1   **The importance of cylinder passivation chemistry for preparation and long-term**
2   **stability of multicomponent monoterpene primary reference materials**
3
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13
14   **Abstract**
15   Monoterpenes play an important role in atmospheric chemistry due to their large anthropogenic
16   and biogenic emission sources and high chemical reactivity. As a consequence, measurements
17   are required to assess how changes in emissions of monoterpenes impact air quality. Accurate
18   and comparable measurements of monoterpenes in indoor and outdoor environments require
19   gaseous primary reference materials (PRMs) that are traceable to the international system of
20   units (SI). PRMs of monoterpenes are challenging to produce due to the high chemical
21   reactivity and low vapour pressures of monoterpenes and also their propensity to convert into
22   other compounds, including other terpenes.
23
24   In this paper, the long-term stability of gravimetrically prepared static monoterpene PRMs
25   produced in differently passivated cylinders, including sampling canisters, was assessed. We
26   demonstrate that static PRMs of multiple monoterpenes can be prepared and used as a suitable
27   long-term standard. For the first time the effect of cylinder pressure and decanting from one
28   cylinder to another on the chemical composition and amount fraction of monoterpenes was also
29   studied. Gravimetrically prepared PRMs of limonene in high pressure cylinders were compared
30   to a novel portable dynamic reference gas generator based on dilution of pure limonene vapour
31   emitted from a permeation tube.
32
33   **Keywords**
36
37
38   **1. Introduction**
39   Terpenes are a large and diverse family of naturally occurring organic compounds that are a
40   major biosynthetic building block (de Meijere, Hadjiarapoglou et al. 1998, Nicklaus, Minnaard
41   et al. 2013). Vegetation including forests and agricultural crops (Ormeño, Gentner et al. 2010,
42   Curtis, Helmig et al. 2014, Gentner, Ormeno et al. 2014) emit substantial quantities of isoprene
43   (a hemiterpene (C_5H_8)), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) (Tao and Jain
44   2005, Barkley, Palmer et al. 2008, Smolander, He et al. 2014, Squire, Archibald et al. 2014,
45   Jokinen, Berndt et al. 2015).
46
47   Terpenes play an important role in atmospheric chemistry due to their high reactivity
48   influencing the HO_x and NO_x budgets (Presto, Hartz et al. 2005, Ng, Chhabra et al. 2007,
49   Forester and Wells 2011, Carslaw, Fletcher et al. 2017). The photochemical reactions of

50 terpenes can lead to the production of tropospheric ozone, which is highly toxic to humans
51 (Wolkoff, Clausen et al. 2000), and the formation of secondary organic aerosol with
52 implications for climate (Lee, Goldstein et al. 2006, Ng, Chhabra et al. 2007, Vibenholt,
53 Norgaard et al. 2009) that influence climate (Coleman, Lunden et al. 2008).

55 Terpenes are also known to be emitted from building materials (Allen, Brewer et al. 2016) and
56 household products, in which they are primarily used as fragrances and flavourings (Wolkoff,
57 Schneider et al. 1998, Lamorena and Lee 2008, Steinemann, MacGregor et al. 2011, Wang,
58 Barratt et al. 2017), impacting indoor air quality (Singer, Destaillats et al. 2006, Nazaroff and
59 Goldstein 2015). In particular, the exposure of the public to terpenes in indoor air quality is
60 poorly understood due to a lack of available data, despite the toxicity of their photochemical
61 products (Jones 1999, Wolkoff and Nielsen 2001, Wang, Ang et al. 2007, Wang, Barratt et al.
62 2017).

64 A variety of techniques have been used for the sampling and analysis of complex mixtures of
65 terpenes (Batterman, Zhang et al. 1998, Koch, Winterhalter et al. 2000, Birmili, Berresheim et
66 al. 2003, Pollmann, Ortega et al. 2005, Qiu, Smuts et al. 2017). However, the accurate
67 measurement of terpene amount fractions in indoor and outdoor air is highly dependent upon
68 the availability of appropriate SI traceable gaseous PRMs (Rhoderick 2010).

70 The World Meteorology Organisation (WMO) Global Atmosphere Watch (GAW) programme
71 is a framework to provide reliable scientific data and information on the long-term trends in
72 the chemical composition of the atmosphere. In WMO-GAW Report No. 171 Global Long-
73 Term Measurements of Volatile Organic Compounds (VOCs) new data quality objectives were
74 created for priority VOC compounds including monoterpenes. These data quality objectives
75 stipulated 20 % accuracy and 15 % precision for monoterpene measurements reported by GAW
76 stations. Further recommendations by GAW's scientific advisory group for reactive gases have
77 been made to lower these data quality objectives to 5 % accuracy (Hoerger, Claude et al. 2015).
78 In order to meet the 5% uncertainty target and prevent the reference material dominating the
79 uncertainty requires stable PRMs of monoterpenes with uncertainties of better than 1 %. There
80 is also a requirement for performing reliable sampling or dynamic calibration methods for the
81 in-situ calibration of instruments during field campaigns or at long-term atmospheric
82 monitoring stations and for independent verification of the gaseous PRMs.

84 PRMs containing monoterpenes are challenging because monoterpenes are highly reactive
85 compounds and can isomerise, tautomerise or react to form a wide range of other compounds
86 including other terpenes (Findik and Gunduz 1997, Allahverdiev, Gunduz et al. 1998, Foletto,
87 Valentini et al. 2002). This has led to observations that the amount fraction of some
88 monoterpenes increase overtime, including the observation of compounds that were not present
89 when the mixture was first prepared, while the amount fraction of others decline (Rhoderick
90 and Lin 2013). Moreover, cylinder passivation has a big impact on the stability of monoterpene
91 gas mixtures. Rhoderick and Lin (2013) demonstrated that specific passivation types, such as
92 'Experis' (Quantum) manufactured by Air Products, looked the most promising for
93 monoterpenes.

95 In this paper, multicomponent monoterpene static gaseous PRMs containing α-pinene, 3-
96 carene, R-limonene and 1,8-cineole, as well as a mixture containing β-pinene were prepared
97 gravimetrically at high pressure in cylinders with different surface passivations (the coating
98 applied to the internal surface of a cylinder to reduce adsorptive losses). The effects of
99 adsorption to the cylinder walls and the cylinder pressure were assessed through a series of

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100   decanting experiments for these different cylinder passivations. The monoterpene PRM in the
101   most suitable cylinder passivation treatment was analysed repeatedly over a two year period to
102   assess the long-term stability building on the previous shorter-term stability studies of
103   Rhoderick et al. (Rhoderick 2010, Rhoderick and Lin 2013). The PRM containing limonene
104   was compared to a new dynamic system based on permeation known as Reactive Gas Standard
105   2 (ReGaS2) developed by the Federal Institute of Metrology (METAS), (Pascale, Guillevic et
106   al. 2017), that is based on permeation to evaluate any systematic biases between the two
107   different approaches. A portion of a monoterpene PRM was decanted into a SilcoNert 2000®
108   (Silcotek) treated sampling canisters to study the stability and their suitability for short-term
109   storage after field sampling.
110

111   **2. Experimental**
112
113   **2.1. Gravimetric preparation of PRMs**

114   PRMs containing the four monoterpenes, α-pinene (both the minus and plus optical isomers),
115   3-carene, R-limonene and 1,8-cineole and n-octane, that was used as an internal reference
116   standard, were prepared independently, in a balance of high purity dry nitrogen (BIP+, Air
117   Products) in accordance with ISO 6142 (ISO 2015). Each monoterpene compound was
118   prepared gravimetrically as a binary mixture (mixtures A – E) at an amount fraction of
119   nominally $5 - 10$ µmol mol^{-1} by liquid injection of each monoterpene, via a transfer vessel, into
120   individual 10 L evacuated cylinders ($<4.0 \times 10^{-7}$ mbar). A balance of high purity dry nitrogen
121   (BIP+, Air Products) was added by direct filling through an additional purifier (Microtorr,
122   SP600F, SAES Getters) to remove trace impurities such as hydrocarbons and water to below
123   < 1 nmol mol^{-1}. Two β-pinene mixtures were also produced in a similar way (mixtures F and
124   G). The compound and the amount fraction of the parent PRMs were: limonene 4.968 ± 0.044
125   µmol mol^{-1} (mixture A), $\pm$-α-pinene 9.942 ± 0.029 µmol mol^{-1} (mixture B), 1,8-cineole 5.007
126   ± 0.028 µmol mol^{-1} (mixture C), 3-carene 4.954 ± 0.036 µmol mol^{-1} (mixture D), octane 9.995
127   ± 0.038 µmol mol^{-1} (mixture E), $\pm$-β-pinene 9.829 ± 0.090 µmol mol^{-1} (mixture F) and 10.492
128   ± 0.175 µmol mol^{-1} (mixture G) with all uncertainties in the gravimetric preparation expanded
129   ($k = 2$).
130

131   All 'pure' liquid compounds were purchased from commercial suppliers (Fluka and Sigma
132   Aldrich) and were purity analysed following the guidelines stipulated in ISO 19229:2015 by
133   gas chromatography with a flame ionisation detector prior to use. Impurities were identified
134   and quantified by percentage area. The purity of all the monoterpenes was between 93.5 and
135   99.5 % (Table S1, supporting information).
136

137   A PRM of nominally 100 nmol mol^{-1} (mixture AA, see Table 1) containing the four
138   monoterpenes and n-octane was prepared by direct transfer of a portion (10 – 25 g) of each
139   gravimetrically prepared parent mixture (A – E) and topped up with a balance of filtered high
140   purity dry nitrogen (BIP+, Air Products) that was again added by direct filling through the
141   Microtorr, SP600F, SAES Getters. A final dilution stage was carried out to prepare a PRM at
142   nominally 2 nmol mol^{-1} (mixture BB, Table 1). A second nominal 2 nmol mol^{-1} mixture
143   (mixture CC) was prepared in the same way to mixture BB for the long-term stability
144   comparison. All of the PRMs were prepared in 10 litre Experis passivated cylinders from Air
145   Products, Belgium.
146

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147 **Table 1.** Gravimetric compositions of monoterpene PRMs made by dilution of the parent
148 mixtures (mixtures A-E). Amount fractions are all in nmol mol^{-1}, uncertainties in the
149 gravimetric preparation are expanded ($k = 2$) and do not include uncertainties arising from the
150 verification process.
151

Compound	Cylinder assignment		
	AA	BB	CC
limonene	93.1 ± 0.8	2.009 ± 0.018	2.042 ± 0.019
α-pinene	96.1 ± 0.8	2.075 ± 0.019	2.109 ± 0.019
1,8-cineole	94.2 ± 0.5	2.033 ± 0.012	2.066 ± 0.012
3-carene	91.1 ± 0.7	1.967 ± 0.015	1.999 ± 0.015
n-octane	89.0 ± 0.46	1.920 ± 0.010	1.952 ± 0.010

152

153 **2.2. Analytical set-up**

154 All of the measurements were performed using a gas chromatograph (Varian CP-3800) with
155 an FID. The system uses a sample pre-concentration trap containing glass beads cooled by
156 liquid nitrogen and held at -100 °C during sampling to collect and focus the analytes prior to
157 injection and separation on a GC column (Varian CP-Sil 13; 75 m x 0.53 mm, phase thickness
158 = 2.0 µm). All mixtures were connected to the GC using SilcoNert 2000® passivated 1/16″
159 stainless steel tubing. The lines were thoroughly purged and flow rates were allowed to stabilise
160 for at least 10 minutes before commencing analysis.

161

162 The PRMs were connected using a minimal dead volume connector and the flow rate was set
163 to 50 ml min^{-1} using a custom flow restrictor. For the dynamic ReGaS2 system a flow of 50 ml
164 min^{-1} could not be achieved and the volume flowed across the trap was recorded by a mass
165 flow meter, calibrated with BIP+ nitrogen, and subsequently corrected to match the sample
166 volume of the high pressure gas standards. Mixtures were compared by running a series of up
167 to six replicate analyses in blocks with the unknown mixture being analysed between two
168 blocks of the PRM mixture to correct for any instrumental drift during analysis. The observed
169 relative standard deviations in the peak areas of all compounds were between 0.3 – 1.5 %.

170 **2.3. Decanting experiments**

171

172 A schematic illustrating the decanting procedure is shown in Figure 1. The decanting
173 experiments were performed in 10 L aluminium Luxfer cylinders that had been treated with
174 different types of cylinder passivation, these included Experis, sometimes referred to as as
175 Quantum, (Air Products), SPECTRA-SEAL (BOC) and 'in-house' treated BOC SPECTRA-
176 SEAL. It has been observed that this propriety 'in-house' passivation provides improved
177 stability for a wide range of compounds at low amount fractions. All cylinders had a 10 L
178 internal volume. Initially, a new PRM, identified as cylinder 1 in Figure 1 was prepared
179 gravimetrically (as described in Section 2.2) at an amount fraction of nominally 2 nmol mol^{-1}
180 and a pressure of 120 bar (cylinder '1') from a dilution of a 100 nmol mol^{-1} PRM (mixture
181 AA).

182

183 Once a new PRM (cylinder '1') had been prepared at 120 bar (day 1), the mixture was analysed
184 by GC-FID and compared against the reference PRM, mixture BB (day 2). The following day
185 (day 3) approximately 50 bar of cylinder '1' was decanted by direct fill (a short well-purged
186 transfer line) to cylinder '2' leaving 70 bar in cylinder '1'. Both cylinder '1' and '2' were then

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187   analysed by GC-FID and compared against reference PRM, mixture BB. Finally (day 4),
188   approximately 20 bar of cylinder '2' was decanted to cylinder '3' leaving 30 bar in cylinder '2'
189   and both cylinder '2' and '3' were then analysed by GC-FID and compared against reference
190   PRM, mixture BB (differences in the gravimetric values between the PRM and the reference
191   standard were normalised). All of the cylinders were evacuated and the decant procedure was
192   repeated for a second time.
193
194   All of the analyses was performed using GC-FID as described in Section 2.2. The certified
195   valve of the decanted cylinder was determined through a comparison with a nominal 2 nmol
196   mol^{-1} reference PRM (mixture BB). If there were no losses then the certified amount fraction
197   of the decanted cylinders should be the same as those of the PRM cylinder '1'. Decant losses
198   were determined for each compound by calculating the response factor (RF_{decant}) for the
199   decanted mixture:
200

201
$$RF_{decant} = \frac{Area_{avgdecant}}{Grav_{decant}}$$

202   where, $Area_{avdecant}$ is the average peak area for a set of GC runs of the decanted mixture and
203   $Grav_{decant}$ is the gravimetrically assigned value of the compound. The response factor of the in-
204   house reference PRM, mixture BB was also determined by:
205

206
$$RF_{BB} = \frac{Area_{avgBB}}{Grav_{BB}}$$

207   where, $Area_{avgBB}$ is the average peak area for a set of GC runs of in-house reference PRM,
208   mixture BB and $Grav_{BB}$ is the gravimetrically assigned value of the compound in mixture BB.
209
210   To determine the effects of decanting, results were normalised to take into account the
211   gravimetric difference between the in-house reference PRM (mixture BB) and the decanted gas
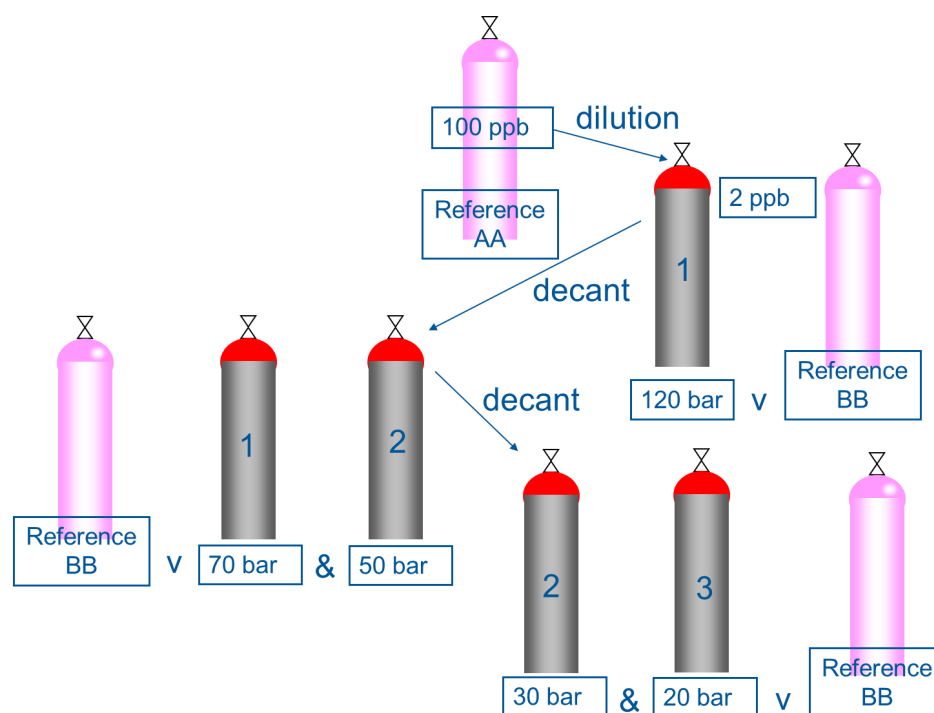212   mixture and the difference between the areas were determined by:
213

214
$$Normalised\ ratio = \frac{RF_{decant}}{RF_{BB}}$$

215   From the normalised ratio percentage differences between the in-house reference PRM
216   (mixture BB) and the decanted mixture were determined.
217
218

Figure 1: Schematic of the decanting procedure that was performed for the monoterpenes using 10 L Luxfer cylinders treated with different passivation types (Experis, SPECTRA-SEAL and an in-house treated SPECTRA-SEAL).

2.4. Short and long-term stability study of monoterpene PRMs

To determine the short and long-term stability of the four component monoterpene reference PRM, mixture BB was regularly run over a three month (75 day) period. GC peak area responses of each terpene were ratioed to *n*-octane, which is known to be stable in this passivation type for more than two years (Grenfell, Milton et al. 2010) and was present in the mixtures as an internal standard. The long-term stability of mixture BB (prepared on 2nd June 2015) was determined by preparing a fresh nominal 2 nmol mol^{-1} mixture (mixture CC), prepared two and a half years later (904 days) on the 22nd November 2017, and comparing the peak areas and their response factor.

β-Pinene, which is known to decompose in the presence of other terpenes over time (Foletto, Valentini et al. 2002), was prepared at 10 µmol/mol in 2015. An independently prepared *β*-pinene binary was prepared two and a half years later and the areas and response factors were compared to determine stability.

2.5. Canister experiment

A large number of samples are collected in the field during measurement campaigns. It is imperative that these samples can be collected and stored in a way that preserves the contents

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244   until they are analysed. One commonly used option is the use of sampling canisters or vessels
245   that have been evacuated prior to use. It has been well documented that the use of stainless
246   steel canisters for sampling terpenes can be problematic (Batterman, Zhang et al. 1998,
247   Rhoderick 2010). Here we decant a portion of our 2 nmol mol^{-1} in-house reference PRM
248   (mixture BB) into a SilcoNert 2000® treated 2 L sampling canister to determine their suitability
249   for short-term storage of monoterpenes. The content was analysed by GC-FID and compared
250   against the same nominal 2 nmol mol^{-1} reference PRM (mixture BB) to determine if any losses
251   were observed over a three month period (83 days).
252

253   **2.6. ReGaS2 dynamic system**

254   An alternative to PRM preparation in high pressure cylinders is dynamic preparation using
255   permeation. The ReGaS2 is a mobile generator that can produce traceable reference gas
256   mixtures, including terpenes (Pascale, Guillevic et al. 2017).
257

258   The method is based on permeation and subsequent dynamic dilution: a permeation tube
259   containing the pure terpene is stored in an oven used as permeation chamber. The pure
260   substance permeates at a constant rate into the matrix gas and was diluted to give the desired
261   amount fraction. The mass loss over time of the permeation tube is precisely calibrated using
262   a traceable magnetic suspension balance. All parts in contact with the reference gas were coated
263   with SilcoNert2000®.
264

265   The ReGaS2 mobile gas generator was fitted with a limonene permeation tube and set to
266   dynamically generate an output of nominally 4 nmol mol^{-1}. The amount fraction of the
267   limonene produced by the dynamic system was measured using the same analytical set-up as
268   was described in Section 2.2 and compared to our nominal 2 nmol mol^{-1} reference PRM
269   (mixture BB).

270
271
272   **2.7. Uncertainty calculations**

273   The evaluation of measurement uncertainty was in accordance to the 'Guide to the expression
274   of uncertainty in measurement' (Joint Committee for Guides in Metrology 2008).
275

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

278

279
$$\bar{r} = \frac{2A_{u,avg}}{(A_{s,avg1} + A_{s,avg2})}$$

280

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

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286

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

$$x_u = x_s \bar{r}$$

290

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

293

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

295

296 $u(x_s)$ is the uncertainty of the reference standard $u(\bar{r})$ is the uncertainty of the ratio, it includes
297 e.g. repeatability, internal blanks, peak shape (error of integration), error in the sample
298 volume. The uncertainty in $\bar{r}$ is calculated by:
299

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

301

302 **3. Results and discussion**
303
304
305 **3.1. Decanting experiments and selection of passivation treatment for long-term stability**
306   **measurements**

307 The adsorption of the monoterpenes to the internal surfaces of the cylinder and valve were
308 investigated through a series of decanting experiments as detailed in Section 2.3. The results
309 for the different passivation types at 120 bar are shown in Figure 2. There is a tabulated
310 summary of the results of the decanting experiments in Tables S2 – S7.
311

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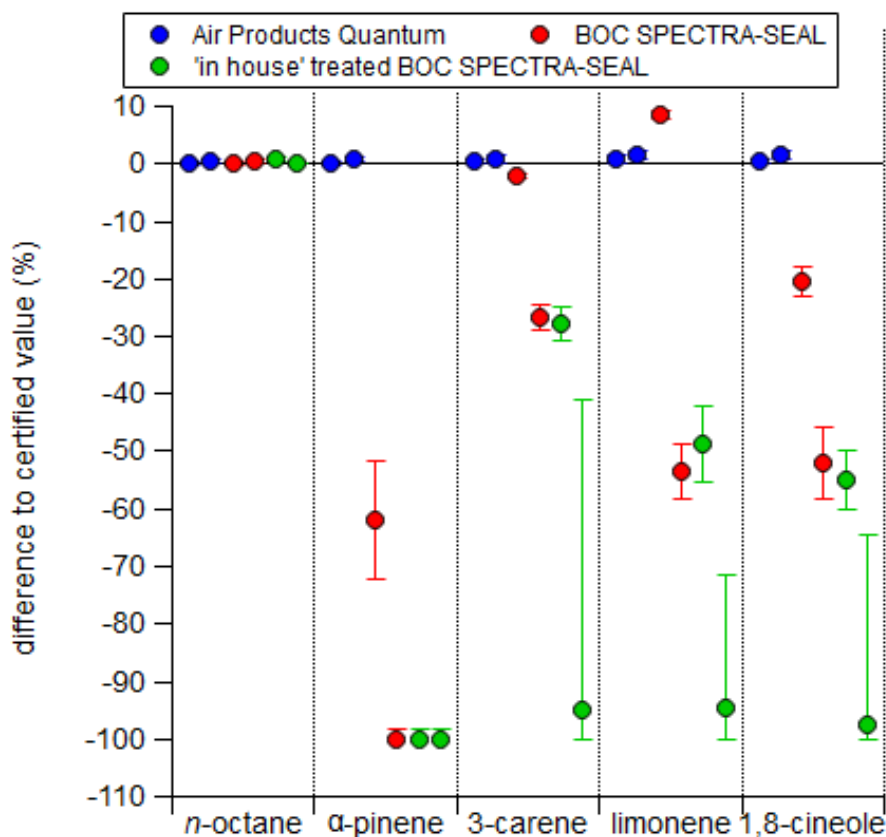
Figure 2: The relative difference between the certified amount fraction of the decanted
mixtures and the gravimetric amount fraction of the reference PRM (mixture BB). Each decant
was performed twice for each passivation type.

Decant losses of monoterpenes in the 10 L cylinders internally passivated with Air Products
Experis treatment were minimal (Tables S2 and S3). No obvious trends or patterns were
observed, therefore it can be confirmed, in agreement with Rhoderick et al. (Rhoderick and Lin
2013) that Experis cylinders are highly suitable for containing monoterpene PRMs. Figure 3
shows that the amount fraction does not appear to be strongly influenced by the pressure within
the cylinder, down to low pressure at 30 bar, as all agree within the measurement uncertainty
and there is no overall directional trend. Below 30 bar we observe that the ratio is less than 1
for all components. While the results are within the measurement uncertainty, wall factors
could have an influence on composition at low pressures (< 30 bar) (Brewer, Brown et al.
2018).

Figure 2 and Tables S3 and S4, show the initial decant, and repeat decant at 120 bar, in 10 L
cylinders passivated internally with BOC SPECTRA-SEAL treatment. Aside from the *n*-octane
a significant decrease in the amount fraction of all monoterpenes was observed (except for

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332 limonene in the first decant) relative to the reference PRM (BB). No further decants were
333 performed for this cylinder type as the passivation was shown to be unsuitable for
334 monoterpenes, with strong degradation observed by gas chromatograph (Figure 4) within less
335 than 24 hours after making the initial PRM. In an attempt to improve the stability of trace
336 monoterpenes in SPECTRA-SEAL passivated cylinders, further in-house treatment was
337 applied to a new set of cylinders. The results of this are shown in Figure 2 and Tables S5 and
338 S6, however no improvement was observed and all of the monoterpenes showed significant
339 losses when the PRM was analysed by gas chromatograph, less than 24 hours after preparation.
340
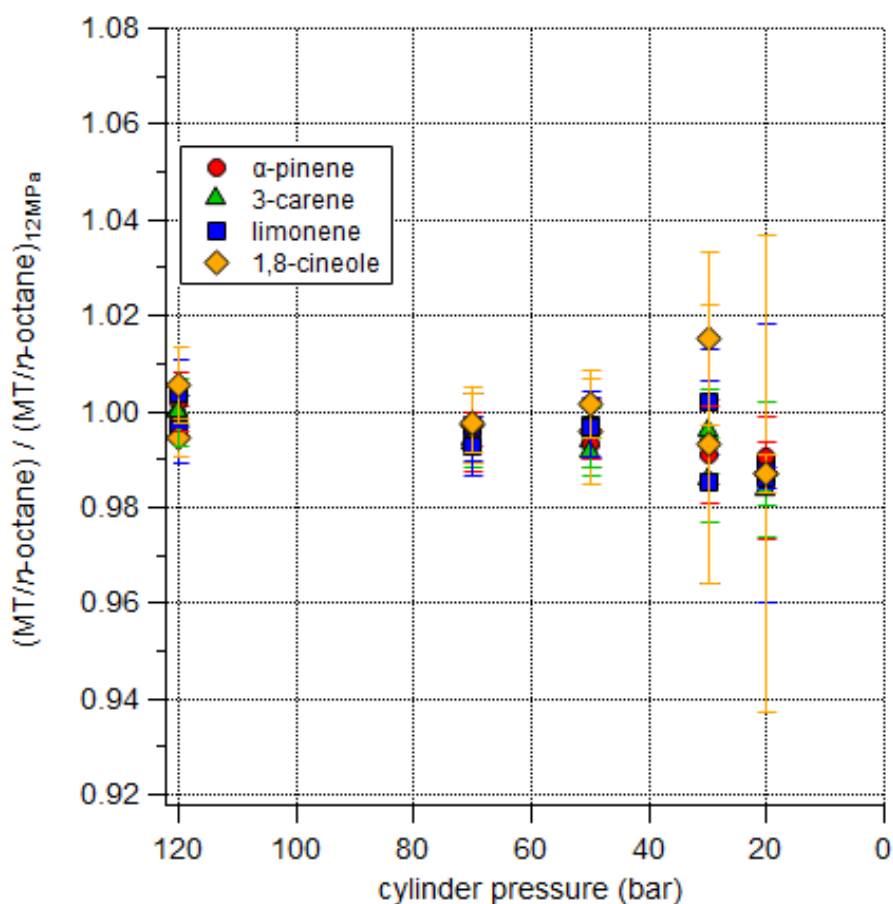
341
342
343 **Figure 3:** The relationship between cylinder pressure and monoterpene amount fraction after
344 normalisation to *n*-octane.
345
346 A sample of a monoterpene mixture in an internally treated SPECTRA-SEAL cylinder was
347 loaded onto a set of Chromasorb-106 and a set of Tenax sorbent tubes (both packed in-house)
348 and their contents analysed on a Thermal-Desorption Gas Chromatograph Mass Spectrometer
349 (TD-GC-MS) to identify the major degradation components. Similarly, a portion of the
350 reference PRM (mixture BB) was also loaded onto Chromasorb-106 and Tenax sorbent tubes
351 and analysed by TD-GC-MS. Five major peaks were consistently observed in the

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352 chromatograms of the desorbed tubes (Figure 4). The peaks observed in the sample from the
353 SPECTRA-SEAL cylinder were identified as the following monoterpenes; (a) α-terpinene, (b)
354 τ-terpinene, (c) terpinolene, (d) cymene and (e) camphene based on retention time and MS
355 library matching to the NIST database. Mass spectrometry was used for compound
356 identification and good forward match (FM) and reverse match (RM) values, predominantly
357 >900 and all above 860 were obtained (see Tables S8 and S9 for details of the elution times,
358 FM and RM values and Figure S1 for mass spectra).

360 Interestingly, α-terpinene is produced industrially by acid-catalysed rearrangement of α-pinene
361 and camphene by oxidation of α-pinene (Findik and Gunduz 1997), which had disappeared
362 from the SPECTRA-SEAL passivated cylinders after 24 hours (Figure 4). A sample of the
363 reference PRM (mixture BB) was also loaded onto Chromasorb-106 and Tenax sorbent tubes.
364 No other terpenes or peaks were observed except for the expected α-pinene, 3-carene, R-
365 limonene and 1,8-cineole and n-octane. Kovats' Retention Indices were used to confirm the
366 assignment of terpene compounds (Table S10 and Figure S2).
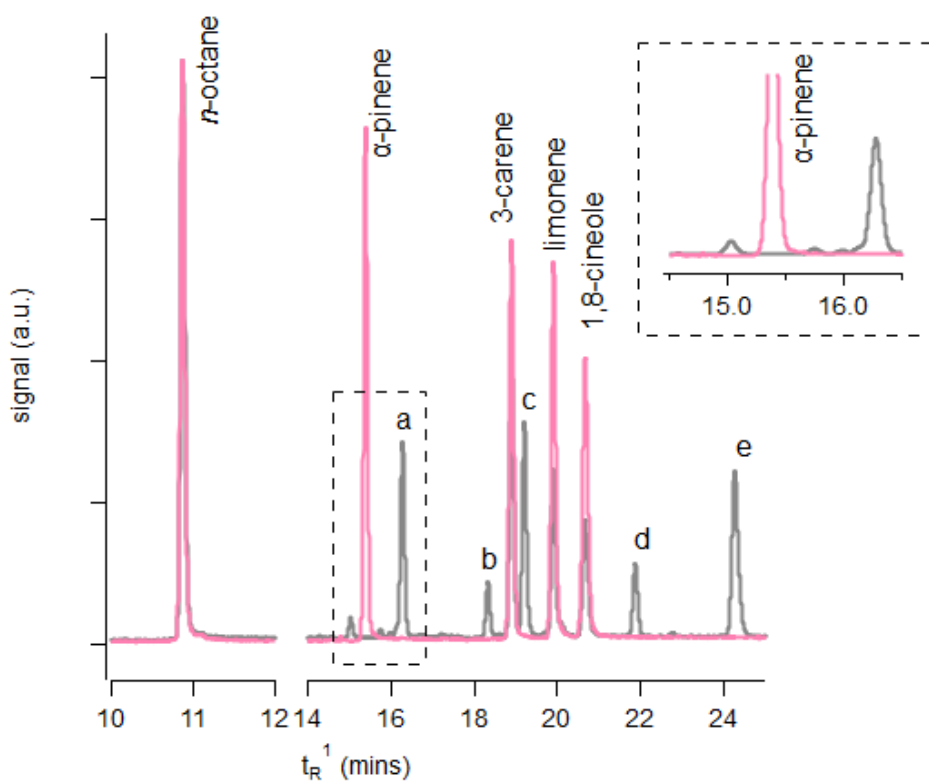
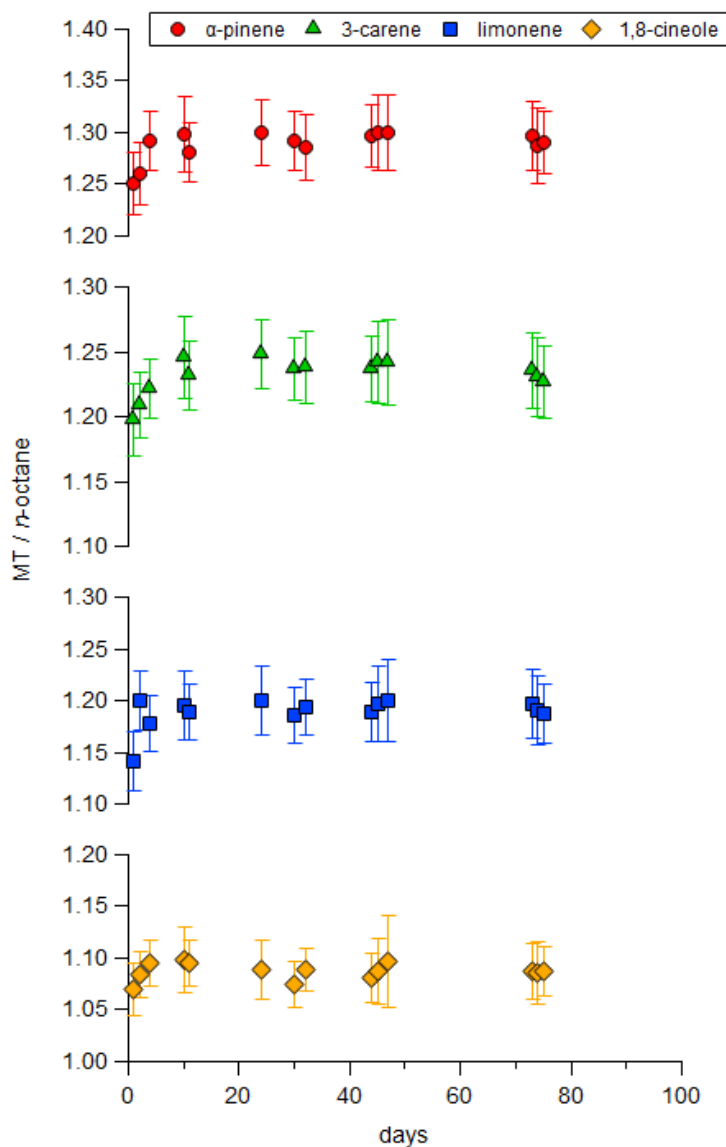**Figure 4**: The nominally 2 nmol mol^{-1} reference PRM, mixture BB (shown in pink) in an Air
Products Experis cylinder was made from the same parent PRM as the PRM made in the
internally passivated BOC SPECTRA-SEAL cylinder (shown in grey). The SPECTRA-SEAL
cylinder was analysed less than 24 hours after preparation and shows significant degradation
of the terpene compounds. The zoomed in portion of the chromatogram focuses on the α-pinene
peak (inset), showing that all of this compound has been lost. The additional peaks observed in

376 the analysis of the SPECTRA-SEAL passivated cylinder, labelled as a – e, correspond to those
377 named in the main text and to the observed MS shown in Figure S1.
378

379 **3.2. Short- and long-term stability study of monoterpene PRM**

380 The short-term and long-term stability of mixture BB was determined through a series of
381 experiments as detailed in Section 2.4. Over the first three month period that mixture BB was
382 run the ratio of the monoterpene to *n*-octane appears to remain fairly constant despite a few
383 outlying points.

384

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385 **Figure 5:** The short-term stability of reference PRM (mixture BB) at nominally 2 nmol mol^{-1}
386 compared as a ratio of the area of each monoterpene normalised relative to the *n*-octane internal
387 standard. Error bars are included to account for the relative standard deviation of the mean (k
388 = 2).
389
390
391 Mixture BB was prepared on 2nd June 2015 and mixture CC was more than two years later (904
392 days) on the 22nd November 2017. A set of measurements were run to compare mixture BB
393 and CC. This was repeated twice in the space of two days. Gravimetric values were normalised
394 and the peak areas of the monoterpenes were then compared and the differences recorded
395 (Table 2). It was found that, unsurprisingly, *n*-octane shows the best agreement and smallest
396 difference, however all the monoterpenes agreed well and differences were no greater than 2.5
397 % between mixtures BB and CC. The relative standard deviations of the peak areas was
398 between 0.1 – 1.5 % with the larger relative standard deviations correlating to the highest
399 differences between the gas mixtures suggesting that the measurement is one of the largest
400 sources of uncertainty in the experimental differences. The comparison infers that the
401 monoterpene mixtures in Experis treated cylinders are stable for over two and a half years.
402
403 Mixture F and G containing *β*-pinene were prepared 976 days apart (approximately 2 years and
404 8 months difference), and were compared. Agreement for *β*-pinene, once normalised to take
405 into account gravimetric differences, was better than 0.5 % and the relative standard deviation
406 in the peak areas were 0.7 – 1.1 %. No systematic bias was observed. This suggests that in
407 Experis treated cylinders there is little or no decay of *β*-pinene at the μmol/mol level when
408 prepared as a binary mixture. Stability has been demonstrated for greater than two and a half
409 years suggesting that it is the interaction of *β*-pinene with other monoterpenes in
410 multicomponent gas standards that is the likely cause of their degradation.
411
412
413 **Table 2:** Comparison showing the percentage difference between PRM mixtures prepared
414 more than two years apart to assess the long-term stability of mixture BB and mixture F.
415 Gravimetric values were normalised and the peak areas compared.

	The difference when comparing PRMs		
Compound	**Mixture BB v CC**		**Mixture F v G**
limonene	0.24 %	0.94 %	
α-pinene	0.06 %	1.61 %	
1,8-cineole	1.96 %	-0.22 %	
3-carene	-0.75 %	1.35 %	
β-pinene			0.45 %
n-octane	-0.75 %	0.24 %	

416

417 **3.3. Short-term stability of monoterpenes in treated sampling canisters**
418

419 Field campaign measurements require the short-term storage of VOC samples. Sampling
420 canisters made from electropolished steel are frequently used despite losses being observed
421 (Batterman, Zhang et al. 1998). Another solution is to use SilcoNert 2000® treated canisters
422 (silanisation treatment, Silcotek). However, the SPECTRA-SEAL cylinders that performed
423 poorly in the decant experiments, also use a silanisation surface treatment, therefore it was
424 important to determine the suitability of SilcoNert 2000® treated canisters for short-term
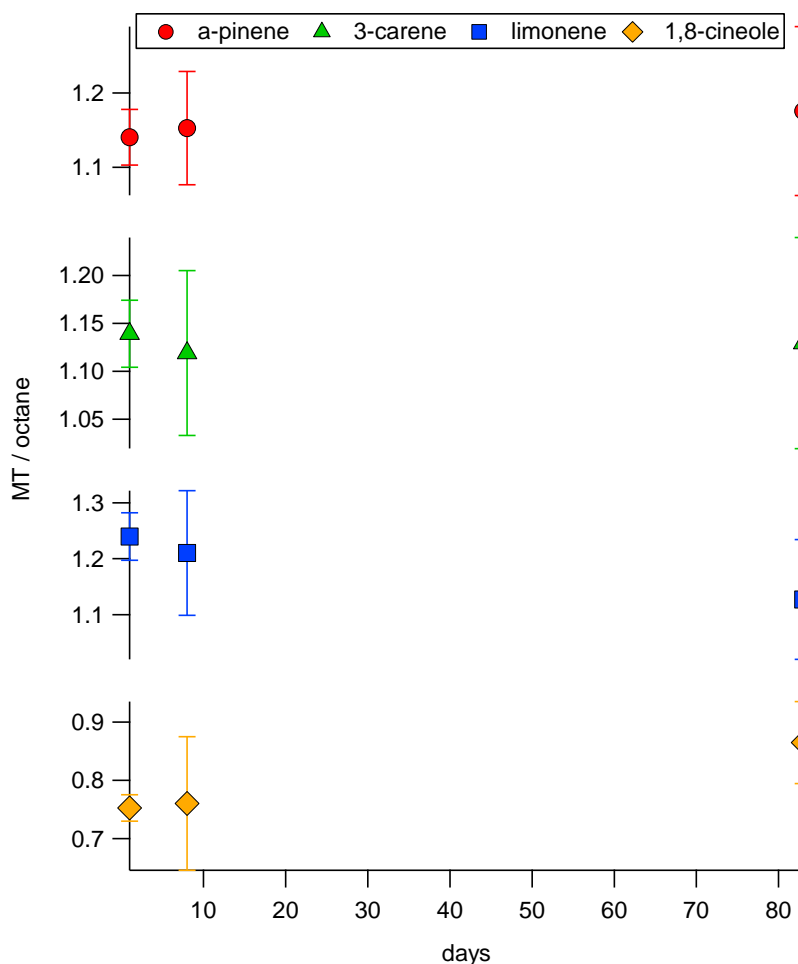
425 storage of monoterpenes. Following decant of mixture BB into the SilcoNert 2000® treated
426 canister the contents were compared against mixture BB the following day (day 1) a week later
427 (day 8) and nearly three months later (day 83). The results of this are shown in Figure 6.
428
429
430

431
432 **Figure 6:** The short-term stability of mixture BB decanted into a SilcoNert 2000® treated
433 canister compared as a ratio of the area of each monoterpene normalised relative to the *n*-octane
434 internal standard. Error bars are included to account for the relative standard deviation of the
435 mean ($k = 2$).
436
437 No statistically significantly trends were observed for the stability although higher than normal
438 relative standard deviations in the GC peak areas were observed (≤ 4 % for all components
439 except 1,8-cineole which was $\leq 8\%$). This can be attributed to changes in the flow of gas from
440 the canister samples during measurement due to the volume and pressure of gas contained.
441
442 It appears that unlike the SPECTRA-SEAL passivated cylinders, the SilcoNert 2000® treated
443 canisters would allow the storage of multi-component monoterpene standards for up to three

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444 months and still meet the data quality objective criteria recommended by GAW and its
445 scientific advisory group (Hoerger, Claude et al. 2015). Nevertheless, this does not mean that
446 a whole air sample containing terpenes or a broad array of terpenes together would behave in
447 the same way due to the impact of humidity, therefore more work is required to determine this.
448 However, it would suggest that decanting of PRMs for transport into the field in small
449 SilcoNert 2000® treated canister should be possible.

450 **3.4. Comparison of dynamic and static PRM**

451

452 From the weighing of the limonene permeation tube and from the data that was logged for the
453 nitrogen flow and subsequent dilution it was calculated that the ReGaS2 mobile gas generator
454 was outputting 4.41 ± 0.32 nmol mol^{-1} of limonene with an expanded uncertainty of 7.3 % (k
455 = 2). Using the PRM static standards gravimetrically produced the output of the ReGaS2
456 dynamic system was estimated to be 3.57 ± 0.11 nmol mol^{-1} of limonene with an expanded
457 uncertainty of 2.9 % ($k = 2$).

458

459 The static PRM that was used in this comparison (mixture BB) was also one of the mixtures
460 used as part of the CCQM-K121 monoterpene key comparison at nominally 2.5 nmol mol^{-1}
461 Results from CCQM-K121 demonstrated that all of the participants (Korea Research Institute
462 of Standards and Science, KRISS; National Institute of Standards and Technology, NIST and
463 NPL) agree within the $k = 2$ expanded uncertainties for all of the monoterpenes evaluated,
464 including limonene.

465

466 Reasons for the systematic bias between the two approaches are supposed, include the
467 temperature at which the permeator was operated was observed to have a strong influence on
468 the reproducibility of the permeation rate. At lower temperatures, such as 30°C (which was the
469 temperature used for the comparison), the permeator does not reach a true steady state and it
470 was observed that the variability on the permeation rate for the same temperature between two
471 measurements was between 8 and 10 %. A shift in the permeation rate of this magnitude
472 coupled to uncertainties in temperature would be enough to compensate for the systematic bias
473 observed between the two approaches.

474

475 The second reason is the decrease in the permeation rate: to investigate this further the
476 permeation rate of limonene from the ReGaS2 dynamic system was measured over an 11 month
477 period between March 2017 and February 2018. The decrease in the permeation rate was
478 determined to be 35 % over this temporal period (Figure S3) for the same temperature. The
479 measurement of the permeation rate in the magnetic suspension balance lasted between two
480 and seven days with an associated uncertainty between 0.5 and 1.5 % for one measurement at
481 one temperature.

482

483 A decrease in the permeation rate of this magnitude coupled to the high uncertainties at such
484 low temperatures would be enough to compensate for the systematic bias observed between
485 the two approaches. Despite the systematic bias observed between the two methods at this trace
486 level, the results of this first comparison are encouraging and show that state-of-the-art
487 developments are being made with dynamic systems capable of delivering reliable outputs
488 suitable for calibrating in the field systems.

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491 ## 4. Conclusions

492 In this paper we have investigated the short-term and long-term stability of monoterpenes in
493 differently internally passivated cylinders. The choice of cylinder passivation is critically
494 important in the preparation of monoterpene gas mixtures. We have demonstrated that Experis
495 treated cylinders are the most appropriate for containing low amount fraction monoterpene
496 PRMs and that the amount fraction is not influenced by pressure dependency between 120 and
497 30 bar.
498
499 The need for suitable storage and transport of PRMs into the field has driven us to investigate
500 the suitability of using SilcoNert 2000® treated canisters for monoterpenes. It was discovered
501 that SilcoNert 2000® treated canisters could hold monoterpenes for up to three months with
502 an uncertainty of 10 %, in line with GAW data quality objectives.
503
504 We compared the ReGaS2 dynamic mobile generator against high pressure static PRMs
505 gravimetrically prepared at NPL. It was found that the output of limonene from dynamic
506 ReGaS2 was 15 - 20 % lower than calculated. These differences correspond to less than 0.5
507 nmol mol^{-1} and it has been suggested that the bias may be attributed to the reproducibility of
508 the limonene permeator at low temperature due to the permeation rate not reaching equilibrium.
509 This first comparison of a dynamic terpene standard against a traditional static standard is the
510 first step in providing the community with traceable reference materials suitable for in the field
511 measurements to meet GAW data quality objectives.
512

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