CCQM-K121 – Monoterpenes in Nitrogen at 2.5 nmol mol^{-1}

Final Report

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Field

Amount of substance

Subject

Comparison of monoterpenes in nitrogen

Participants

KRISS, NIST, NPL

Organizing body

CCQM-GAWG

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Abstract

The growing awareness of climate change, and continuing concerns regarding tropospheric and stratospheric chemistry, will require future measurements and standards for compounds linked to these issues. To globally monitor and control the emissions of these species in the atmosphere, it is necessary to demonstrate measurement equivalence at the highest levels of accuracy for assigned values of standards. This report describes the results of a key comparison for several important monoterpene species, which are relevant to atmospheric chemistry and climate. The comparison samples include α-pinene, 3-carene, R-limonene and 1,8-cineole in a nitrogen matrix gas, at a 2.5 nmol mol^{-1} amount-of-substance fraction. The objective of this key comparison is to evaluate the participants' capabilities to measure trace-level monoterpenes using their own calibration techniques.

1 Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry and climate. They contribute to photochemical processes that lead to the production of tropospheric ozone and chemical smog, act as a sink to hydroxyl radicals that oxidize methane and other greenhouse gases, and form secondary organic aerosols (SOAs), which contribute to fine particle pollution and cloud condensation nuclei [1, 2]. VOC sources can be either biogenic or anthropogenic, with the most important biogenic VOCs being isoprene, isoprenoids and monoterpenes [3].

There has been considerable interest in measuring ambient levels of monoterpenes in the atmosphere and their emission rates from terrestrial vegetation. In support of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program for VOC measurements, several National Metrology Institutes (NMIs) have researched the preparation of stable monoterpene gas standards. Several monoterpene-in-nitrogen standards have been developed and compared between a limited number of NMIs with some success. Therefore, it is advantageous for the NMIs to take part in a key comparison of these monoterpene compounds.

This report describes the results of a key comparison of several important monoterpenes at elevated atmospheric amount-of-substance fraction levels. The mixtures used for this comparison are comprised of α-pinene, 3-carene, R-limonene and 1,8-cineole in a balance of nitrogen, at a nominal amount-of-substance fraction of 2.5 nmol mol^{-1}. The objective of this key comparison is to assess participant measurement capabilities for monoterpenes at trace levels.

2 Design and organization of the key comparison

2.1 Quantities and units

The measurand in this comparison is the amount-of-substance fraction of monoterpenes in a matrix of high-purity nitrogen, and is expressed as nmol mol^{-1}, i.e., parts per billion (ppb).

2.2 Participants

Table 1 lists the participants in this key comparison.

Table 1. Lists of participants in CCQM-K121

Acronym	Country	Institute
KRISS	KR	Korea Research Institute of Standards and Science Daejeon, Republic of Korea
NIST	US	National Institute of Standards and Technology Gaithersburg, Maryland, United States of America
NPL	GB	National Physical Laboratory Teddington, United Kingdom

2.3 Schedule

The schedule for this key comparison is shown in Table 2.

Table 2. CCQM-K121 schedule

Date	Task completed
October 2014	Preparation, verification and stability testing of mixtures by NIST
July 2015	Receipt of cylinder gas mixtures by participants
September 2015	Analysis of mixtures by participants
January 2016	Return of cylinders to NIST
February 2016	Data submitted to NIST Reanalysis of mixtures for stability check
April 2016	Discussion of data at CCQM/GAWG meeting
August 2016	Distribution of Draft A report
December 2016	Distribution of Draft B report to participants
April 2017	Presentation of Draft B to GAWG
October 2017	Final approval by GAWG

2.4   Measurement samples

The measurement samples for this key comparison were prepared in 20-L aluminum gas cylinders treated with *Experis*, a proprietary process by Air Products, Belgium used to passivate the internal walls [1]. Previously reported research on monoterpenes in cylinders demonstrates that this container/treatment combination provides the most consistent stability results [4, 5]. Each sample was prepared by gravimetric dilution of a parent mixture containing nominally 225 nmol mol⁻¹ monoterpenes in nitrogen.

2.4.1   *Parent mixtures*

Two gravimetric primary standard mixtures (PSMs), APE1135902 and APE1082180 (Table 3), were used as parent mixtures for the preparation of the key comparison samples, as well as five in-house PSMs that were used to verify them. The parent mixtures were made with four monoterpenes (*α*-pinene, 3-carene, *R*-limonene and 1,8-cineole) plus an alkane (used as an internal standard) in nitrogen, at a nominal amount-of-substance fraction of 225 nmol mol⁻¹. All pure monoterpene starting materials were analyzed for purity prior to their use in the parent mixtures (Figure 1).

Table 3. Gravimetric values of parent mixtures used for CCQM-K121

Compound	Amount-of-Substance Fraction (nmol mol⁻¹)[a]	
	APE1135902	*APE1082180*
α-Pinene	222.53 ± 0.39	229.70 ± 0.40
3-Carene	229.83 ± 0.51	224.24 ± 0.38
R-Limonene	221.35 ± 0.33	231.86 ± 0.48
1,8-Cineole	236.97 ± 0.37	227.46 ± 0.49
Internal Standard[b]	243.24 ± 0.32	225.39 ± 0.43

[a] Expanded uncertainties represent approximate 95 % confidence intervals.
[b] Included in mixture to track stability: *n*-octane for APE1135902; *n*-hexane for APE1082180.

The parent mixtures were analyzed against each other over approximately 15 months to verify their gravimetric values (Figure 2). All analyses were performed using a gas chromatograph with flame ionization detection (GC-FID), coupled to a cryogenic preconcentrator. A 60 m × 0.32 mm capillary column with 0.25 μm of AT-wax was used with the following temperature program: hold at 50 °C for 12 minutes; ramp to 110 °C at 4 °C min⁻¹; hold for 1 min. The detector temperature was set to 250 °C. Sample volumes of 50 mL and 200 mL were cryogenically trapped for mixtures at 225 nmol mol⁻¹ and 2.5 nmol mol⁻¹, respectively. A representative chromatogram of parent mixture APE1135902 is shown in Figure 3.

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[1] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
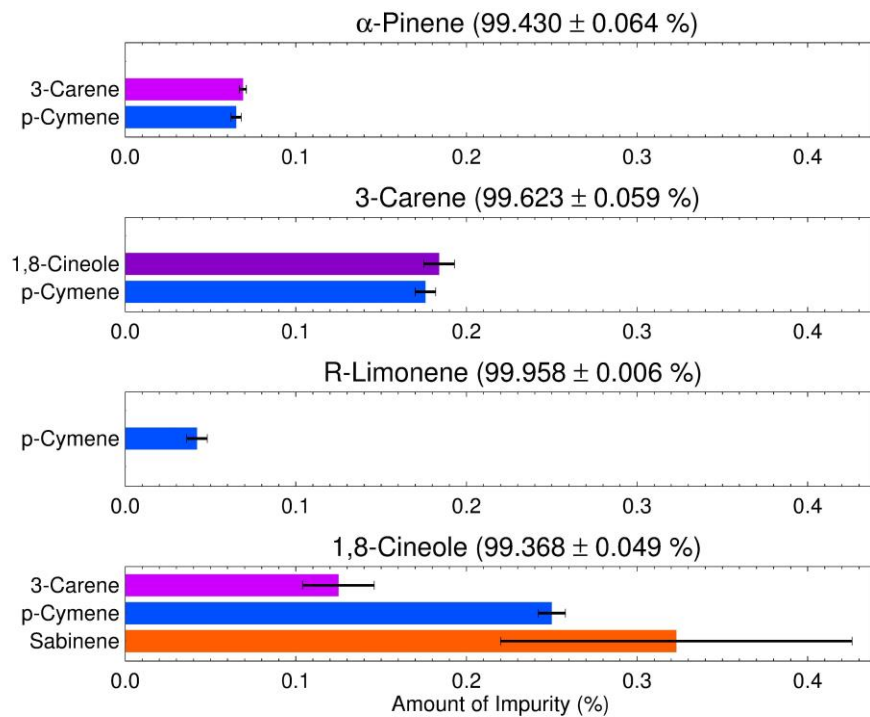
Figure 1. Purity analysis of monoterpenes used in the preparation of parent mixtures APE1135902 and APE1082180. The uncertainties shown represent the standard uncertainties of the analysis.
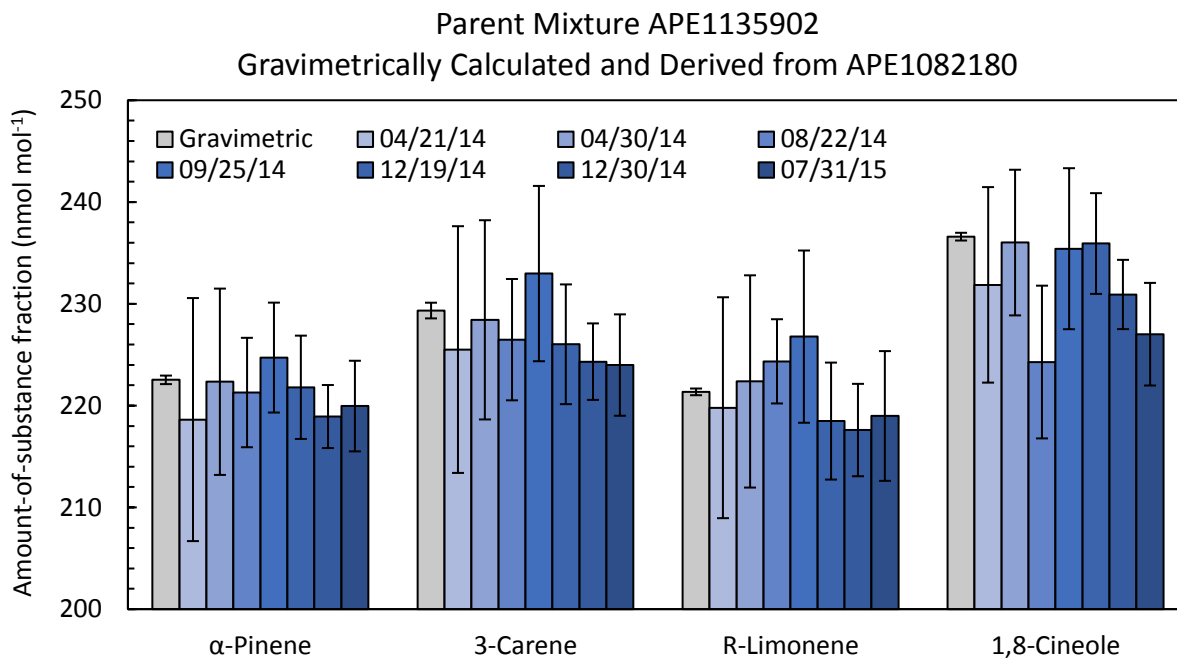

Figure 2. Verification of APE1135902 (prepared April 2014) using APE1082180 (prepared August 2013). Gray bars represent gravimetric values; blue bars represent predicted values using a single-point calibration with APE1082180. Error bars represent approximate 95 % confidence intervals.
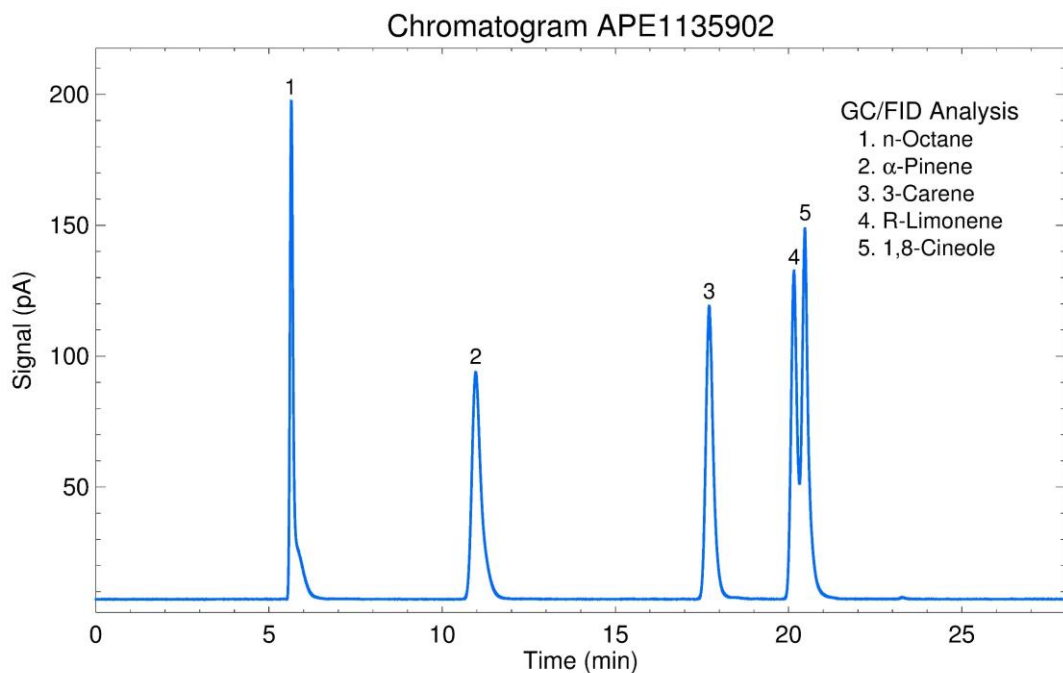
Figure 3. Sample chromatogram of parent mixture APE1135902, nominal 225 nmol mol^{-1} monoterpenes and *n*-octane in nitrogen.

The chosen chromatographic method does not baseline-separate *R*-limonene and 1,8-cineole. Baseline separation of these two compounds can be achieved using a different coated capillary. However, NIST is also tracking long-term stability of these and other standard mixtures containing many monoterpenes. The column used in these measurements baseline-separates all the monoterpenes being studied except for *R*-limonene and 1,8-cineole. Changing to a different coated capillary would alter the characteristics of elution, thus changing the ratio between the monoterpenes and the internal standard. NIST used the same column and dedicated instrument to maintain stability throughout this comparison, to understand the behavior of the comparison mixtures over time.

Mixtures APE1135902 and APE1082180 contained internal standards of *n*-octane and *n*-hexane, respectively, which were used to track stability of the monoterpenes over time. A consistent response ratio of each monoterpene to the internal standard ensures that the mixture is stable. Both parent mixtures were rigorously analyzed for stability prior to use for the key comparison samples. Figures 4i and 4ii indicate that both parent mixtures were stable for several months prior to preparation of the key comparison samples, and have maintained stability for approximately 2+ years.
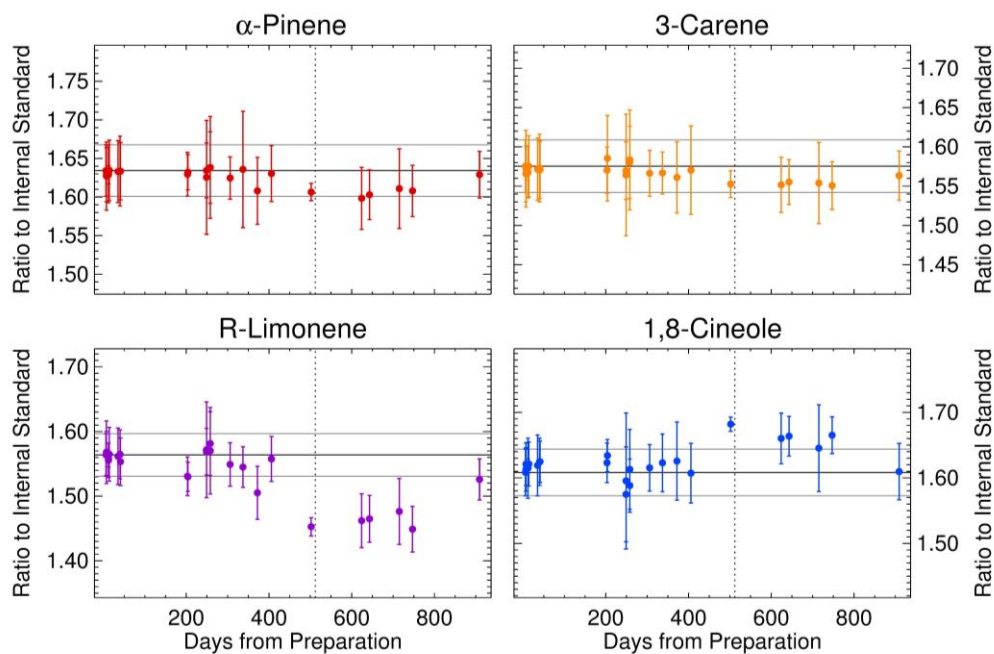
7
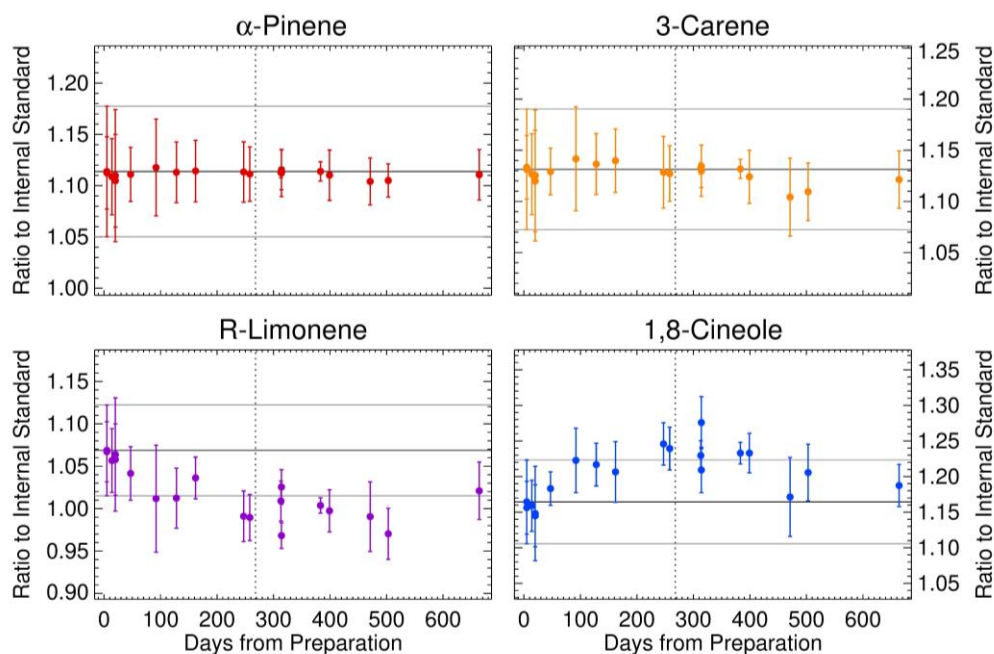
Figure 4. Stability testing of parent mixtures (i) APE1135902 and (ii) APE1082180 over time from the date of mixture preparation. Individual data points represent response ratios of each monoterpene to the internal standard. Error bars represent approximate 95 % confidence intervals. Dark and light gray lines represent the initial response ratios and their approximate 95 % confidence intervals, respectively. Dotted vertical lines indicate when preparation of the key comparison samples began.

Since the measurement samples for this key comparison were prepared via dilution of aliquots of the parent mixtures, a mother-daughter test was performed to determine whether any loss of monoterpenes occurred during cylinder mixture transfer. Approximately 1.4 MPa of parent mixture APE1082180 (mother) was transferred into an evacuated *Experis* cylinder (daughter), and the ratio of the response of the daughter to that of the mother was calculated (Figure 5). Since the response ratios were unity within the error bars, it was determined that there was no significant monoterpene loss due to cylinder transfer.
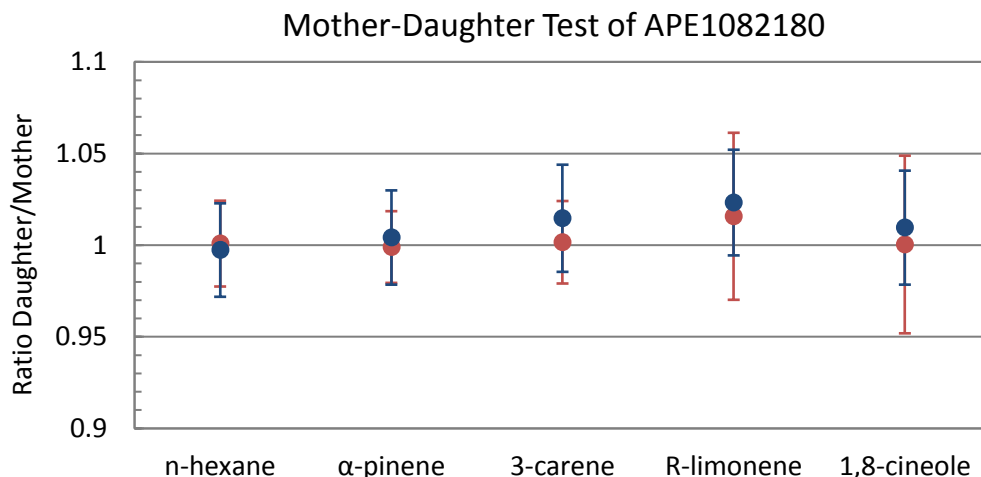

Figure 5. Mother-daughter analysis of APE1082180. Each data point represents the ratio of the response of the daughter cylinder to that of the mother cylinder. Error bars represent approximate 95 % confidence intervals.

2.4.2   *NIST in-house primary standard mixtures*

Five monoterpene PSMs, ranging from approximately (1.5 to 3.5) nmol mol^{-1}, were prepared to validate the amount-of-substance fractions in the key comparison samples. All calculations for the gravimetric values of the PSMs were reviewed for sources of persistent ("systematic") and volatile ("random") error [6, Paragraph (5e)]. The major sources of uncertainty included: (a) the mass of the parent mixture added, (b) the mass of the nitrogen balance gas added, (c) the purity of the balance gas, (d) the molecular masses of the monoterpenes and components of the balance nitrogen, and (e) the composition of the parent mixture. The combined uncertainties (u_{grav}) assigned to the PSMs were calculated independently for each analyte in the mixture from all known sources of error in the gravimetric method, using Formula (4) from ISO 6142-1 [7].

The gravimetric values and uncertainties for each PSM are listed in Table 4. The final uncertainties are expressed as expanded uncertainties, $U = ku_{grav}$, where the coverage factor, k, equals 2. The true amount-of-substance fractions are therefore asserted to lie within the interval defined by the gravimetric value $\pm U$ with about 95 % confidence.

Table 4. Gravimetric amount-of-substance fractions of NIST in-house PSMs

Cylinder	Amount-of-Substance Fraction (nmol mol^{-1})[a]				
	α-Pinene	*3-Carene*	*R-Limonene*	*1,8-Cineole*	*Int Std*[d]
APE1145326[b]	2.518 ± 0.022	2.600 ± 0.023	2.504 ± 0.022	2.681 ± 0.023	2.752 ± 0.024
APE1145327[b]	3.411 ± 0.029	3.522 ± 0.030	3.392 ± 0.028	3.632 ± 0.030	3.728 ± 0.031
APE1145334[c]	1.576 ± 0.019	1.538 ± 0.019	1.591 ± 0.020	1.561 ± 0.019	1.546 ± 0.019
APE1145336[c]	3.093 ± 0.021	3.020 ± 0.020	3.122 ± 0.021	3.063 ± 0.021	3.035 ± 0.020
APE1161693[b]	2.111 ± 0.017	2.180 ± 0.018	2.100 ± 0.017	2.248 ± 0.018	2.308 ± 0.018

[a] Expanded uncertainties represent approximate 95 % confidence intervals.
[b] Prepared from parent mixture APE1135902.
[c] Prepared from parent mixture APE1082180.
[d] Int Std, internal standard; *n*-octane from APE1135902, *n*-hexane from APE1082180.

The PSMs were verified using ISO 6143 GenLine linear regression [8, 9] by means of an external control cylinder, ND02720. The resulting linear regression shows that the predicted amount-of-substance fractions agree with their gravimetric values (Figure 6).
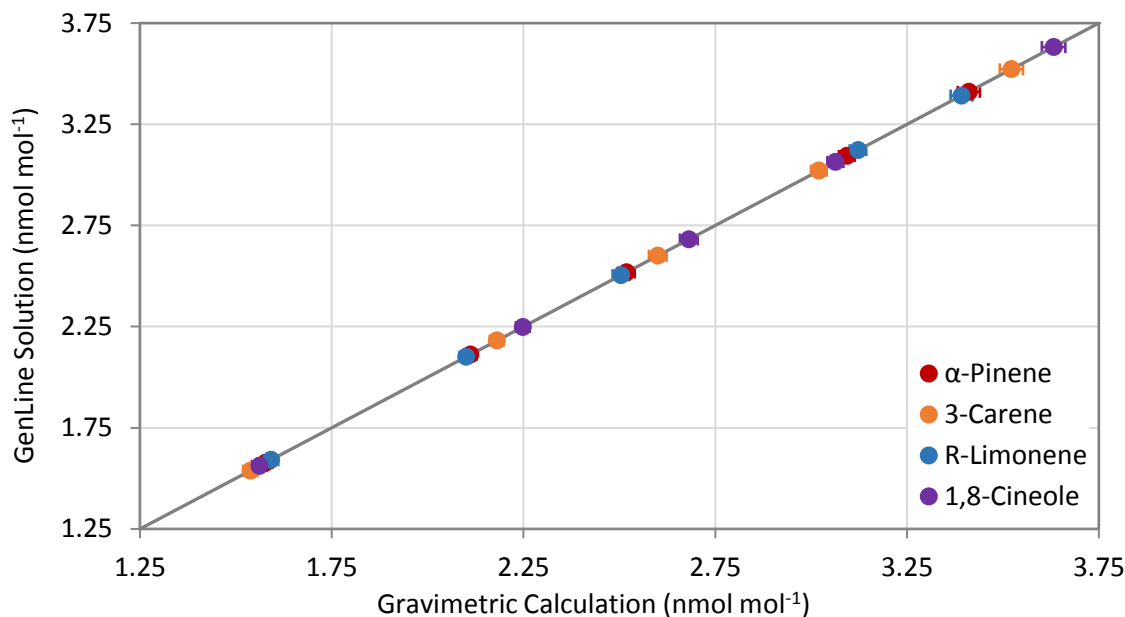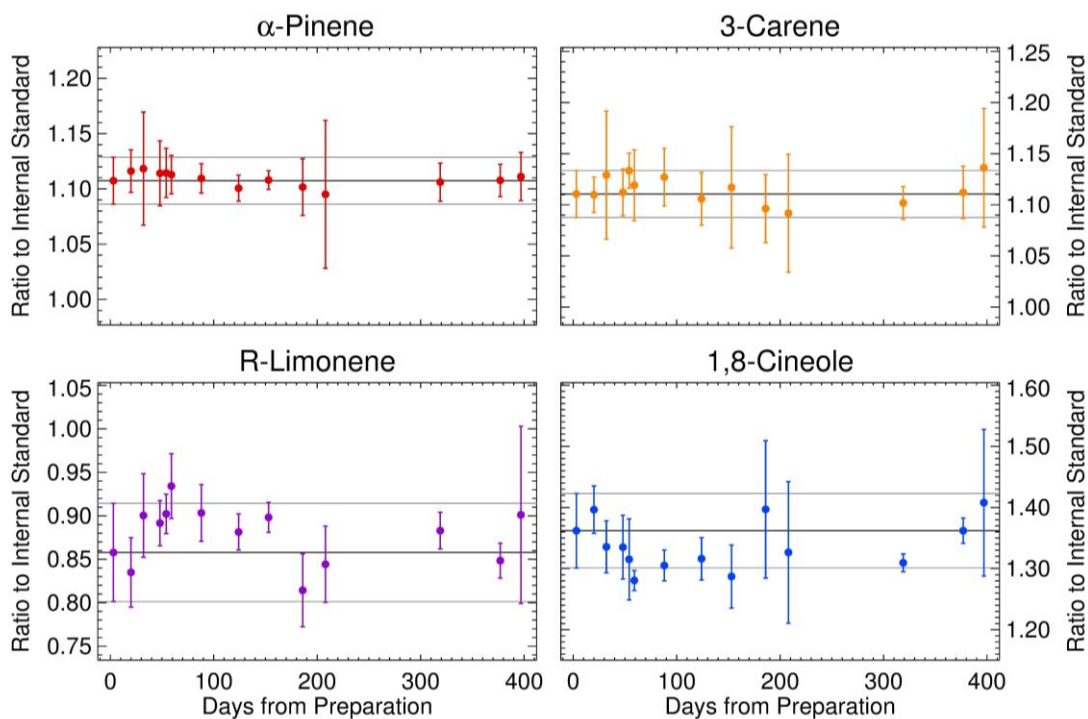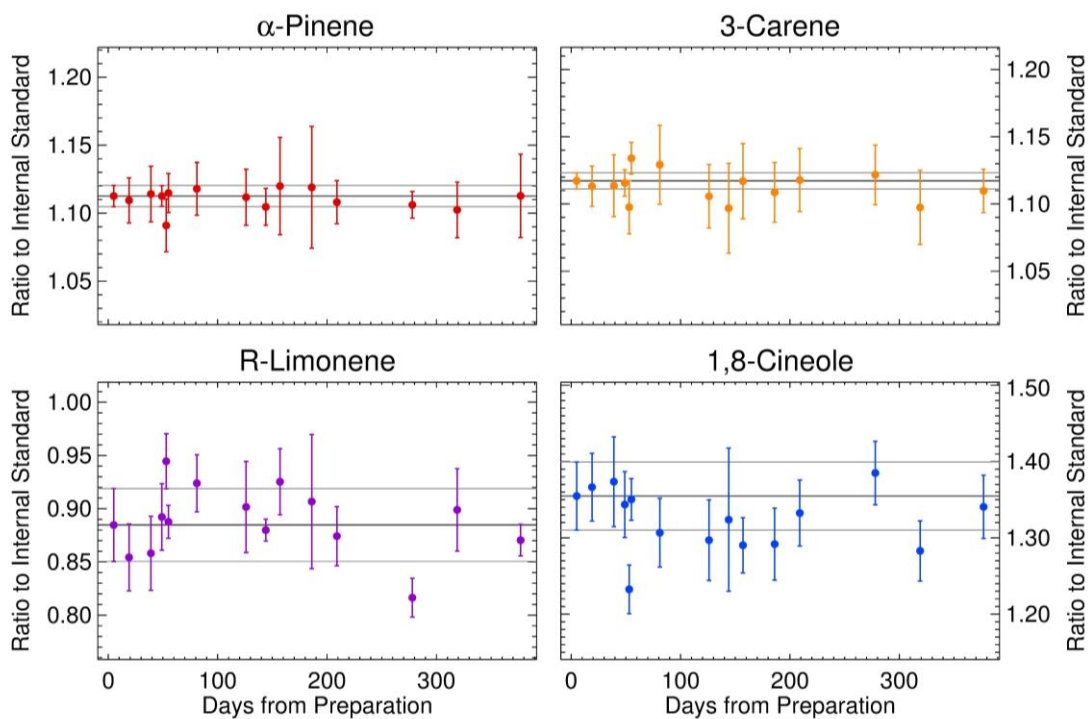

Figure 6. Results from ISO 6143 GenLine analysis, showing the linear regression solution versus the gravimetric value for each PSM used in this key comparison. Error bars represent approximate 95 % confidence intervals on the gravimetric values.

As with their parent mixtures, the PSMs were tracked for stability prior to and throughout the duration of the key comparison. These mixtures have remained stable for approximately 400 days (Figures 7i through 7v).

(i)　Stability of Monoterpenes in APE1145326

α-Pinene

3-Carene

R-Limonene

1,8-Cineole

Ratio to Internal Standard

Days from Preparation

(ii)　Stability of Monoterpenes in APE1145327

α-Pinene

3-Carene

R-Limonene

1,8-Cineole

Ratio to Internal Standard

Days from Preparation

11

(iii)   Stability of Monoterpenes in APE1145334

α-Pinene

3-Carene

R-Limonene

1,8-Cineole
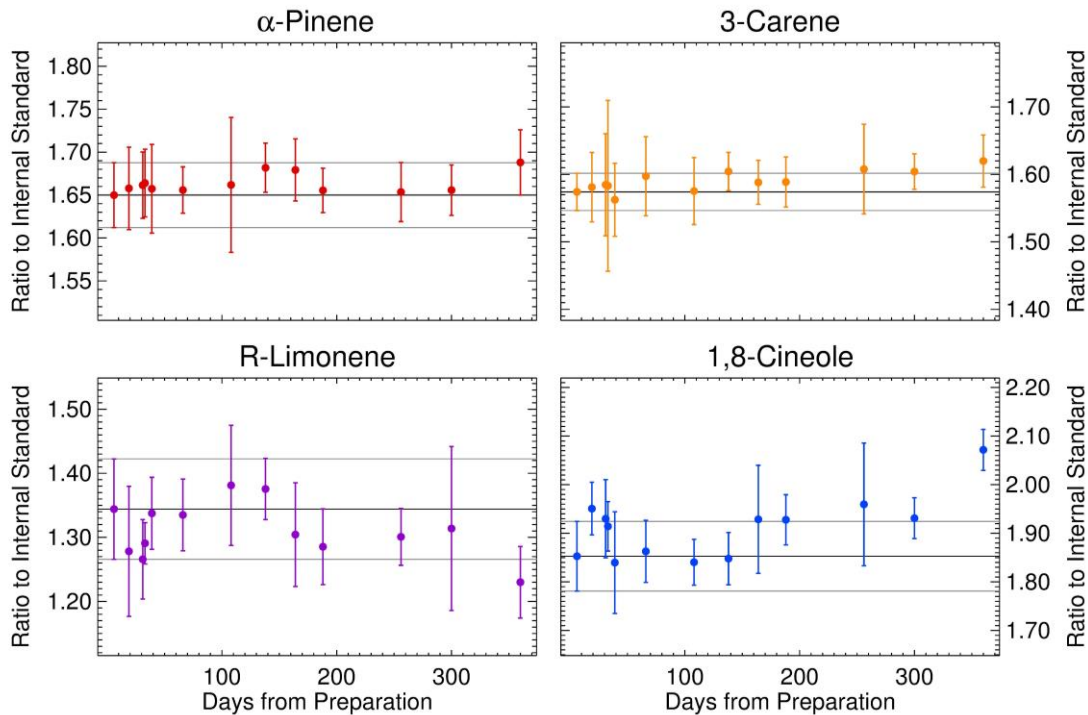
(iv)   Stability of Monoterpenes in APE1145336

α-Pinene

3-Carene

R-Limonene

1,8-Cineole

12
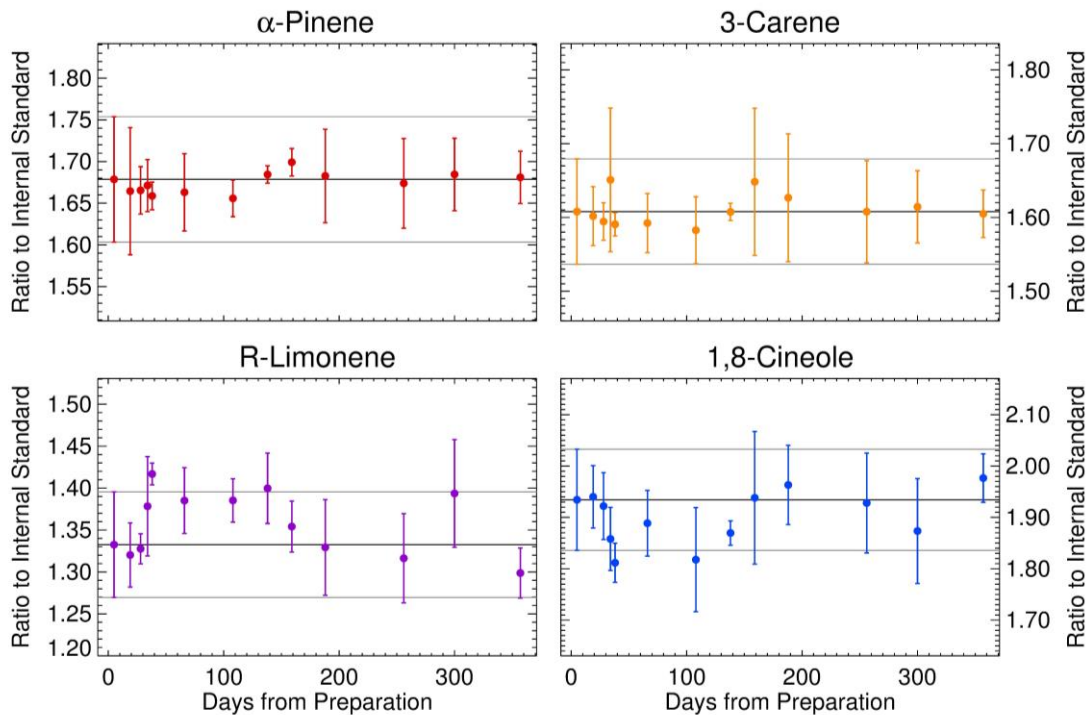
Figure 7. Stability testing of NIST in-house PSMs from the date of preparation. Individual data points represent response ratios of 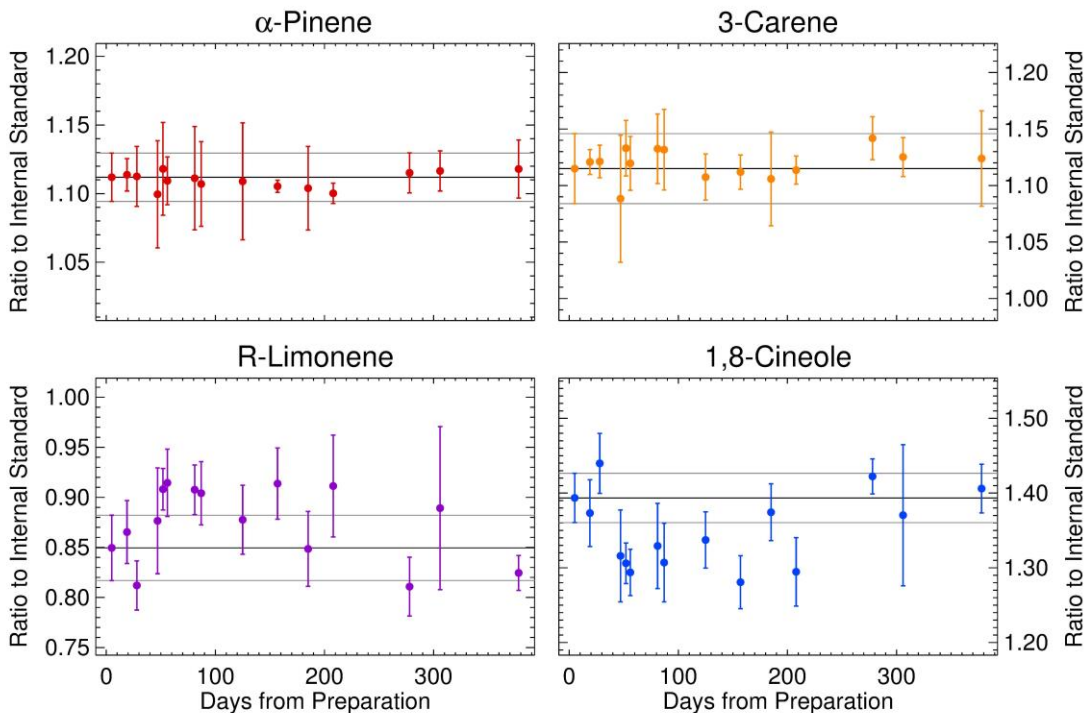each monoterpene to the internal standard. Error bars represent $k = 2$ expanded uncertainties. Dark and light gray lines represent the initial response ratios and $k = 2$ expanded uncertainties, respectively.

2.4.3   Key comparison samples

The key comparison sample mixtures were prepared via dilution of parent mixture APE1135902 to a nominal amount-of-substance fraction of 2.5 nmol mol^{-1}. All gravimetric calculations were reviewed for sources of systematic and random error, in the same manner as discussed in Section 2.4.2.

The gravimetric amount-of-substance fractions of each key comparison sample were verified against the NIST in-house PSMs over approximately 4 months (March through July 2015) using ISO 6143 GenLine linear regression [8, 9]. Based on the agreement between the predicted (x_{ver}) and gravimetric (x_{grav}) values (see Figure 8 and Table 5), the samples were deemed appropriate for this key comparison and delivered to the participants. The verification amount-of-substance uncertainties, $u(x_{ver})$, were computed for each comparison sample from the PSMs fitted to GenLine.

To ensure that no significant changes to the monoterpene mixtures occurred over the course of the key comparison, the key comparison samples were reverified upon their return to NIST. Cylinders APE1145315 and APE1145321 were reverified in November through December 2015; cylinder APE1145320 was reverified in May 2016 due to a delay in sample return. To conserve gas in the NIST

PSMs, cylinder APE1145320 was analyzed by comparison against one PSM (APE1161693), using the same control cylinder (ND02720) as previously discussed. Results from both verification periods are shown in Figure 8; the consistency between the two indicates that the mixtures remained stable throughout the key comparison.

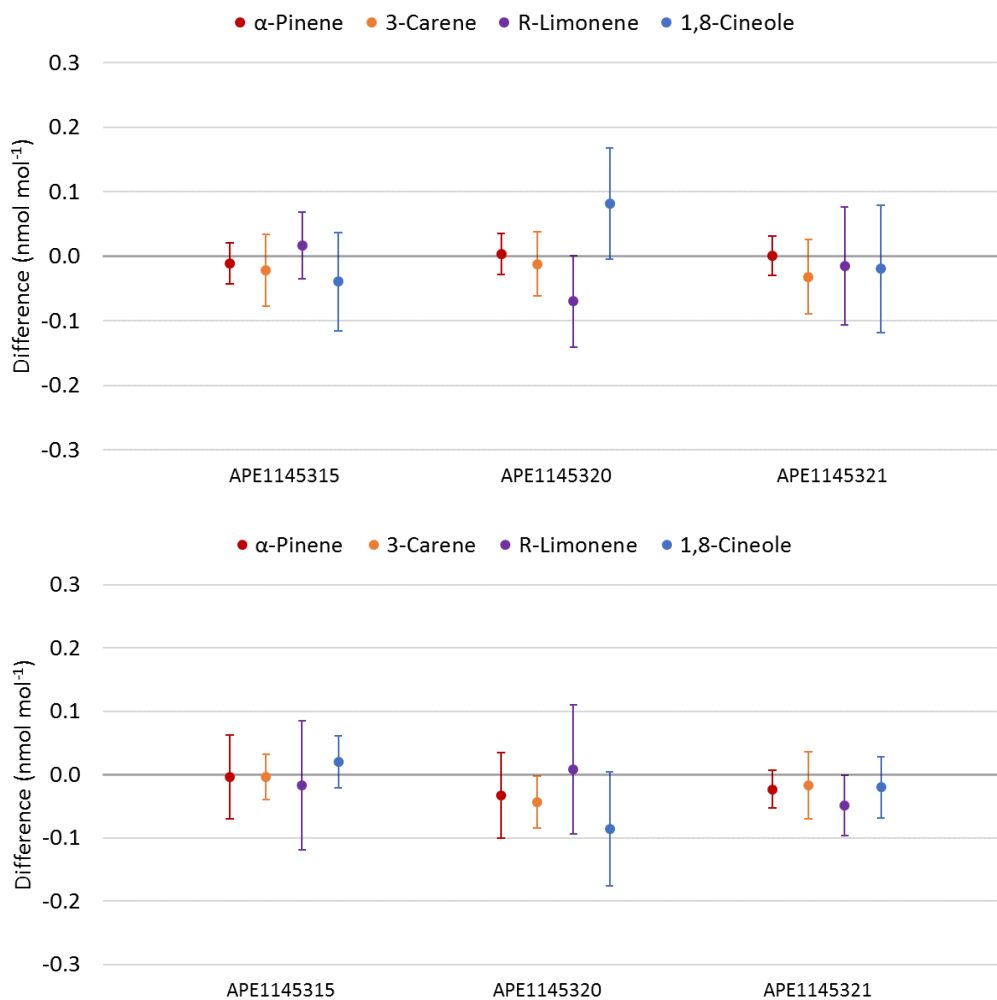**Figure 8.** Differences between the predicted and gravimetric amount-of-substance fractions for each key comparison sample, expressed as nmol mol^{-1}. The top and bottom figures represent the initial verification and reverification analyses, respectively. Error bars represent combined standard uncertainties.

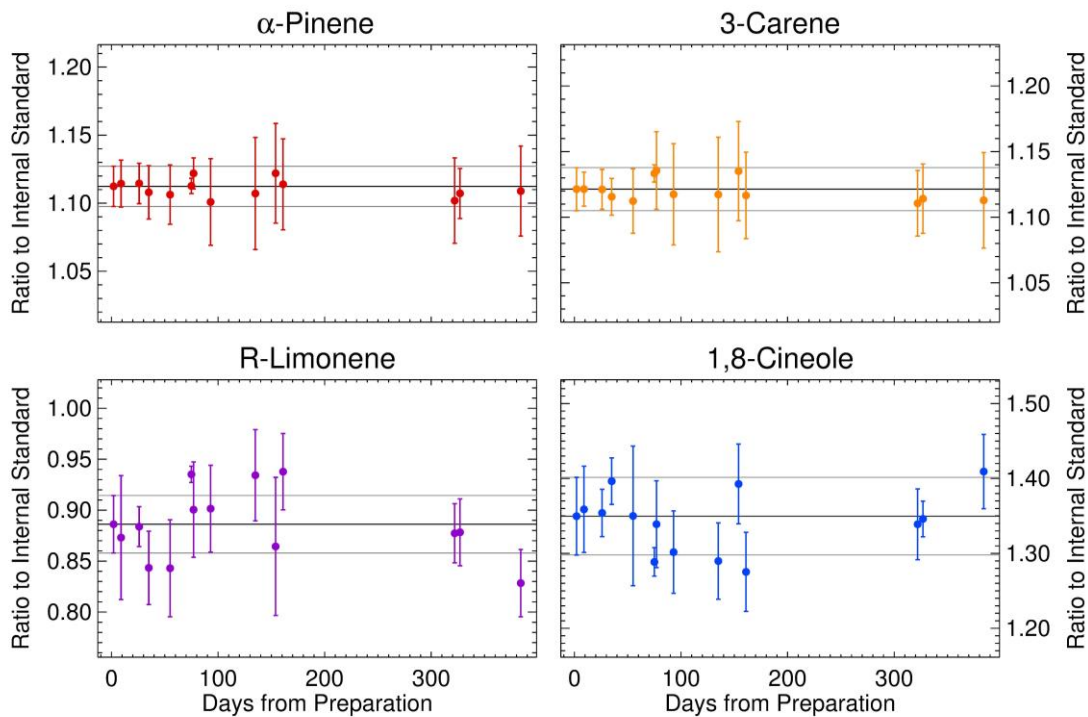**Table 5.** Verification analysis of CCQM-K121 key comparison samples[a]

	APE1145315		APE1145320		APE1145321	
	value	u[b]	*value*	u[b]	*value*	u[b]
α-Pinene						
x_{ver} (nmol mol^{-1})	2.520	0.027	2.523	0.031	2.534	0.028
x_{grav} (nmol mol^{-1})	2.531	0.016	2.520	0.007	2.533	0.012
Difference (nmol mol^{-1})	*-0.011*	*0.031*	*0.003*	*0.031*	*0.001*	*0.030*
Difference (%)	*-0.434%*	*1.236%*	*0.135%*	*1.247%*	*0.026%*	*1.201%*
3-Carene						
x_{ver} (nmol mol^{-1})	2.592	0.052	2.590	0.049	2.584	0.056
x_{grav} (nmol mol^{-1})	2.614	0.017	2.602	0.008	2.616	0.013
Difference (nmol mol^{-1})	*-0.022*	*0.055*	*-0.012*	*0.050*	*-0.032*	*0.058*
Difference (%)	*-0.827%*	*2.121%*	*-0.457%*	*1.911%*	*-1.217%*	*2.229%*
R-Limonene						
x_{ver} (nmol mol^{-1})	2.534	0.049	2.436	0.070	2.504	0.091
x_{grav} (nmol mol^{-1})	2.517	0.016	2.506	0.007	2.519	0.012
Difference (nmol mol^{-1})	*0.017*	*0.051*	*-0.070*	*0.071*	*-0.015*	*0.092*
Difference (%)	*0.676%*	*2.024%*	*-2.790%*	*2.899%*	*-0.599%*	*3.657%*
1,8-Cineole						
x_{ver} (nmol mol^{-1})	2.656	0.075	2.765	0.086	2.678	0.098
x_{grav} (nmol mol^{-1})	2.695	0.017	2.683	0.008	2.697	0.013
Difference (nmol mol^{-1})	*-0.039*	*0.077*	*0.082*	*0.086*	*-0.019*	*0.099*
Difference (%)	*-1.459%*	*2.882%*	*3.042%*	*3.119%*	*-0.718%*	*3.693%*

[a] Comprised of 3 separate analyses, each consisting of at least 3 individual measurements, performed over an analytical period of approximately 4 months (March through July 2015).

[b] u, combined standard uncertainty.

In addition to reverification, the key comparison samples were tracked for stability using the internal standard, *n*-octane, both prior to and after analysis by the participants (Figure 9). The internal standard was also tracked for stability by comparison to other *n*-octane PSMs (not shown).

(i)   Stability of Monoterpenes in APE1145315

α-Pinene

3-Carene

R-Limonene

1,8-Cineole

Ratio to Internal Standard

Days from Preparation

(ii)   Stability of Monoterpenes in APE1145320

α-Pinene

3-Carene

R-Limonene

1,8-Cineole

Ratio to Internal Standard

Days from Preparation

16
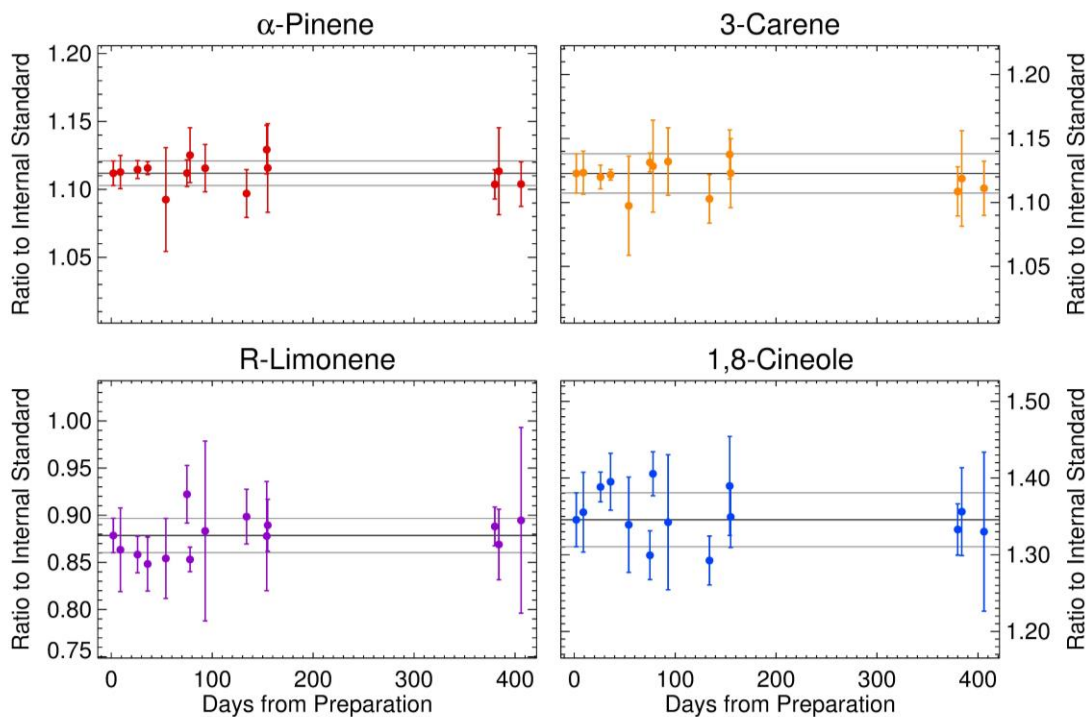
Figure 9. Stability testing of the key comparison samples over time from the date of mixture preparation. Individual data points re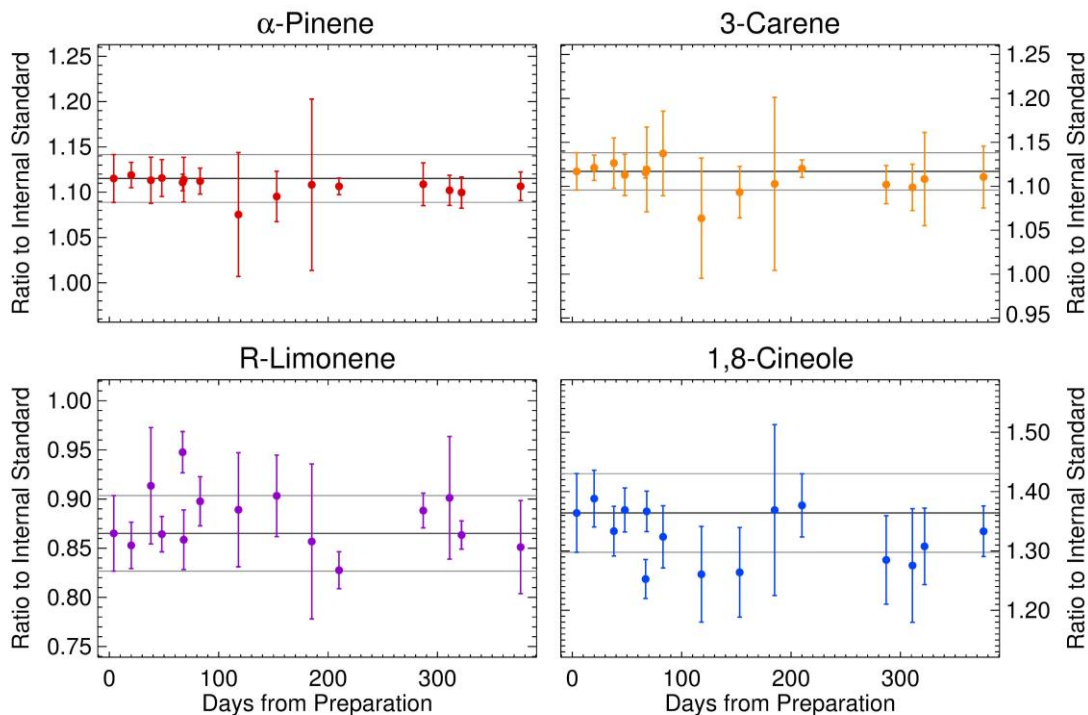present the response ratios of each monoterpene to the internal standard. Error bars represent approximate 95 % confidence intervals. Dark and light gray lines represent the initial response ratios and their approximate 95 % confidence intervals, respectively.

Based on a statistical analysis of the key comparison stability data, only α-pinene in sample APE1145321 yielded a slope significantly different from zero, and was -4.6 × 10^{-5} nmol mol^{-1} day^{-1} (Figure 10). This sample was measured by NIST for this key comparison approximately 228 days after preparation; therefore, the overall change in the amount-of-substance fraction of α-pinene was -0.010 nmol mol^{-1} (-0.40 % relative). Since this change fell within the combined standard uncertainty of the gravimetric value (0.012 nmol mol^{-1}), no correction for drift was applied.
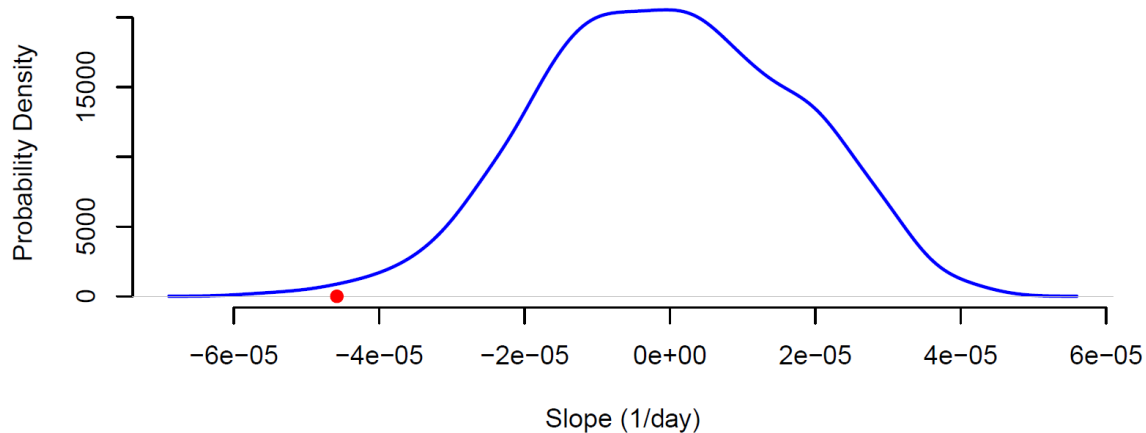
Figure 10. Smooth histogram of the slopes obtained in a permutation test for the slope of the relation between the ratio and day, for α-pinene in APE1145321. For only 6 of 1000 permutations of the data over the days did the slope have a value farther from 0 than obtained with the data in their actual temporal order (indicated by the red dot).

2.4.4 Key comparison reference values (KCRVs) and uncertainties

The key comparison reference value (x_{KCRV}) for each monoterpene in this comparison is the gravimetric amount-of-substance fraction determined from all preparation mass measurements and purities of the components. The final uncertainty is a combined standard uncertainty defined as:

$$u(x_{KCRV}) = \sqrt{u^2(x_{grav}) + u^2(x_{ver})},\qquad(1)$$

where $u(x_{grav})$ and $u(x_{ver})$ represent the gravimetric and verification uncertainties, respectively. The KCRVs and associated uncertainties for each sample in this comparison are listed in Table 6. The final uncertainties are expressed as expanded uncertainties, $U(x_{KCRV}) = ku(x_{KCRV})$, where the coverage factor, k, equals 2. The true amount-of-substance fractions are therefore asserted to lie within the interval defined by the gravimetric value $\pm\, U(x_{KCRV})$ with about 95 % confidence.

Table 6. Amount-of-substance fractions and uncertainties of CCQM-K121 samples[a]

Sample	Component	x_{KCRV}	$u(x_{grav})$[b]	$u(x_{ver})$[b]	$u(x_{KCRV})$[b]	$U(x_{KCRV})$[c]
APE1145315						
	α-Pinene	2.531	0.016	0.027	0.031	0.062
	3-Carene	2.614	0.017	0.052	0.055	0.110
	R-Limonene	2.517	0.016	0.049	0.051	0.102
	1,8-Cineole	2.695	0.017	0.075	0.076	0.153
	Int Std[d]	2.766	0.018			
APE1145320						
	α-Pinene	2.520	0.007	0.031	0.031	0.063
	3-Carene	2.602	0.008	0.049	0.050	0.099
	R-Limonene	2.506	0.007	0.070	0.071	0.141
	1,8-Cineole	2.683	0.008	0.086	0.086	0.172
	Int Std[d]	2.754	0.008			
APE1145321						
	α-Pinene	2.533	0.012	0.028	0.030	0.061
	3-Carene	2.616	0.013	0.056	0.058	0.115
	R-Limonene	2.519	0.012	0.091	0.092	0.183
	1,8-Cineole	2.697	0.013	0.098	0.099	0.198
	Int Std[d]	2.768	0.013			

[a] All values expressed as nmol mol^{-1}.

[b] u, combined standard uncertainty.

[c] U, expanded uncertainty represents an approximate 95 % confidence interval.

[d] *Int Std*, internal standard; *n*-octane from parent mixture APE1135902.

2.5 Measurement protocol

The measurement protocol requested that participants provide an amount-of-substance fraction value and uncertainty of each monoterpene for at least three individual determinations. A description of the analytical procedure, uncertainty budget and calibration method was also requested.

2.6 Measurement methods

Methods for analysis were used solely at the discretion of the participating laboratory, and are summarized in Table 7 (see the Appendices for more detailed method information provided by the participants).

Table 7. Measurement and calibration methods used by participating laboratories

Laboratory	Measurement method	Calibration method	Traceability
KRISS	GC-FID with preconcentration	Single-point calibration	KRISS-prepared gravimetric standards
NIST	GC-FID with preconcentration	Linear calibration curve, ISO 6143 [8, 9]	NIST-prepared gravimetric standards
NPL	GC-FID with preconcentration	Single-point calibration	NPL-prepared gravimetric standards, ISO 6142 [7]

3 Results

The CCQM-K121 report forms, as submitted by the participants, are in the Appendices. A summary of the results is shown in Table 8. All final amount-of-substance fractions are shown with $k = 2$ expanded uncertainties.

Table 8. Summarized results for CCQM-K121[a]

	KCRV[b]		Measurement		Degree of Equivalence	
	x_{KCRV}	$U(x_{KCRV})$	x_i	$U(x_i)$	d_i	$U(d_i)$
KRISS – APE1145320						
α-Pinene	2.520	0.063	2.516	0.047	-0.004	0.079
3-Carene	2.602	0.099	2.618	0.068	0.016	0.120
R-Limonene	2.506	0.141	2.585	0.074	0.079	0.159
1,8-Cineole	2.683	0.172	2.717	0.087	0.034	0.193
NIST – APE1145321						
α-Pinene	2.533	0.061	2.513	0.055	-0.020	0.082
3-Carene	2.616	0.115	2.573	0.046	-0.043	0.124
R-Limonene	2.519	0.183	2.505	0.052	-0.014	0.190
1,8-Cineole	2.697	0.198	2.689	0.027	-0.008	0.200
NPL – APE1145315						
α-Pinene	2.531	0.062	2.55	0.08	0.02	0.10
3-Carene	2.614	0.110	2.54	0.05	-0.07	0.12
R-Limonene	2.517	0.102	2.48	0.05	-0.04	0.11
1,8-Cineole	2.695	0.153	2.58	0.13	-0.12	0.20

[a] All values are shown as amount-of-substance fractions in nmol mol^{-1}. Uncertainties are shown as $k = 2$ expanded uncertainties.

[b] KCRV, key comparison reference value (see Section 2.4.4).

3.1 Degrees of equivalence

The consistency between the participating laboratory result and the KCRV is presented in terms of degrees of equivalence expressed quantitatively in two terms: (1) the deviation of the laboratory result from the KCRV, and (2) the $k = 2$ expanded uncertainty of this deviation. The degree of equivalence is defined as:

$$d_i = x_i - x_{\text{KCRV}} \tag{2}$$

where x_i denotes the amount-of-substance fraction reported by the participant and x_{KCRV} is the KCRV. The expanded uncertainty associated with d_i is defined as:

$$U(d_i) = \sqrt{U^2(x_i) + U^2(x_{\text{KCRV}})} \tag{3}$$

where $U(x_i)$ and $U(x_{\text{KCRV}})$ denote the $k = 2$ expanded uncertainties of the participant value and the KCRV, respectively. The degrees of equivalence and expanded uncertainties associated with the results of this key comparison are shown in Table 8 and Figure 11.

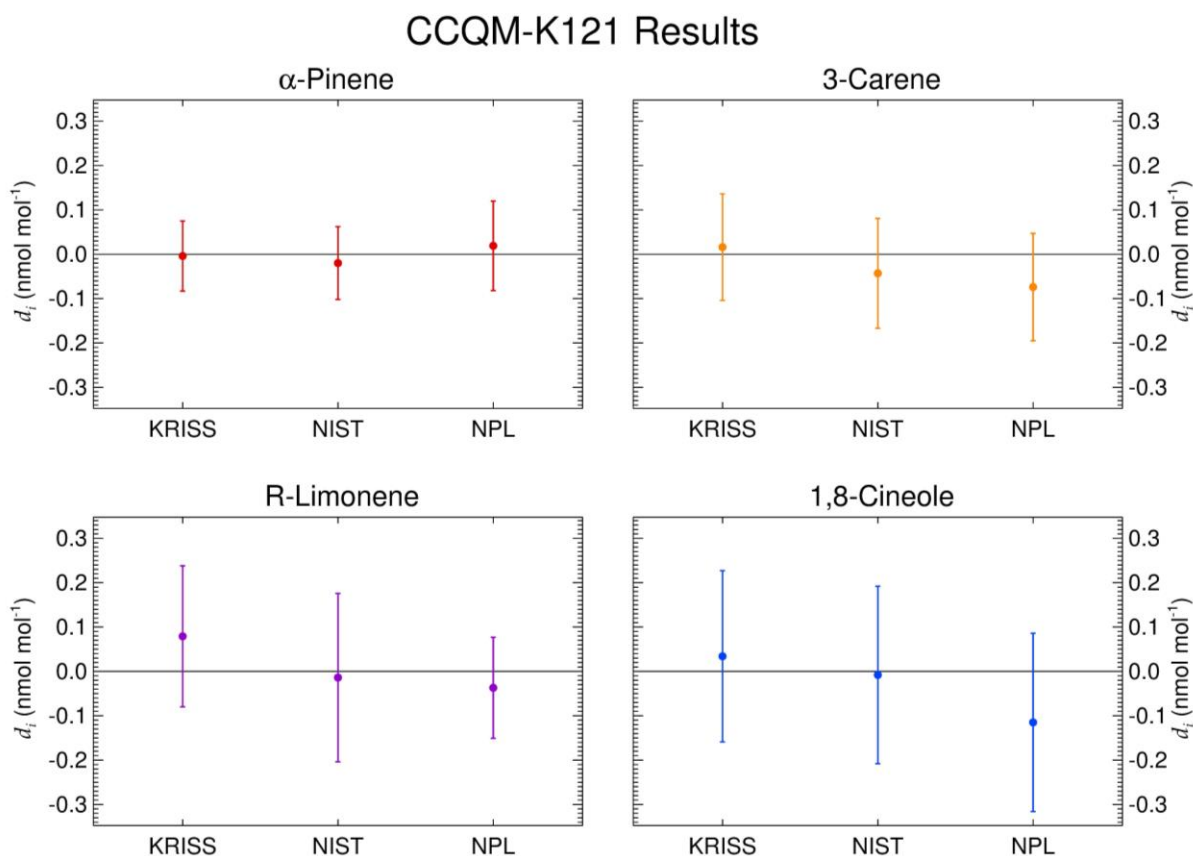**Figure 11.** Degrees of equivalence (d_i) between the participant value (x_i) and the KCRV (x_{KCRV}) for each monoterpene in the key comparison samples. Error bars represent $k = 2$ expanded uncertainties of the degrees of equivalence, $U(d_i)$.

4 Conclusions

All participant results agree with their KCRVs within the $k = 2$ expanded uncertainties for all monoterpenes evaluated in this key comparison.

5 How far the light shines statement (HFTLS)

This key comparison can be used to support CMC claims for the monoterpenes listed in Table 9 in a balance of nitrogen; it can also be used to extrapolate CMC claims for monoterpenes of similar difficulty (Table 10), as they have exhibited cylinder stability over time (see Figure 12). Furthermore, this key comparison may be used to extrapolate CMC claims for the above monoterpenes in a matrix of synthetic dry air, as preliminary testing demonstrates cylinder stability for approximately 300 days (Figure 13).

Table 9. How far the light shines for the monoterpenes measured in this key comparison

Component[a]	Accepted Range of Values
α-Pinene	1 to 500 nmol mol^{-1}
3-Carene	1 to 500 nmol mol^{-1}
R-Limonene	1 to 500 nmol mol^{-1}
1,8-Cineole	1 to 500 nmol mol^{-1}

[a] Monoterpene component in a balance of nitrogen or air.

Table 10. How far the light shines for additional monoterpenes of similar difficulty

Component[a]	Accepted Range of Values
β-Pinene	1 to 500 nmol mol^{-1}
Camphene	1 to 500 nmol mol^{-1}
α-Terpinene	1 to 500 nmol mol^{-1}
p-Cymene	1 to 500 nmol mol^{-1}

[a] Monoterpene component in a balance of nitrogen or air.

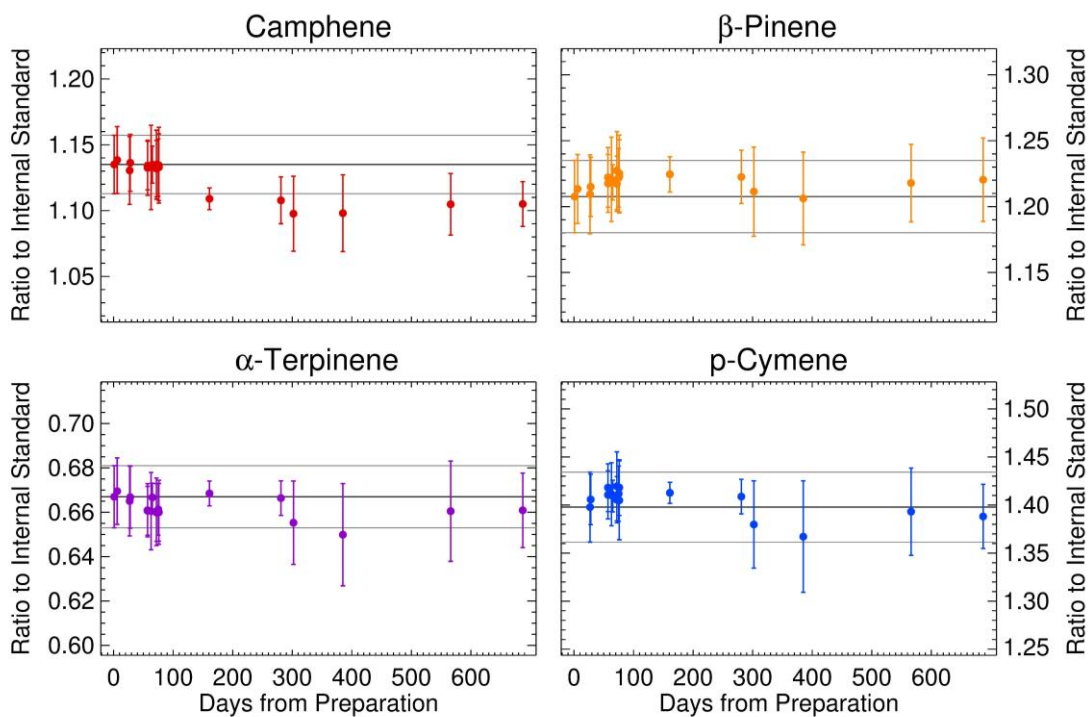**Figure 12.** Stability testing of monoterpene-in-nitrogen sample APE1135917, nominal amount-of-substance fraction of 225 nmol mol^{-1}. Individual data points represent response ratios of each monoterpene to the internal standard (*n*-octane). Error bars represent *k* = 2 expanded uncertainties. Dark and light gray lines represent the initial response ratios and *k* = 2 expanded uncertainties, respectively.
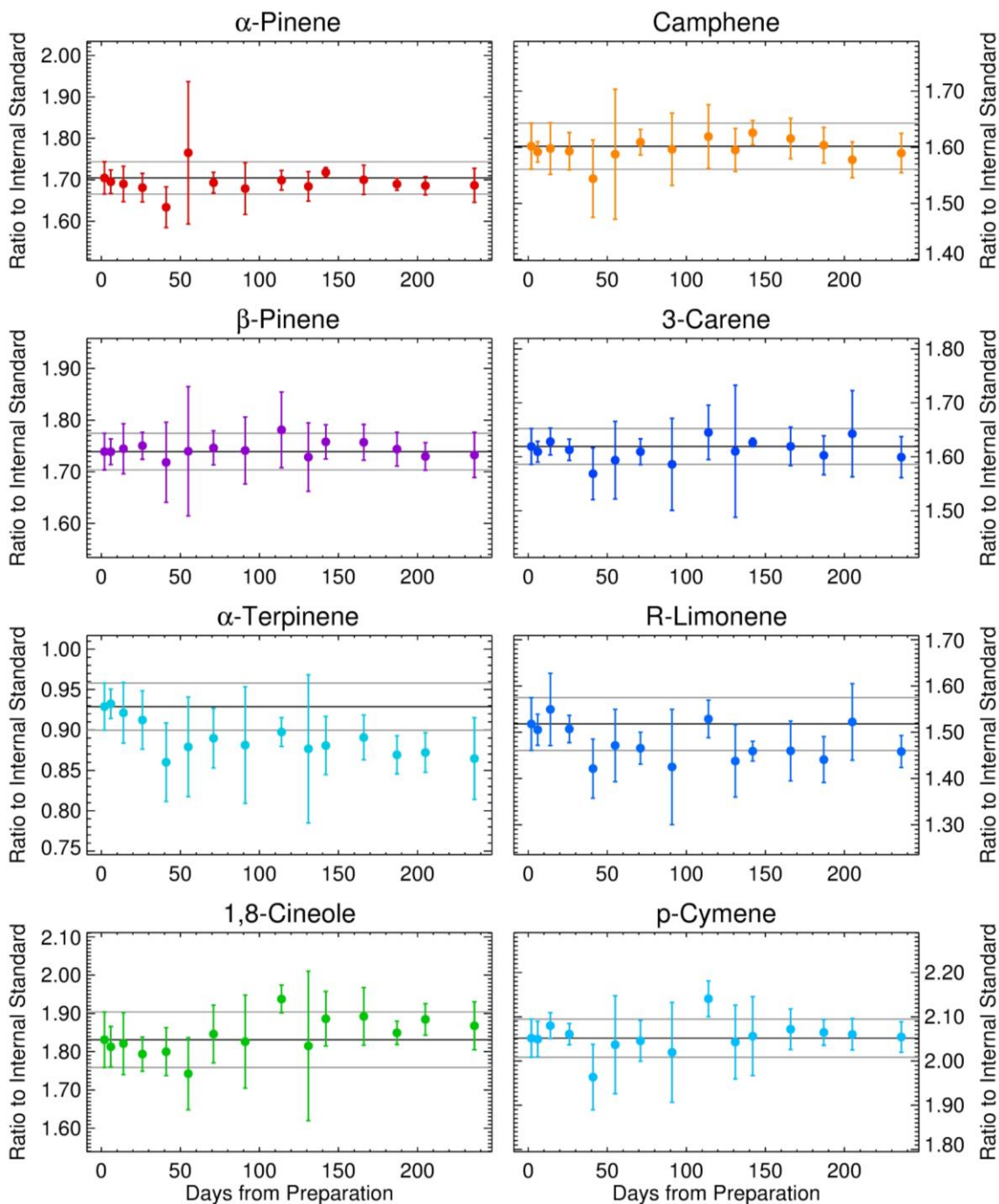
Figure 13. Stability testing of monoterpene-in-air sample APE1145335, diluted to a nominal amount-of-substance fraction of 2 nmol mol^{-1} from parent mixtures APE1135917 and APE1082180. Individual data points represent response ratios of each monoterpene to the internal standard (*n*-hexane). Error bars represent $k = 2$ expanded uncertainties. Dark and light gray lines represent the initial response ratios and $k = 2$ uncertainties, respectively.

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Appendix A

Measurement Report: KRISS

CCQM-K121 Measurement Report: Monoterpenes in Nitrogen

Laboratory: Korea Research Institute of Standards and Science
Laboratory code: KRISS
Participants: Yong Doo KIM, Dal Ho KIM, Sangil LEE

Cylinder No.: APE1145320
Nominal Concentration: 2.5 nmol mol^{-1}

Measurement No. 1	Date	Result (nmol mol^{-1})	Stand. deviation (% relative)	# of sub-measurements
α-pinene		2.517	0.05	
3-carene	9-December-2015	2.619	0.04	3
R-limonene		2.588	0.07	
1,8-cineole		2.718	0.13	

Measurement No. 2	Date	Result (nmol mol^{-1})	Stand. deviation (% relative)	# of sub-measurements
α-pinene		2.516	0.13	
3-carene	10-December-2015	2.617	0.21	3
R-limonene		2.585	0.06	
1,8-cineole		2.711	0.06	

Measurement No. 3	Date	Result (nmol mol^{-1})	Stand. deviation (% relative)	# of sub-measurements
α-pinene		2.515	0.23	
3-carene	12-December-2015	2.619	0.17	3
R-limonene		2.585	0.04	
1,8-cineole		2.726	0.08	

Summary Results:

Gas Mixture Component	Result (assigned value) (nmol mol^{-1})	Coverage factor	Assigned expanded uncertainty (nmol mol^{-1})
α-pinene	2.516		0.047
3-carene	2.618	2	0.068
R-limonene	2.585		0.074
1,8-cineole	2.717		0.087

Reference Method:
All analysis was carried out using GC-FID (6890, Agilent Technologies) with a cryogenic
concentrator (7200 Preconcentrator, Entech Instruments). Table 1 and 2 describe the method
parameters of the GC-FID and the cryogenic concentrator, respectively.

Table 1. Method parameters for the GC-FID system

GC-FID (Agilent 6890)	
Column	DB-624 (60m × 320 μm × 1.8 μm)
	Flow 2 mL/min (He)
Oven	130 °C (isothermal, 18 min), 20 °C /min, 210 °C (isothermal, 0.5 min)
Detector	250 °C (isothermal), H_2: 35 mL/min, Air: 300 mL/min, Makeup: 15 mL/min

Table 2. Method parameters for the cryogenic concentrator

	Trap temperature, °C	M1→ M2 temperature, °C	M2→M3 temperature, °C	Inject temperature, °C	Bake out temperature, °C
Mod 1 Trap	-10	10			150
Mod 2 Trap	-130	-130	230		220
Mod 3 Trap			-150	100	
Trapping sample					
Sample flow	100 mL/min				
Sample volume	500 mL				

Calibration Standards:
A set of primary standard gas mixtures (PSMs) was gravimetrically prepared for the comparison.
All source reagents were analyzed using GC-FID to determine their purities (based on peak
areas). Micro syringes were used to transfer the source reagents into cylinders for gravimetrically
prepared PSMs at 10 μmol/mol. The PSMs were further diluted with nitrogen to 150 nmol/mol
and then 2.5 nmol/mol (Figure 1). The PSMs at each step were analyzed against each other for
verification. Table 3 describes details of the composition of the reference PSM (D254233),
which was used to analyze the NIST mixture (one point calibration).
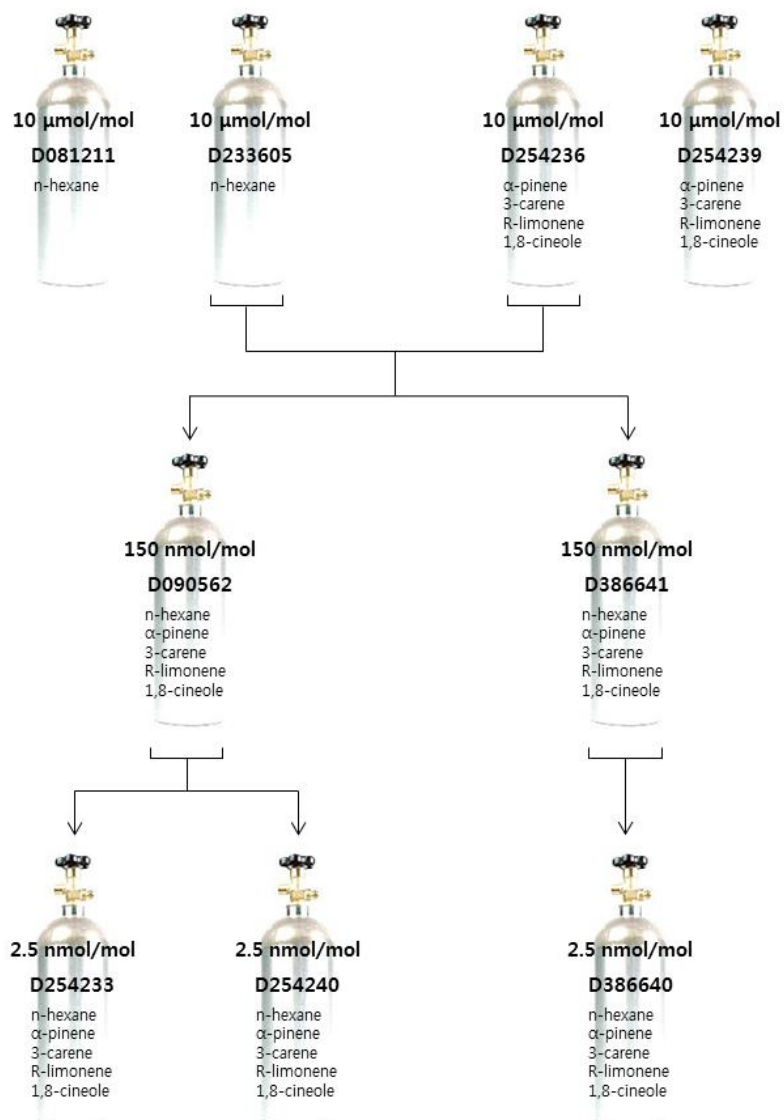
Figure 1. Hierarchy of KRISS PSMs

D254233 Component	Amount fraction, nmol mol^{-1}	Relative expanded uncertainty, %
α-pinene	2.634	1.8
3-carene	2.461	2.5
R-limonene	2.489	2.8
1,8-cineole	2.491	3.1

Instrument Calibration:
The KRISS and the NIST mixture were analyzed using a GC-FID with a cryogenic concentrator. The analysis method consisted of six sample injections by alternating between the two cylinders (i.e., $PSM_{KRISS} - PSM_{NIST} - PSM_{KRISS} - PSM_{NIST} - PSM_{KRISS} - PSM_{NIST} - PSM_{KRISS}$).

Sample Handling:
After its arrival, the NIST mixture was stored in an analytic laboratory, together with the KRISS mixture, until the comparison analysis.

Uncertainty:
The measurement uncertainty consists of uncertainties from two sources such as the gravimetric preparation of the KRISS PSM and the comparison analysis. The gravimetric preparation uncertainty includes uncertainties from impurity analysis, molecular weight, weighing process, short-term stability (i.e., absorption on the internal surface of a cylinder), and internal consistency (i.e., the reproducibility of the gravimetric preparation). The analytical uncertainty is comprised of reproducibility, repeatability, and drift of GC measurements.
The amount mole fractions of NIST cylinder are determined by the following equation.

$$x_{NIST} = x_{KRISS} \times R_{avg}$$

(1)

where x_{NIST} is the amount mole fraction of NIST PSM, x_{KRISS} is the amount mole fraction of KRISS PSM, and R_{avg} is the average of GC peak area ratios (i.e., peak area of NIST PSM to peak area of KRISS PSM) for nine measurements during three days.

The combined standard uncertainty is estimated as

$$u(x_{NIST}) = \sqrt{u^2(x_{KRISS}) + u^2(R_{avg})}$$

Table 3. Uncertainty budget for α-pinene

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$, nmol mol^{-1}
Gravimetric preparation (x_{KRISS})	2.634 nmol mol^{-1}	Normal distribution	0.024 nmol mol^{-1}	x_{NIST}/x_{KRISS}	$0.009 \times x_{NIST}$
Response ratio	0.956	Normal distribution	0.002	x_{NIST}/R_{avg}	$0.002 \times x_{NIST}$

Coverage factor: 2
Expanded uncertainty: 0.047 nmol mol^{-1}

Table 4. Uncertainty budget for 3-carene

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$, nmol mol^{-1}
Gravimetric preparation (x_{KRISS})	2.461 nmol mol^{-1}	Normal distribution	0.031 nmol mol^{-1}	x_{NIST}/x_{KRISS}	$0.013 \times x_{NIST}$
Response ratio	1.064	Normal distribution	0.003	x_{NIST}/R_{avg}	$0.003 \times x_{NIST}$

Coverage factor: 2
Expanded uncertainty: 0.068 nmol mol^{-1}

Table 5. Uncertainty budget for R-limonene

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$, nmol mol^{-1}
Gravimetric preparation (x_{KRISS})	2.489 nmol mol^{-1}	Normal distribution	0.035 nmol mol^{-1}	x_{NIST}/x_{KRISS}	$0.014 \times x_{NIST}$
Response ratio	1.039	Normal distribution	0.002	x_{NIST}/R_{avg}	$0.002 \times x_{NIST}$

Coverage factor: 2
Expanded uncertainty: 0.074 nmol mol^{-1}

Table 6. Uncertainty budget for 1,8-cineole

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$, nmol mol^{-1}
Gravimetric preparation (x_{KRISS})	2.491 nmol mol^{-1}	Normal distribution	0.039 nmol mol^{-1}	x_{NIST}/x_{KRISS}	$0.016 \times x_{NIST}$
Response ratio	1.091	Normal distribution	0.004	x_{NIST}/R_{avg}	$0.004 \times x_{NIST}$

Coverage factor: 2
Expanded uncertainty: 0.087 nmol mol^{-1}

Appendix B

Measurement Report: NPL

CCQM-K121 Measurement Report: Monoterpenes in Nitrogen

Laboratory: National Physical Laboratory
Cylinder No.: D201796
Nominal Concentration: 2.5 nmol/mol

Measurement 1 : GC-FID

Component	Date	Result (nmol/mol)	standard uncertainty (nmol/mol)	No. of replicates
α-pinene	23/09/2015	2.56	0.08	3
3-carene	23/09/2015	2.53	0.05	3
R-limonene	23/09/2015	2.48	0.07	3
1,8-cineole	23/09/2015	2.59	0.19	3

Measurement 2 : GC-FID

Component	Date	Result (nmol/mol)	standard uncertainty (nmol/mol)	No. of replicates
α-pinene	24/09/2015	2.55	0.07	3
3-carene	24/09/2015	2.54	0.07	3
R-limonene	24/09/2015	2.48	0.05	3
1,8-cineole	24/09/2015	2.61	0.07	3

Measurement 3 : GC-FID

Component	Date	Result (nmol/mol)	standard uncertainty (nmol/mol)	No. of replicates
α-pinene	27/10/2015	2.54	0.11	3
3-carene	27/10/2015	2.53	0.06	3
R-limonene	27/10/2015	2.47	0.06	3
1,8-cineole	27/10/2015	2.57	0.22	3

Measurement 4 : GC-FID

Component	Date	Result (nmol/mol)	standard uncertainty (nmol/mol)	No. of replicates
α-pinene	28/10/2015	2.55	0.09	6
3-carene	28/10/2015	2.54	0.06	6
R-limonene	28/10/2015	2.48	0.04	6
1,8-cineole	28/10/2015	2.58	0.10	5

Measurement 5 : GC-FID

Component	Date	Result (nmol/mol)	standard uncertainty (nmol/mol)	No. of replicates
α-pinene	28/10/2015	2.55	0.08	6
3-carene	28/10/2015	2.54	0.06	6
R-limonene	28/10/2015	2.48	0.05	6
1,8-cineole	28/10/2015	2.58	0.08	5

Summary Results:

Component	Date	Result (nmol/mol)	expanded uncertainty (nmol/mol)	coverage factor
α-pinene	24/11/2015	2.55	0.08	2
3-carene	24/11/2015	2.54	0.05	2
R-limonene	24/11/2015	2.48	0.05	2
1,8-cineole	24/11/2015	2.58	0.13	2

Reference Method

The amount fraction of the monoterpene components in the comparison mixture were measured using a gas chromatograph (Varian CP3800) with flame ionisation detector (GC-FID). The system uses a sample pre-concentration trap containing glass beads to accumulate the analytes prior to injection and separation on the GC column (Varian CP-Sil 13 column, 75 m x 0.53 mm, 2.0 μm phase thickness).

Calibration Standards

Two NPL Primary Reference Gas Mixtures (PRGMs) containing the four monoterpene components and *n*-octane with nominal concentrations of 2.5 nmol/mol in a nitrogen matrix were prepared independently in accordance with ISO 6142. Four binary mixtures of each monoterpene component were prepared at 5 μmol/mol by liquid injection (via a transfer vessel) of individual pure monoterpene components into evacuated cylinders followed by the addition of nitrogen by direct filling. A 10 μmol/mol parent mixture of *n*-octane was prepared in the same way. A 100 nmol/mol mixture of the five components was then prepared by direct transfer of the parent mixtures and dilution with nitrogen. A final dilution stage was carried out to prepare the PRGMs used in the comparison (D090584 and D386637). Mixtures were prepared in 10 litre treated cylinders from Air Products, Belgium.

Both mixtures were used to determine the amount fractions of the monoterpene components in the comparison mixture. The amount fraction of the PRGM (D090584) was 2.361 ± 0.013 nmol/mol *n*-octane, 2.551 ± 0.023 nmol/mol α-pinene, 2.418 ± 0.018 nmol/mol 3-carene, 2.470 ± 0.022 nmol/mol R-limonene and 2.499 ± 0.015 nmol/mol 1,8-cineole. The amount fraction of the PRGM (D386637) was 2.511 ± 0.013 nmol/mol *n*-octane, 2.587 ± 0.023 nmol/mol α-pinene, 2.828 ± 0.021 nmol/mol 3-carene, 2.517 ± 0.023 nmol/mol R-limonene and 2.500 ± 0.015 nmol/mol 1,8-cineole. Expanded (*k* = 2) uncertainties are stated.

Instrument Calibration

The PRGMs were prepared with monoterpene amount fractions that had nominally similar composition to the comparison mixture. This was to minimise any uncertainty contribution for non-linear deviations in the analyser response. The samples were collected in the sample pre-concentration trap to ensure peaks were sufficiently large to reduce measurement uncertainty.

Sample Handling

The mixture being analysed was connected to the GC using Silcosteel-passivated 1/16" stainless steel tubing via a minimised dead volume connector. The flow rate was set to 50 ml min^{-1} using an in-line NPL-designed flow restrictor and maintained throughout the analysis.

The lines were thoroughly purged and flow rates were allowed to stabilise for at least 10 minutes before commencing analysis. The method was set up to alternate between the NPL and comparison mixture. Up to 6 injections of each mixture were performed in order to obtain a comprehensive dataset.

Uncertainty

The ratio of the GC-FID response from the comparison mixture and the NPL PRGM was calculated using:

$$r = \frac{2A_{u,m}}{(A_{s,m} + A_{s,m+1})}$$

Where $A_{u,m}$ is the peak area from repeat m of the comparison mixture, and $A_{s,m}$ is the peak area from repeat m of the NPL PRGM.

And the average ratio ($\bar{r}$) is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Where n is the number of ratios. The amount fraction of the target component in the comparison mixture, x_u, is then calculated by:

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

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:

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

The table which follows details the uncertainty analysis for an example measurement of α-pinene.

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_s	nmol/mol	2.551	0.0161	1.0013	0.0161	A	normal
$\bar{r}$	-	1.0013	0.0307	2.5507	0.0782	A	normal
x_u	nmol/mol	2.554					
$u(x_u)$	nmol/mol	0.0799					
$U(x_u)$	nmol/mol	0.1597					

To obtain the final result for α-pinene, an average was taken for the five measurements. The following table shows the calculation of the final results and its uncertainty.

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_1	nmol/mol	2.560	0.0752	0.20	0.0150	A	normal
x_2	nmol/mol	2.554	0.0733	0.20	0.0147	A	normal
x_3	nmol/mol	2.541	0.1078	0.20	0.0216	A	normal
x_4	nmol/mol	2.550	0.0871	0.20	0.0174	A	normal
x_5	nmol/mol	2.554	0.0799	0.20	0.0160	A	normal
x_f	nmol/mol	2.552					
$u(x_f)$	nmol/mol	0.038					
$U(x_f)$	nmol/mol	0.077					

Where x_1-x_5 is the measurement number and x_f is the final value of the amount fraction of α-pinene in the comparison mixture.

Authorship

Nicholas D C Allen, Marivon Corbel, David R Worton, Richard J C Brown and Paul J Brewer

Appendix C

Measurement Report: NIST

CCQM-K121 Measurement Report: Monoterpenes in Nitrogen

Laboratory: National Institute of Standards and Technology (NIST)
Laboratory code: NIST

Cylinder No.: APE1145321
Nominal Concentration: 2.5 nmol mol^{-1}

Measurement No. 1	Date	Result (nmol mol^{-1})	Stand. deviation (nmol mol^{-1})	# of sub-measurements
α-Pinene		2.521	0.015	3
3-Carene	8 Sept 2015	2.632	0.018	3
R-Limonene		2.540	0.012	3
1,8-Cineole		2.678	0.018	3

Measurement No. 2	Date	Result (nmol mol^{-1})	Stand. deviation (nmol mol^{-1})	# of sub-measurements
α-Pinene		2.527	0.010	3
3-Carene	9 Sept 2015	2.581	0.010	3
R-Limonene		2.487	0.050	3
1,8-Cineole		2.697	0.017	3

Measurement No. 3	Date	Result (nmol mol^{-1})	Stand. deviation (nmol mol^{-1})	# of sub-measurements
α-Pinene		2.524	0.012	3
3-Carene	10 Sept 2015	2.610	0.012	3
R-Limonene		2.480	0.013	3
1,8-Cineole		2.691	0.011	3

Summary Results:

Gas Mixture Component	Result (assigned value) (nmol mol^{-1})	Coverage factor	Assigned expanded uncertainty (nmol mol^{-1})
α-Pinene	2.513	2	0.055
3-Carene	2.573	2	0.046
R-Limonene	2.505	2	0.052
1,8-Cineole	2.689	2	0.027

Reference Method:
Describe your instrument(s) (principles, make, type, configuration, data collection, etc.):

All measurements were taken on an Agilent 7890 GC/FID. The FID was operated at 250 °C with a fuel mixture of 30 mL min^{-1} hydrogen and 400 mL min^{-1} air. The instrument was equipped with a 60 m by 0.32 mm capillary column coated with a 0.25 μm film of AT-Wax. All GC samples were cryogenically trapped on the head of a pre-column using a Nutech 3351DS preconcentrator. A 200-mL sample was collected at a flow rate of 100 mL min^{-1} prior to injection.

Agilent Chemstation data system was used for peak area integration with the data transferred to Excel via macro program.

Calibration Standards:
Describe your calibration standards for the measurements (preparation method, purity analyses, estimated uncertainty, etc.):

The 4-component monoterpene-in-nitrogen PSMs were prepared in 20-L aluminum gas cylinders, equipped with DIN-1 stainless steel valves and pretreated with the proprietary process Experis by Air Products, Belgium. The cylinders were connected to a fill manifold, along with Airgas built in purifier (BIP) N_2. The contents of the cylinders were vented and evacuated to a pressure of approximately 3 µm Hg. The cylinders were then filled with 300 psi of BIP N_2, rolled, and re-evacuated to approximately 3 µm Hg. Mass measurements were determined for each of the evacuated cylinders using a Mettler SR64001 single-pan balance, with a capacity of 64 kg and a sensitivity of 0.1 g. The cylinders were weighed a total of five times. Cylinders APE1161693, APE1145326 and APE1145327 were connected to the fill manifold with parent mixture APE1135902, nominal 200 nmol mol^{-1} α-pinene, 3-carene, R-limonene and 1,8-cineole, with n-octane as an internal standard. Each cylinder was filled to a predetermined pressure with the parent mixture and set aside to equilibrate for approximately 2 hours.

Cylinders APE1145334 and APE1145336 were connected to the fill manifold with parent mixture APE1082180, nominal 200 nmol mol^{-1} α-pinene, 3-carene, R-limonene and 1,8-cineole, with n-hexane as an internal standard. Each cylinder was filled to a predetermined pressure with the parent mixture and set aside to equilibrate overnight. Five mass measurements were taken for each cylinder after addition of the parent mixture.

All cylinders were connected to the fill manifold along with Airgas BIP N_2 balance gas then filled with N_2 to a predetermined pressure and allowed to equilibrate overnight. Five mass measurements were taken for each cylinder after addition of the balance gas. After final weighing, all cylinders were rolled a minimum of 3 hours.

Several Airgas BIP N_2 cylinders were used in the preparation of these five PSMs. Each cylinder was analyzed individually for argon (Ar) and monoterpene impurities. The assay of the N_2 balance gas was considered as a collective lot of one Ar concentration (17.72 $\pm$ 4.90 µmol mol^{-1}).

Table 1: Gravimetric concentrations of components in PSM cylinders

PSM	Amount-of-Substance Fraction (nmol mol^{-1})[a]				
Cylinder No.	α-Pinene	3-Carene	R-Limonene	1,8-Cineole	Int Std[b]
APE1161693	2.111 ± 0.017	2.180 ± 0.018	2.100 ± 0.017	2.248 ± 0.018	2.308 ± 0.018
APE1145326	2.518 ± 0.022	2.600 ± 0.023	2.504 ± 0.022	2.681 ± 0.023	2.752 ± 0.024
APE1145327	3.411 ± 0.029	3.522 ± 0.030	3.392 ± 0.028	3.632 ± 0.030	3.728 ± 0.031
APE1145334	1.576 ± 0.019	1.538 ± 0.019	1.591 ± 0.020	1.561 ± 0.019	1.546 ± 0.019
APE1145336	3.093 ± 0.021	3.020 ± 0.020	3.122 ± 0.021	3.063 ± 0.021	3.035 ± 0.020

[a]Expanded uncertainties are shown with a confidence interval of approximately 95 %.
[b]Int Std, Internal Standard, included in mixtures for stability testing. Int Std is n-octane in cylinders APE1161693, APE1145326 and APE1145327, and n-hexane in cylinders APE1145334 and APE1145336.

Instrument Calibration:
Describe your calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction, etc.):

The GC-FID was calibrated using a suite of five PSMs ranging in concentration for each of the 4 monoterpene components in a balance of N2 (Table 1). For each measurement, CCQM-K121 sample APE1145321 was used as the analytical control, and was sampled both before and after each PSM measurement to allow for correction of the response for instrument drift. CCQM-K121 was rigorously compared to the PSM sample a total of five times over three analytical periods. A response ratio for each measurement was determined by dividing the measured monoterpene component response of each sample by the monoterpene component response of the control. The ratios and concentrations for the five PSMs were then plotted to a first-order regression using the ISO 6143 GenLine program, from which the CCQM-K121 sample concentration was determined.

Sample Handling:
How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument (automatic, high pressure, mass-flow controller, dilution, etc.)?

All standards and the K-121 sample were brought into the lab and set next to the GC to be used. They were allowed to stabilize for 24 hours. Stainless steel 2-stage, low dead volume, regulators were used and the sample lines were 0.16 cm stainless steel.   The samples were pre-concentrated in stainless steel traps then cryofocused on the head of the capillary column.

Uncertainty:
There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they either have to be taken into account or they can be neglected.

NIST measured the mass fraction of each terpene in the CCQM-K121 sample by taking the following steps, which are consistent with the guidance in NIST TN 1900 ("Simple Guide for Evaluating and Expressing the Uncertainty of NIST Measurement Results"), an authoritative reference for uncertainty evaluation according to the NIST Quality Manual (QM-I):

(1) We built an analysis function (which was a polynomial of either the first or second degree, depending on the terpene) for the target terpene based on replicated instrumental indications obtained for several standard gas mixtures with certified values of the mass fraction of the terpene as described in ISO 6143 (A-2);

(2) We applied the Monte Carlo method of the GUM Supplement 1 to obtain a sample of 10000 replicates of the analysis function that express the uncertainties associated with the instrumental responses and with the certified mass fractions;

(3) We evaluated each of those 10000 replicates of the analysis function at each replicate of the instrumental response obtained for the CCQM-K121 sample. The measured value of the target terpene's mass fraction was the average of these evaluations, and the associated standard uncertainty was their standard deviation. The expanded uncertainty (for 95 % coverage) was half the length of a 95 % coverage interval for the true mass fraction centered at the measured value.

Coverage factor: 2
Expanded uncertainty: See Summary Table above.