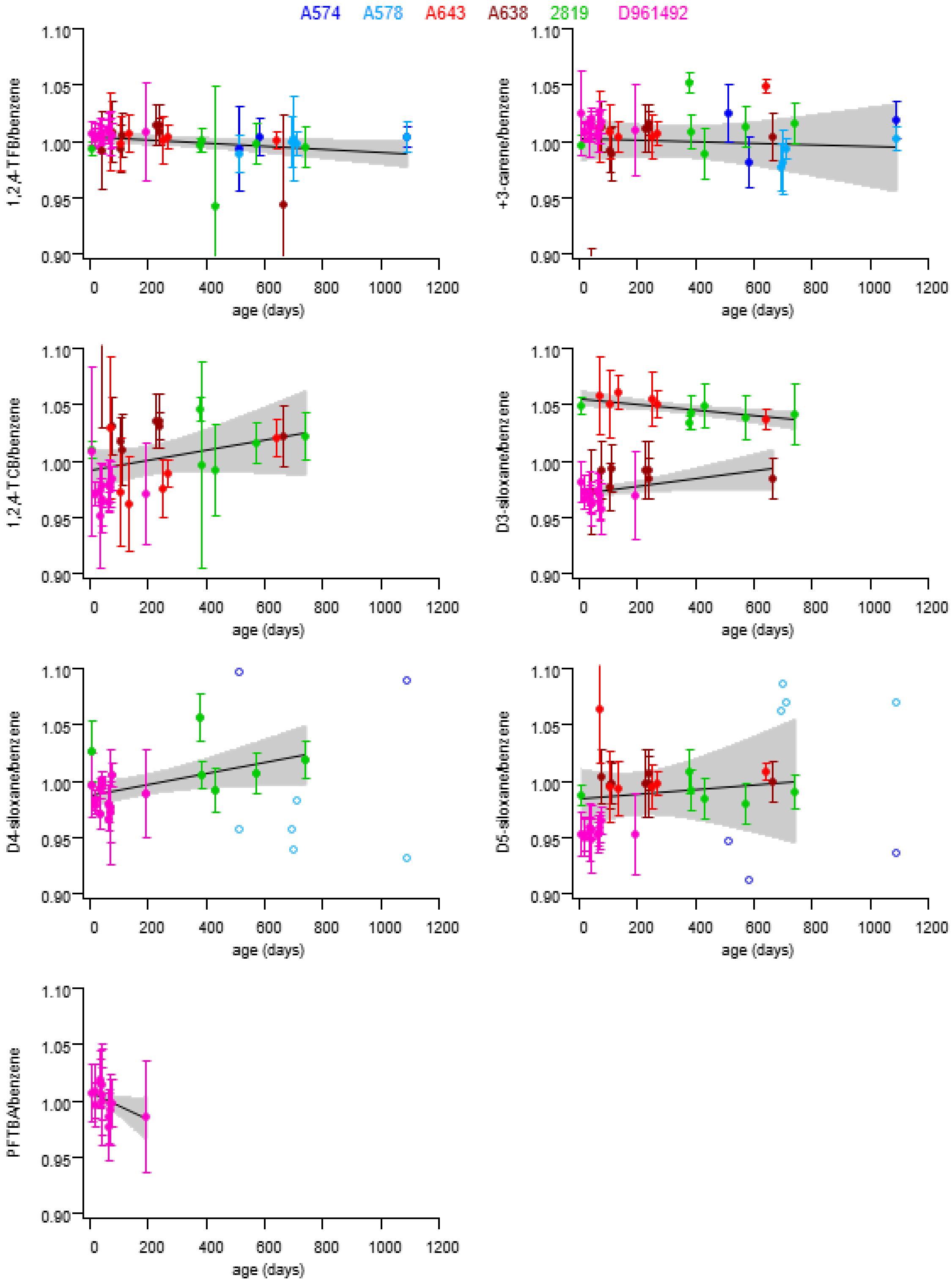


Figure S2. Stability plots of all components present in the PTR-MS transmission curve reference material. The open symbols show the original data before being corrected for biases in the parent mixtures (for methanol, MVK and 1,2,4-TMB) as discussed in the text. The best fit curves from least squares 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.



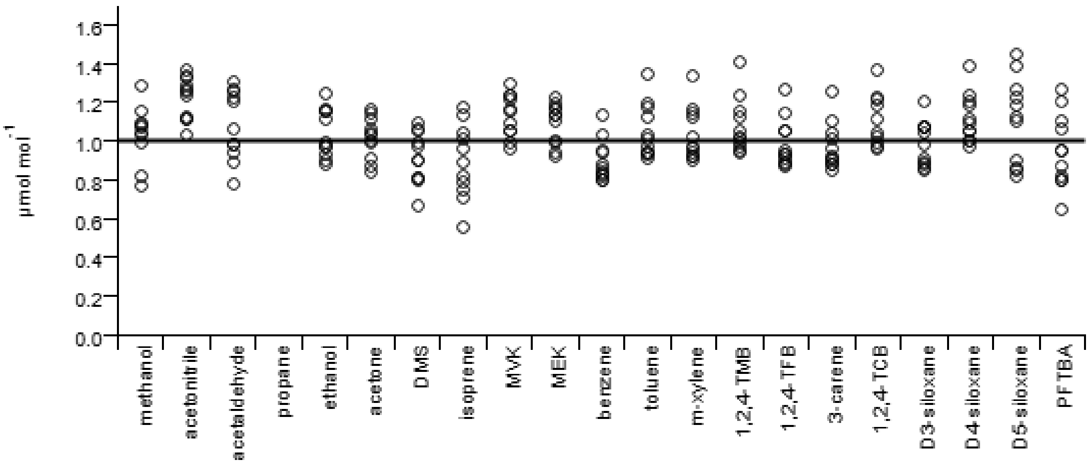

A574
A578
A643
A638
2819
D961492
DMS/benzene
isoprene/benzene
MVK/benzene
MEK/benzene
benzene/isoprene
toluene/benzene
m-xylene/benzene
1,2,4-TMB/benzene
1.10
1.05
1.00
0.95
0.90
1.06
1.04
1.02
1.00
0.98
0.96
0
200
400
600
800
1000
1200
age (days)


A574
A578
A643
A638
2819
D961492
1,2,4-TFB/benzene
+3-carene/benzene
1,2,4-TCB/benzene
D3-siloxane/benzene
D4-siloxane/benzene
D5-siloxane/benzene
PFTBA/benzene
1.10
1.05
1.00
0.95
0.90
0
200
400
600
800
1000
1200
age (days)

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. To prepare the PTRMS 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 NPL 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 NPL PRM D961492, 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.

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



Additional References

Kierkegaard, A. and McLachlan, M. S.: Determination of linear and cyclic volatile methylsiloxanes in air at a regional background site in Sweden, Atmospheric Environment, 80, 322-329, https://doi.org/10.1016/j.atmosenv.2013.08.001, 2013.