Supplement of "The importance of cylinder passivation chemistry for preparation and long-term stability of multicomponent monoterpene primary reference materials"

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Table S1: Overview of purity analysis of chemicals purchased.

	Chemical purity analysed							
Compounds found	**+-α-pinene**	**--α-pinene**	**limonene**	**3-carene**	**1,8-cineole**	***n*-octane**	**+-β-pinene**	**--β-pinene**
±α-pinene	97.95%	98.80%	<0.01%	0.02%	0.03%	<0.01%	1.61%	1.08%
±β-pinene	0.06%	0.11%	<0.01%	0.02%	0.03%	<0.01%	93.82%	95.33%
limonene	0.17%	0.24%	99.04%	0.24%	0.34%	<0.01%	1.48%	0.87%
3-carene	<0.01%	<0.01%	<0.01%	98.23%	<0.01%	<0.01%	<0.01%	<0.01%
1,8-cineole	<0.01%	<0.01%	<0.01%	<0.01%	99.49%	<0.01%	<0.01%	<0.01%
3-carene	<0.01%	<0.01%	<0.01%	<0.01%	0.01%	<0.01%	<0.01%	<0.01%
cis-ocimene	0.01%	0.03%	0.02%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
myrcene	<0.01%	<0.01%	0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
***n*-octane**	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	99.90%	<0.01%	<0.01%
unknown terpene	0.60%	0.42%	0.30%	0.96%	0.04%	<0.01%	3.07%	2.71%
other hydrocarbons	1.21%	0.27%	0.63%	0.53%	0.06%	0.10%	0.02%	0.03%

Table S2: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated Experis cylinder (normalised for gravimetric differences).

Experis		**Difference to the reference standard mixture BB**				
Decant	**Pressure**	***n*-octane**	**+/- α-pinene**	**3-carene**	**R-limonene**	**1,8-cineole**
cylinder '1'	120 bar	0.0%	0.0%	0.6%	0.7%	0.5%
cylinder '1'	70 bar	0.7%	0.4%	0.3%	0.9%	0.9%
cylinder '2'	50 bar	0.7%	0.3%	0.2%	0.9%	0.8%
cylinder '2'	30 bar	0.6%	0.0%	0.3%	0.9%	1.7%
cylinder '3'	20 bar	0.3%	-0.8%	-0.6%	-0.4%	-1.1%

Table S3: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated Experis cylinder repeated (normalised for gravimetric differences).

Quantum repeat		**Difference to the reference standard mixture BB**				
Decant	**Pressure**	***n*-octane**	**+/- α-pinene**	**3-carene**	**R-limonene**	**1,8-cineole**
cylinder '1'	120 bar	0.5%	0.7%	0.9%	1.4%	1.5%
cylinder '1'	70 bar	0.5%	0.8%	0.8%	0.6%	0.8%
cylinder '2'	50 bar	0.3%	0.6%	0.5%	0.9%	1.0%
cylinder '2'	30 bar	0.1%	-0.1%	0.0%	-0.2%	-0.1%
cylinder '3'	20 bar	0.6%	0.4%	0.3%	0.5%	-0.2%

Table S4: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated BOC SPECTRA-SEAL cylinder (normalised for gravimetric differences).

BOC SPECTRA-SEAL		**Difference to the reference standard mixture BB**				
Decant	**Pressure**	***n*-octane**	**+/- α-pinene**	**3-carene**	**R-limonene**	**1,8-cineole**
cylinder '1'	120 bar	0.3%	-61.8%	-2.0%	8.5%	-20.4%
cylinder '1'	70 bar					
cylinder '2'	50 bar					
cylinder '2'	30 bar					
cylinder '3'	20 bar					

Table S5: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated BOC SPECTRA-SEAL cylinder (normalised for gravimetric differences) repeated.

BOC SPECTRA-SEAL repeat		**Difference to the reference standard mixture BB**				
Decant	**Pressure**	***n*-octane**	**+/- α-pinene**	**3-carene**	**R-limonene**	**1,8-cineole**
cylinder '1'	120 bar	0.4%	-100.0%	-26.5%	-53.5%	-52.0%
cylinder '1'	70 bar					
cylinder '2'	50 bar					
cylinder '2'	30 bar					
cylinder '3'	20 bar					

Table S6: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated treated BOC SPECTRA-SEAL cylinder with further proprietary in-house treatment (normalised for gravimetric differences).

In-house treated BOC SPECTRA-SEAL		**Difference to the reference standard mixture BB**				
Decant	**Pressure**	***n*-octane**	**+/- α-pinene**	**3-carene**	**R-limonene**	**1,8-cineole**
cylinder '1'	120 bar	0.7%	-100.0%	-27.8%	-48.8%	-54.9%
cylinder '1'	70 bar					
cylinder '2'	50 bar					
cylinder '2'	30 bar					
cylinder '3'	20 bar					

Table S7: The percentage difference between the reference standard mixture BB and the decanted monoterpene mixture in a 10 L internally passivated treated BOC SPECTRA-SEAL cylinder with further proprietary in-house treatment (normalised for gravimetric differences) repeated.

In-house treated BOC SPECTRA-SEAL repeat	**Difference to the reference standard mixture BB**

Decant	Pressure	*n*-octane	+/- α-pinene	+3-carene	R-limonene	1,8-cineole
cylinder '1'	120 bar	0.1%	-100.0%	-94.9%	-94.5%	-97.4%
cylinder '1'	70 bar					
cylinder '2'	50 bar					
cylinder '2'	30 bar					
cylinder '3'	20 bar					

Table S8: Elution times, forward match (FM) and reverse match (RM) values obtained by mass spectrometry for Mixture BB

Mixture BB			
Compound	**Elution time**	**Forward match**	**Reverse match**
α-pinene	39.25	904	907
3-carene	41.25	909	952
limonene	41.65	894	896
1,8-cineole	41.80	864	900

Table S9: Elution times, forward match (FM) and reverse match (RM) values obtained by mass spectrometry for a terpene mixture in a BOC SPECTRA-SEAL passivated cylinder.

Mixture in BOC SPECTRA-SEAL passivated cylinder			
Compound	**Elution time**	**Forward match**	**Reverse match**
camphene	39.80	946	962
α-terpinene	41.40	921	930
cymene	41.65	937	949
τ-terpinene	42.25	911	931
terpinolene	43.05	938	945

Table S10: The Kovats' Retention Indices on a non-polar column, using a custom temperature program for reference publications 1-8 (Adams 1998, Frizzo, Serafini et al. 2001, Novak, Zitterl-Eglseer et al. 2001, Araujo, Silveira et al. 2003, Dwivedi, Khan et al. 2004, Riu-Aumatell, Castellari et al. 2004, Tuberoso, Kowalczyk et al. 2005, de Marchese, de Heluani et al. 2007).

		Kovats' Retention Indicies value										
Elution time	Compound	1	2	3	4	5	6	7	8	Average	Max value	Min value
39.25	α-pinene	938	937	933		928	934	938	939	935	939	928
39.80	camphene	954		946		955		954	953	952	955	946
41.25	3-carene			1011			1011	1013	1011	1012	1013	1011
41.40	α-terpinene		1017			1024		1020	1018	1020	1024	1017
41.65	p-cymene	1025	1026			1015	1023		1023	1022	1026	1015
41.66	limonene	1029	1029	1020	1017	1028	1029	1034	1031	1027	1034	1017
41.80	1,8-cineole		1033	1020			1036	1031		1030	1036	1020
42.25	γ-terpinene		1058	1051	1057	1058	1059	1063	1062	1058	1063	1051
43.05	terpinolene		1084	1097	1074	1086	1088	1092	1088	1087	1097	1074

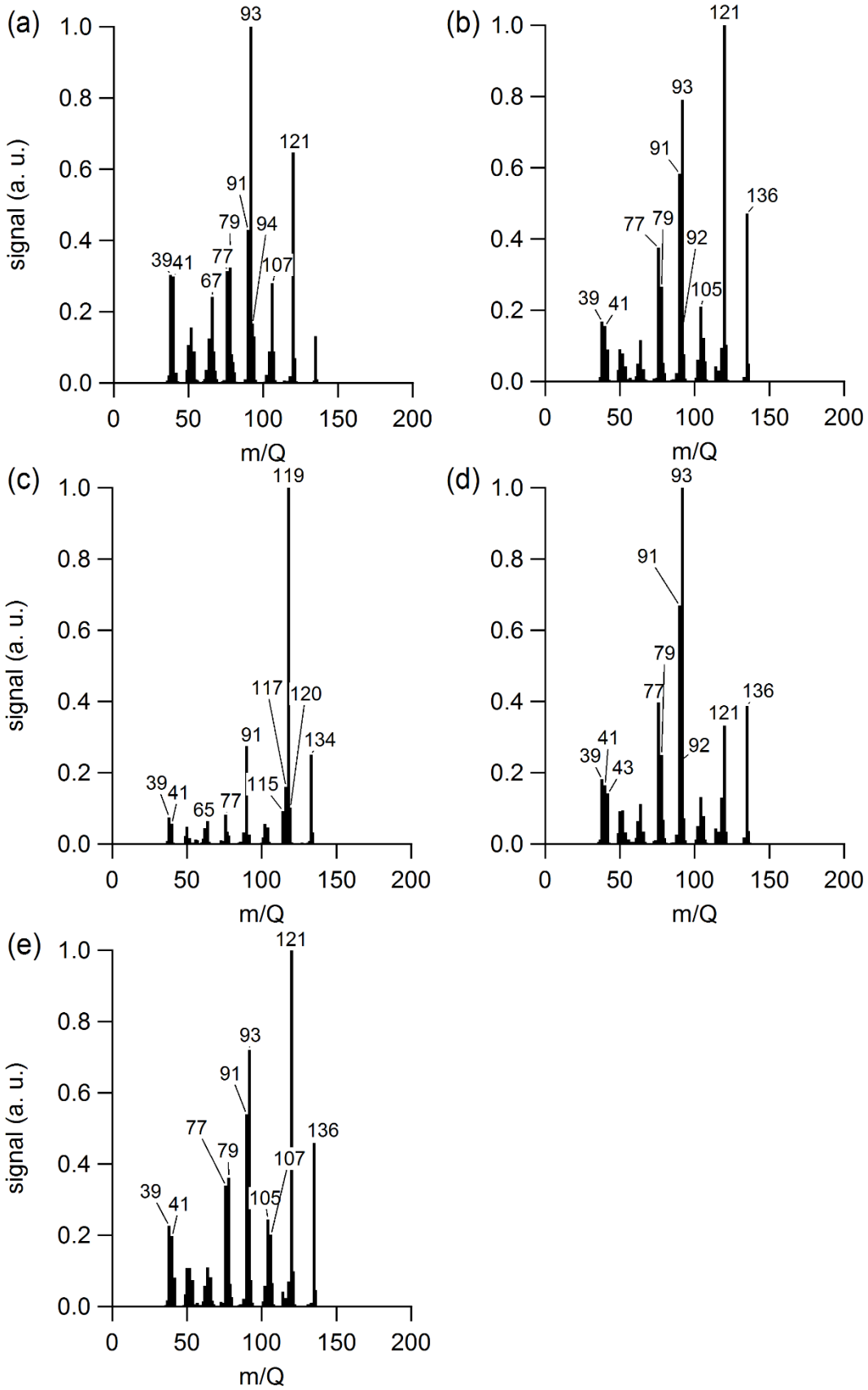

Figure S1: Mass spectrometry ion fragmentation spectrum for (a) camphene (b) *α*-terpinene (c) cymene (d) *τ*-terpinene (e) terpinolene, peaks identified and observed in a BOC SPECTRA-SEAL passivated cylinder.

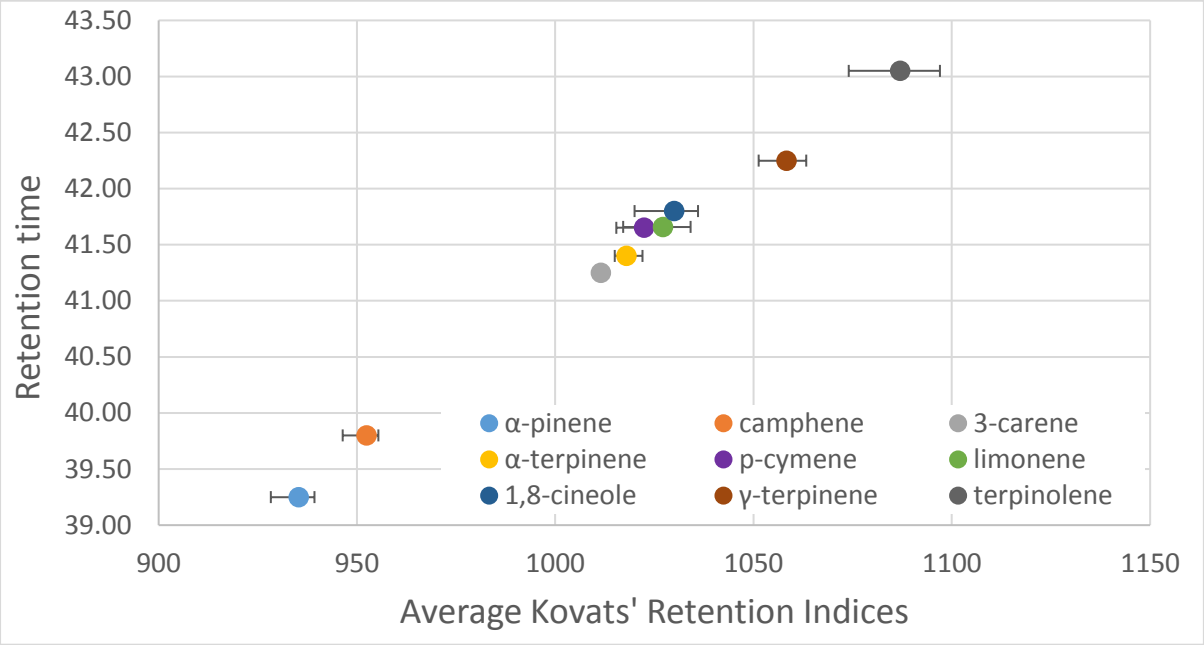

Figure S2: The average Kovats' Retention Indices on a non-polar column, using a custom temperature program for reference publications 1-8 (Adams 1998, Frizzo, Serafini et al. 2001, Novak, Zitterl-Eglseer et al. 2001, Araujo, Silveira et al. 2003, Dwivedi, Khan et al. 2004, Riu-Aumatell, Castellari et al. 2004, Tuberoso, Kowalczyk et al. 2005, de Marchese, de Heluani et al. 2007). Error bars cover the range from minimum to maximum for the Kovats' Retention Indice values.

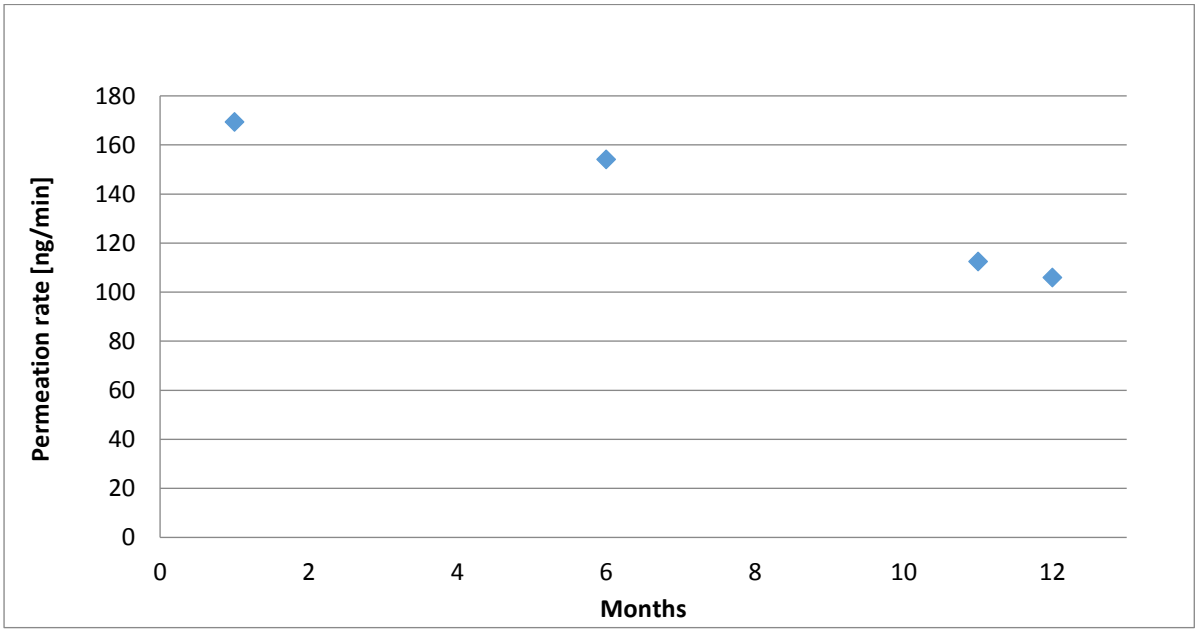

Figure S3: The permeation rate of limonene measured in the magnetic suspension balance over an 11 month period at 30°C with a nitrogen flow of 0.17 l/min.

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