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

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Description of uncertainty analysis procedure

Below is the uncertainty evaluation adopted when comparing the response of an unknown mixture against a validated calibration standard e.g. a PRM:

$$\bar{r} = \frac{2A_{u,avg}}{(A_{s,avg1}+A_{s,avg2})} \quad \text{(S1)}$$

Where $\bar{r}$ is the average ratio, $A_{u,avg}$ is the average peak area from n repeated measurements of the comparison mixture, $A_{s,avg1}$ is the average peak area from n repeated measurements of the calibration standard before running the comparison mixture and $A_{s,avg2}$ is the average peak area from n repeated measurements of the calibration standard after running the comparison mixture.

The amount fraction of the target component in the comparison mixture, x_u, is then calculated by:

$$x_u = x_s\bar{r} \quad \text{(S2)}$$

Where x_s is the amount fraction of the target component in the standard. The standard uncertainty of the measurand, $u(x_u)$, is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{{x_s}^2} + \frac{u(\bar{r})^2}{\bar{r}^2}} \quad \text{(S3)}$$

$u(x_s)$ is the uncertainty of the reference standard $u(\bar{r})$ is the uncertainty of the ratio, it includes e.g. repeatability, internal blanks, peak shape (error of integration), error in the sample volume. The uncertainty in $\bar{r}$ is calculated by:

$$\frac{u(\bar{r})^2}{\bar{r}^2} = \frac{u(A_{u,avg})^2}{{A_{u,avg}}^2} + \frac{u(A_{s,avg1})^2}{(A_{s,avg1}+A_{s,avg2})^2} + \frac{u(A_{s,avg2})^2}{(A_{s,avg1}+A_{s,avg2})^2} \quad \text{(S4)}$$

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 with respect 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).

Experis repeat		**Difference with respect 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 with respect 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	No further decants were performed for this cylinder type as the passivation was shown to be unsuitable for monoterpenes.				
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 with respect 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	No further decants were performed for this cylinder type as the passivation was shown to be unsuitable for monoterpenes.				
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 with respect 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	No further decants were performed for this cylinder type as the passivation was shown to be unsuitable for monoterpenes.				
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 with respect 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	No further decants were performed for this cylinder type as the passivation was shown to be unsuitable for monoterpenes.				
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
ɤ-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; Araujo et al., 2003; de Marchese et al., 2007; Dwivedi et al., 2004; Frizzo et al., 2001; Novak et al., 2001; Riu-Aumatell et al., 2004; Tuberoso et al., 2005).

		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

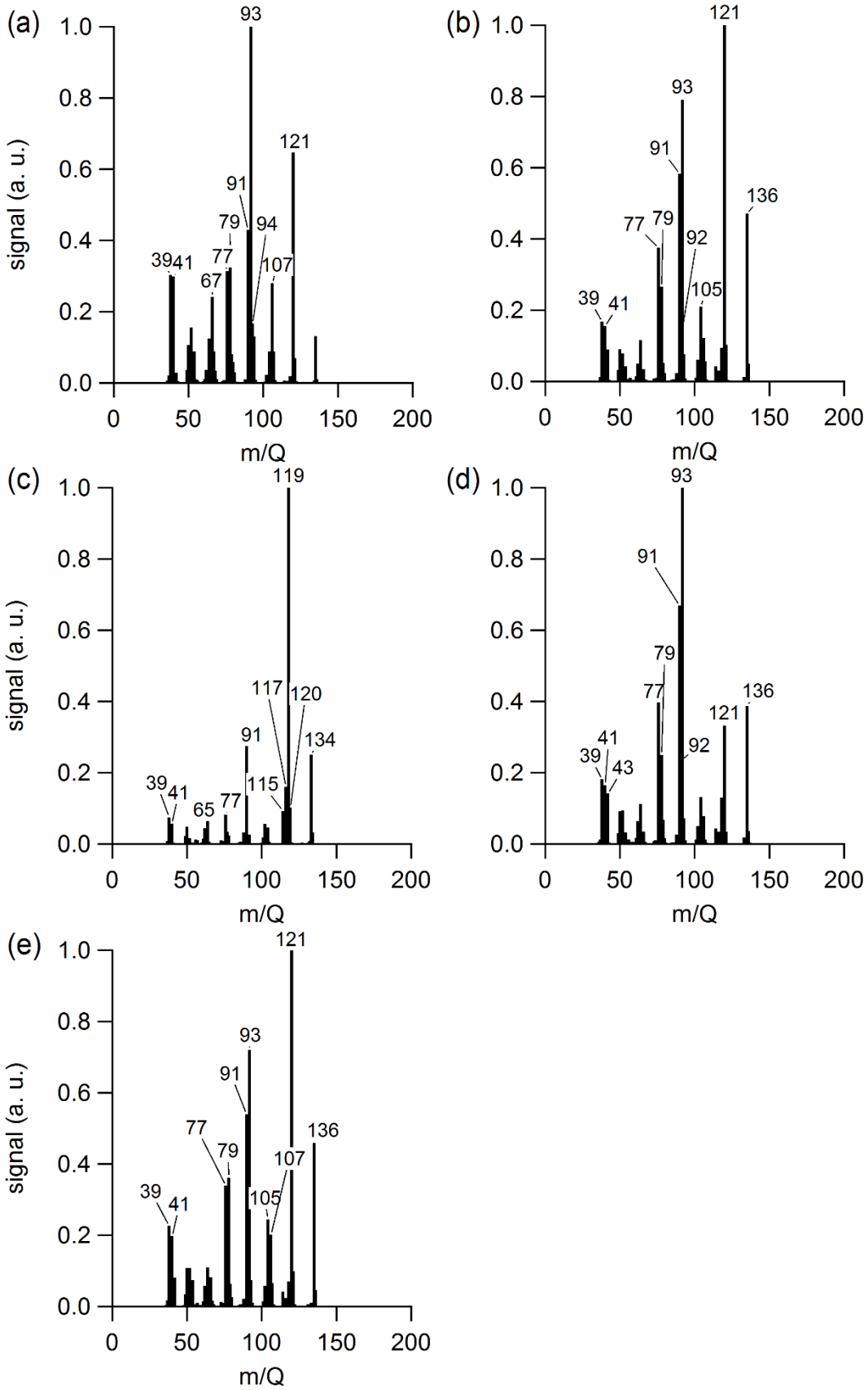

Figure S1: Mass spectrometry ion fragmentation spectra for (a) camphene (b) α-terpinene (c) cymene (d) τ-terpinene (e) terpinolene peaks identified and observed in a BOC SPECTRA-SEAL passivated cylinder.

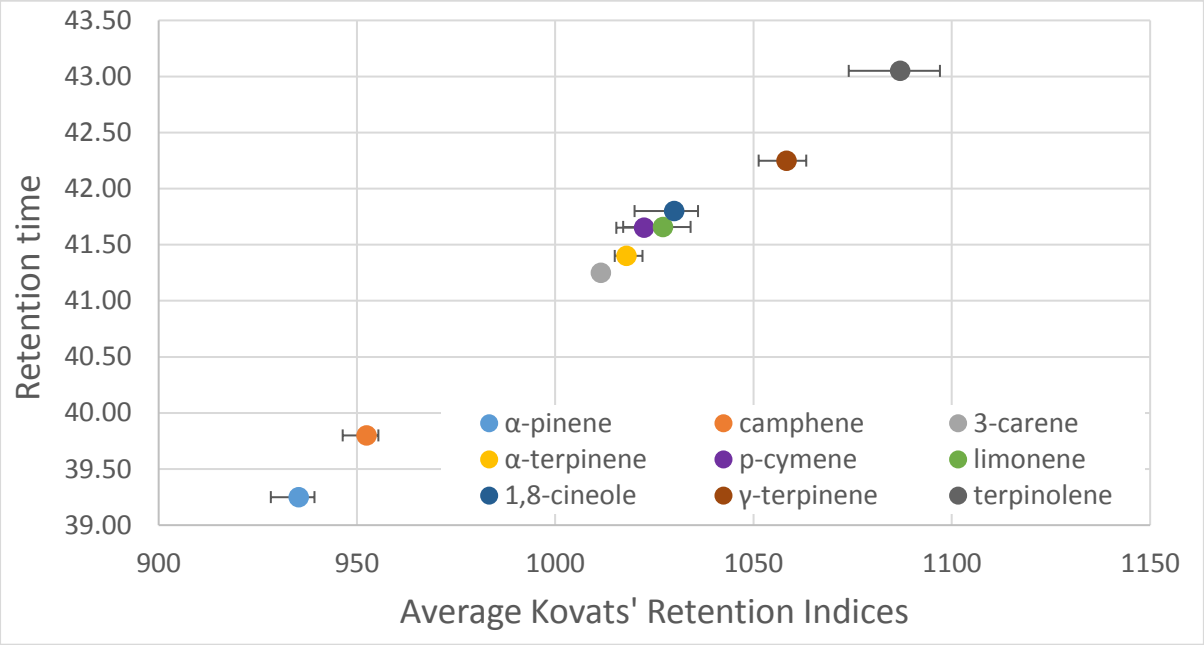

Figure S2: The average Kovats' Retention Indices on a non-polar column, using a custom temperature program for reference publications 1-8 (Adams, 1998; Araujo et al., 2003; de Marchese et al., 2007; Dwivedi et al., 2004; Frizzo et al., 2001; Novak et al., 2001; Riu-Aumatell et al., 2004; Tuberoso et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

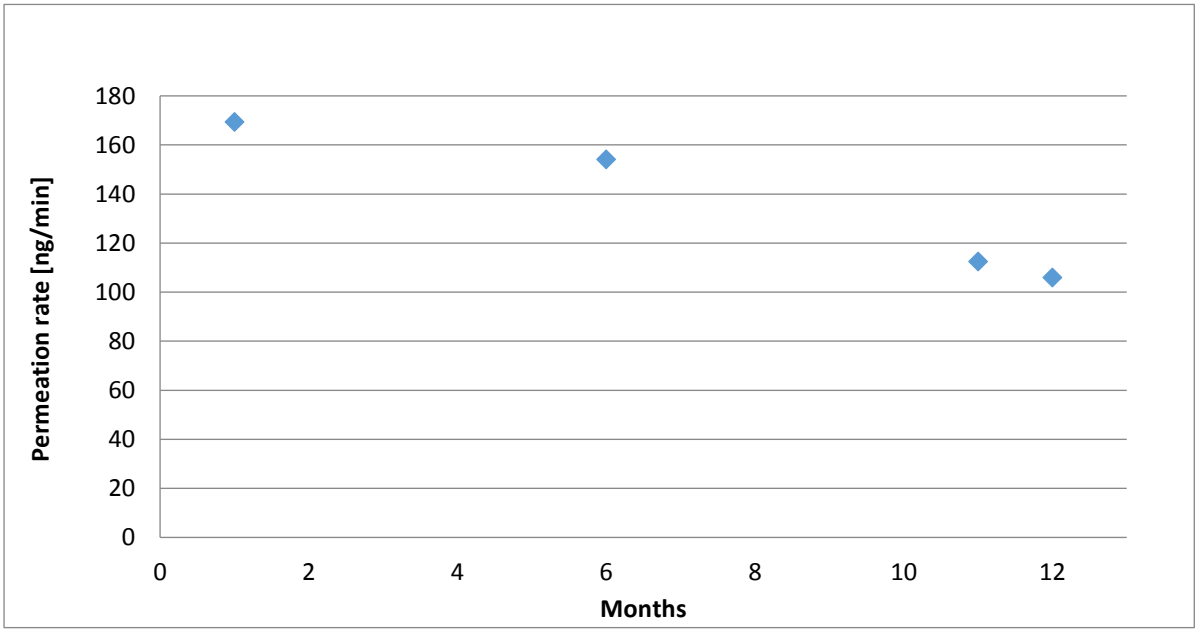

Figure S3: The permeation rate of limonene measured in the magnetic suspension balance over an 11 month period at 30°C with a nitrogen flow of 0.17 l/min.

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