

Pilot Comparison CCQM-P177 – 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

BAM, NIST

Organizing body

CCQM-GAWG

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Abstract

Growing awareness of the impact of monoterpenes on climate, atmospheric chemistry, and indoor air quality has necessitated the development of measurement standards to globally monitor and control their emissions. For National Metrology Institutes to develop such standards, it is essential that they demonstrate measurement equivalence for assigned values at the highest levels of accuracy. This report describes the results of a pilot comparison for 4 key monoterpene species: α -pinene, 3-carene, *R*-limonene and 1,8-cineole, at a nominal amount-of-substance fraction of $2.5 \text{ nmol mol}^{-1}$. The objective of this comparison is to evaluate participant 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 the photochemical production of tropospheric ozone and 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]. In the indoor environment, VOC emissions from construction products (such as building materials and furniture) can have a significant impact on the localized air quality. As a result, VOC measurements have also become a growing concern for the health evaluation of products designated for interior use [3, 4].

VOC sources can be either biogenic or anthropogenic, with the most important biogenic VOCs being isoprene, isoprenoids and monoterpenes [5]. There has been considerable interest in measuring ambient monoterpene levels, along with their emission rates from terrestrial vegetation and industrial processes, which has led to the need for stable, accurate reference standards. 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 these standards in compressed gas cylinders. Several monoterpene-in-nitrogen standards have been developed and compared between a limited number of NMIs with some success; these developments have culminated in key comparison CCQM-K121 of monoterpenes in nitrogen [6].

This report describes the results of a pilot 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 $2.5 \text{ nmol mol}^{-1}$. The objective of this pilot comparison is to assess participant measurement capabilities for monoterpenes at trace levels.

2 Design and organization of the pilot 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 pilot comparison.

Table 1. Lists of participants in CCQM-P177

Acronym	Country	Institute
BAM	DE	Federal Institute for Materials Research and Testing Berlin, Germany
NIST	US	National Institute of Standards and Technology Gaithersburg, Maryland, United States of America

2.3 Schedule

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

Table 2. CCQM-P177 schedule

Date	Task completed
October 2014	Preparation, verification and stability testing of mixtures by NIST
August 2015	Receipt of cylinder gas mixtures by participants
September 2015	Analysis of mixtures by participants
January 2016	Data submitted to NIST
February 2016	Return of cylinders to NIST
March 2016	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 comparison were prepared in 20-L aluminum gas cylinders treated with *Experis*, a proprietary process by Air Products, Belgium used to passivate the internal walls¹. Previously reported research on monoterpenes in cylinders demonstrates that this container/treatment combination

provides the most consistent stability results [7, 8]. 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 pilot 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. More information regarding the preparation and analysis of the parent mixtures can be found in the CCQM-K121 Final Report [6].

Table 3. Gravimetric values of parent mixtures used for CCQM-P177

Compound	Amount-of-Substance Fraction (nmol mol ⁻¹) ^a	
	<i>APE1135902</i>	<i>APE1082180</i>
α -Pinene	222.53 ± 0.39	229.70 ± 0.40
3-Carene	229.83 ± 0.51	224.24 ± 0.38
<i>R</i> -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.

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 pilot comparison samples. 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 [6, Section 2.4.2]. The PSMs were verified using ISO 6143 GenLine linear regression [9, 10] and tested for stability over time, as discussed in the CCQM-K121 Final Report [6].

The gravimetric values and uncertainties for each PSM are listed in Table 4. The final uncertainties are expressed as expanded uncertainties, $U = k \cdot u_{\text{grav}}$, 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.

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.

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

Cylinder	Amount-of-Substance Fraction (nmol mol ⁻¹) ^a				
	<i>α</i> -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.

2.4.3 Pilot comparison samples

The pilot comparison samples 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 of the CCQM-K121 Final Report [6].

The gravimetric amount-of-substance fractions of each pilot comparison sample were verified against the NIST in-house PSMs over approximately 3 months (March through June 2015), using ISO 6143 GenLine linear regression [9, 10]. Based on the agreement between the predicted (x_{ver}) and gravimetric (x_{grav}) values (see Figure 1 and Table 5), the samples were deemed appropriate for this comparison and delivered to the participants. The verification amount-of-substance uncertainties, $u(x_{\text{ver}})$, were computed for each pilot sample from the PSMs fitted to GenLine.

To ensure that no significant changes to the monoterpene mixtures occurred over the course of the comparison, the pilot comparison samples were reverified after analysis by the participants. APE1145321 was reverified using ISO 6143 GenLine in November through December 2015. APE1145316 was reverified by single-point calibration with two NIST PSMs in June through August 2016. Single-point calibration was used in lieu of GenLine to conserve gas pressure in the NIST PSMs. Results from both verification periods are shown in Figure 1; the consistency between the two indicates that the mixtures remained stable throughout the entire pilot comparison.

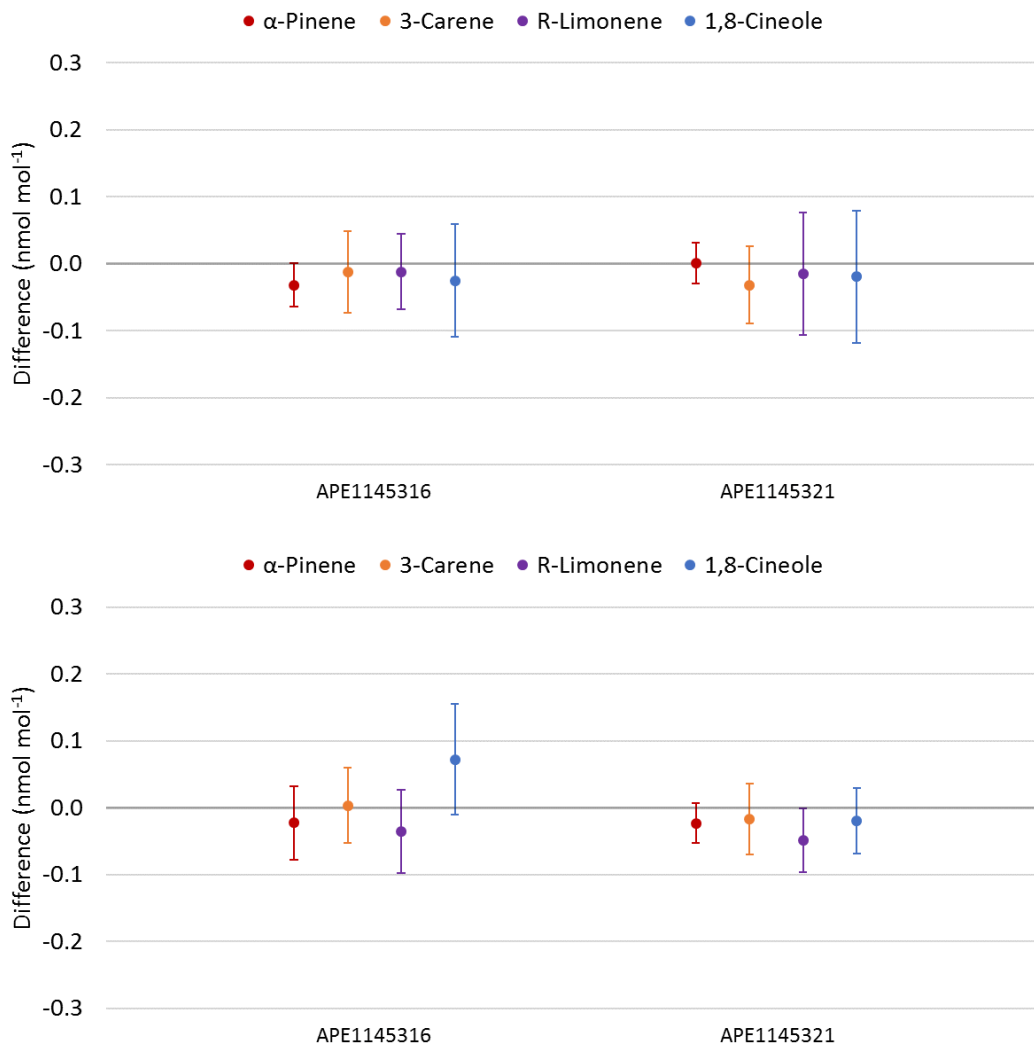


Figure 1. Differences between the predicted and gravimetric amount-of-substance fractions for each pilot comparison sample, expressed as nmol mol^{-1} . The top and bottom figures represent the initial verification and reverification analyses, respectively. Error bars represent combined standard uncertainties.

Table 5. Verification analysis of CCQM-P177 samples^a

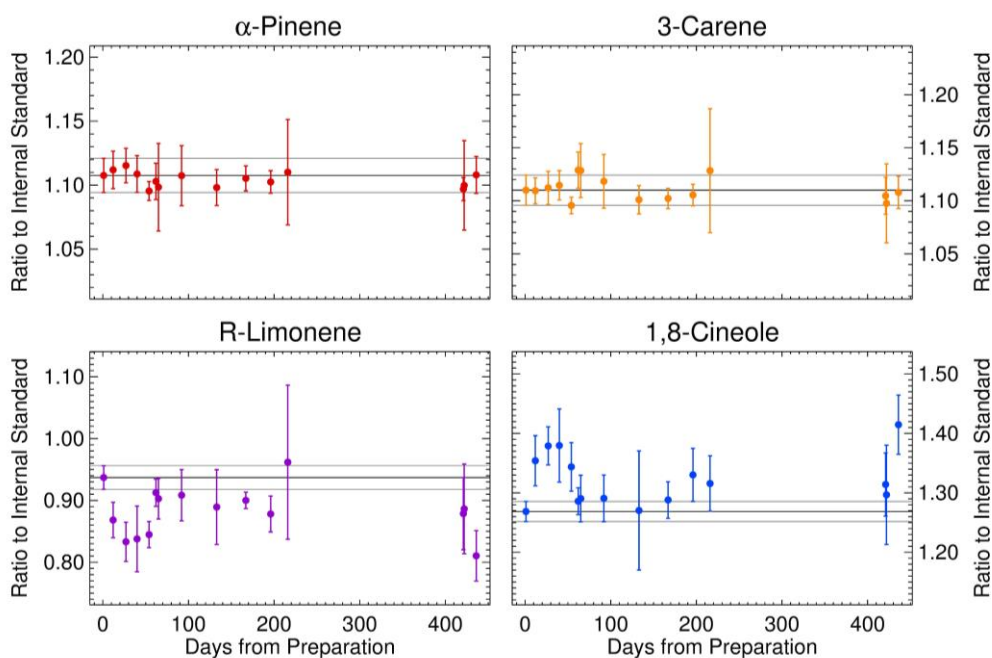
	APE1145316		APE1145321	
	<i>value</i>	<i>u^b</i>	<i>value</i>	<i>u^b</i>
α-Pinene				
x_{ver} (nmol mol ⁻¹)	2.492	0.032	2.534	0.028
x_{grav} (nmol mol ⁻¹)	2.524	0.008	2.533	0.012
<i>Difference (nmol mol⁻¹)</i>	-0.032	0.033	0.001	0.030
<i>Difference (%)</i>	-1.3 %	1.3 %	0.03%	1.2%
3-Carene				
x_{ver} (nmol mol ⁻¹)	2.593	0.060	2.584	0.056
x_{grav} (nmol mol ⁻¹)	2.606	0.008	2.616	0.013
<i>Difference (nmol mol⁻¹)</i>	-0.013	0.061	-0.032	0.058
<i>Difference (%)</i>	-0.49 %	2.4 %	-1.2%	2.2%
R-Limonene				
x_{ver} (nmol mol ⁻¹)	2.498	0.056	2.504	0.091
x_{grav} (nmol mol ⁻¹)	2.510	0.008	2.519	0.012
<i>Difference (nmol mol⁻¹)</i>	-0.012	0.057	-0.015	0.092
<i>Difference (%)</i>	-0.47 %	2.3 %	-0.6%	3.7%
1,8-Cineole				
x_{ver} (nmol mol ⁻¹)	2.662	0.084	2.678	0.098
x_{grav} (nmol mol ⁻¹)	2.687	0.008	2.697	0.013
<i>Difference (nmol mol⁻¹)</i>	-0.025	0.084	-0.019	0.099
<i>Difference (%)</i>	-0.95 %	3.2 %	-0.72%	3.7%

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

^b *u*, combined standard uncertainty.

In addition to reverification, the pilot comparison samples were tracked for stability using the internal standard, *n*-octane, both prior to and after analysis by the participants (Figure 2). The internal standard was also tracked for stability by comparison to other *n*-octane PSMs (not shown).

(i) Stability of Monoterpenes in APE1145316



(ii) Stability of Monoterpenes in APE1145321

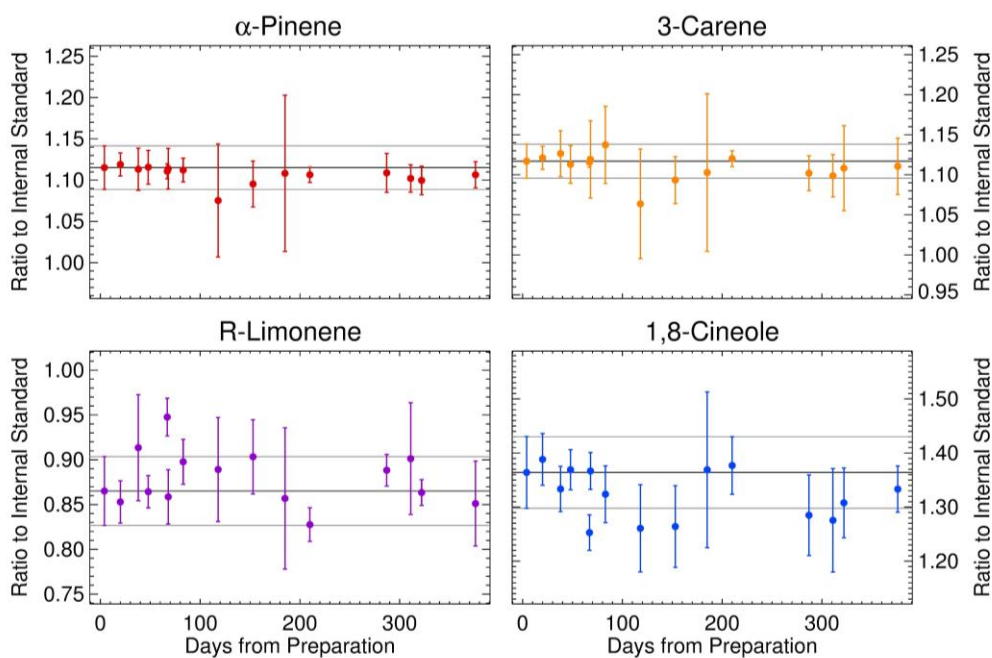


Figure 2. Stability testing of the pilot comparison samples over time from the date of mixture preparation. Individual data points represent response ratios of each monoterpene to the internal standard. Error bars represent approximate 95 % confidence intervals. Dark and light gray lines represent the initial response ratios and their approximate 95 % confidence intervals, respectively.

Based on a statistical analysis of the sample stability data, only α -pinene in sample APE1145321 yielded a slope significantly different from zero: $-4.6 \times 10^{-5} \text{ nmol mol}^{-1} \text{ day}^{-1}$ (Figure 3). Sample APE1145321 was measured by NIST for this pilot comparison approximately 228 days after preparation; therefore, the overall change in the amount-of-substance fraction of α -pinene was $-0.010 \text{ nmol mol}^{-1}$ (-0.40% relative). Since this change fell within the combined standard uncertainty of the gravimetric value ($0.012 \text{ nmol mol}^{-1}$), no correction for drift was applied.

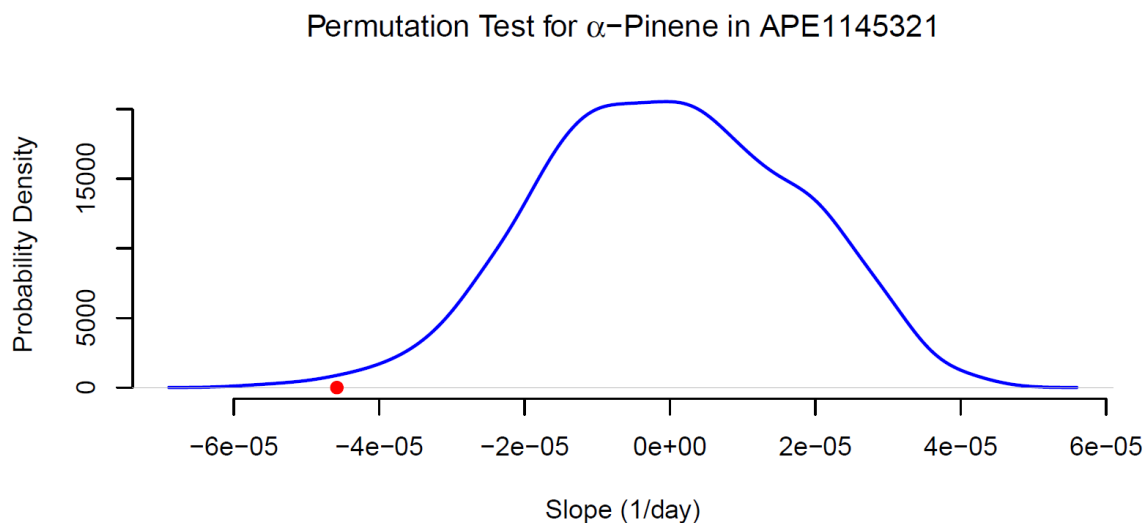


Figure 3. Smooth histogram of the slopes obtained in a permutation test for the slope of the relation between the ratio and day, for α -pinene in APE1145321. For only 6 of 1000 permutations of the data over the days did the slope have a value farther from 0 than obtained with the data in their actual temporal order (indicated by the red dot).

2.4.4 Reference values (RVs) and uncertainties

The reference value (x_{RV}) 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:

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

where $u(x_{grav})$ and $u(x_{ver})$ represent the gravimetric and verification uncertainties, respectively. The RVs and associated uncertainties for each sample in this comparison are listed in Table 6. The final uncertainties are expressed as expanded uncertainties, $U(x_{RV}) = ku(x_{RV})$, 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 $\pm U(x_{RV})$ with about 95 % confidence.

Table 6. Amount-of-substance fractions and uncertainties of CCQM-P177 samples^a

Sample	Component	x_{RV}	$u(x_{grav})^b$	$u(x_{ver})^b$	$u(x_{RV})^b$	$U(x_{RV})^c$
APE1145316						
	α -Pinene	2.524	0.008	0.032	0.033	0.065
	3-Carene	2.606	0.008	0.060	0.061	0.122
	<i>R</i> -Limonene	2.510	0.008	0.056	0.057	0.114
	1,8-Cineole	2.687	0.008	0.084	0.084	0.168
	<i>Int Std</i> ^d	2.758	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
	<i>R</i> -Limonene	2.519	0.012	0.091	0.092	0.183
	1,8-Cineole	2.697	0.013	0.098	0.099	0.198
	<i>Int Std</i> ^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. These methods are summarized in Table 7 and detailed in the Appendices.

Table 7. Measurement and calibration methods used by participating laboratories

Laboratory	Measurement method	Calibration method	Traceability
BAM	GC-MS with thermal desorption	Six-point calibration	BAM-prepared dilution standards
NIST	GC-FID with preconcentration	Linear calibration curve, ISO 6143 [9, 10]	NIST-prepared gravimetric standards

3 Results

The CCQM-P177 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. Please note that the NIST results for this comparison are based on the results from NIST's participation in CCQM-K121 [6].

Table 8. Summarized results for CCQM-P177^a

	RV ^b		Measurement		Difference ($x_i - x_{RV}$)	
	x_{RV}	$U(x_{RV})$	x_i	$U(x_i)$	D_i	$U(D_i)$
BAM – APE1145316						
α -Pinene	2.524	0.065	2.36	0.94	-0.16	0.94
3-Carene	2.606	0.122	2.54	1.02	-0.07	1.03
<i>R</i> -Limonene	2.510	0.114	2.12	0.84	-0.39	0.85
1,8-Cineole	2.687	0.168	1.89	0.76	-0.80	0.78
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
<i>R</i> -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

^aAll values are shown as amount-of-substance fractions in nmol mol⁻¹. Uncertainties are shown as $k = 2$ expanded uncertainties.

^bRV, reference value (see Section 2.4.4).

3.1 Differences

The consistency between the participating laboratory result and the RV is presented in terms of difference, expressed quantitatively in two terms: (1) the deviation of the laboratory result from the RV, and (2) the expanded uncertainty of this deviation. The difference, D_i , is defined as:

$$D_i = x_i - x_{RV} \quad (2)$$

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

$$U(D_i) = \sqrt{U^2(x_i) + U^2(x_{RV})} \quad (3)$$

where $U(x_i)$ and $U(x_{RV})$ denote the $k = 2$ expanded uncertainties of the participant value and the RV, respectively. The differences and expanded uncertainties associated with the results of this comparison are shown in Table 8 and Figure 4.

CCQM-P177 Results

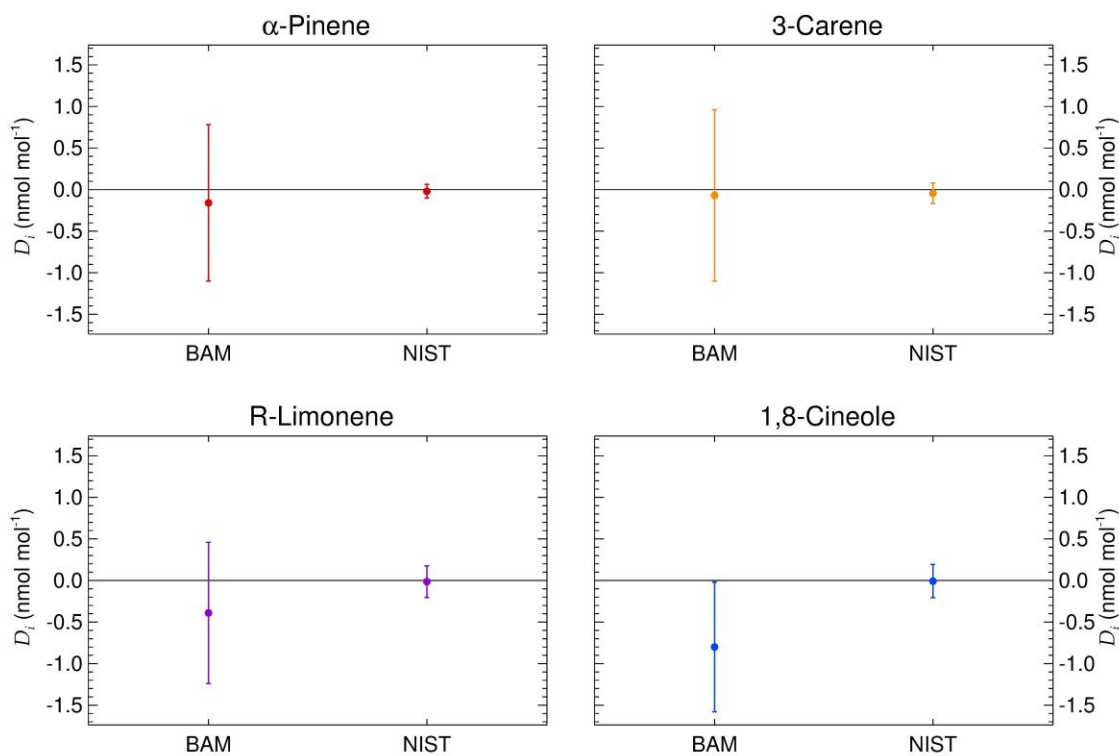


Figure 4. Differences (D_i) between the participant value (x_i) and the RV (x_{RV}) for each monoterpene in the pilot comparison samples. Error bars represent $k = 2$ expanded uncertainties of the difference, $U(D_i)$.

4 Conclusions

All participant results for this comparison agree with their RVs within the $k = 2$ expanded uncertainties, with the exception of BAM's reported value for 1,8-cineole. The uncertainties reported by BAM are more than a factor of 10 greater than those reported by NIST, due to a more complex sampling and analysis procedure.

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Appendix A

Measurement Report: BAM

CCQM-P177 Measurement Report: Monoterpenes in Nitrogen

Laboratory: BAM

Laboratory code:

Cylinder No.: APE1145316

Nominal Concentration: 2.5 nmol mol⁻¹

Measurement No. 1	Date 3.12.2016	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene		2.46	3.7	4
3-Carene		2.65	3.8	4
R-Limonene		2.22	1.3	4
1,8-Cineole		1.97	3.9	4

Measurement No. 2	Date 4.12.2016	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene		2.42	3.1	4
3-Carene		2.55	3.6	4
R-Limonene		2.14	1.7	4
1,8-Cineole		1.87	4.5	4

Measurement No. 3	Date 7.12.2016	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene		2.19	7.4	4
3-Carene		2.41	6.1	4
R-Limonene		2.01	2.0	4
1,8-Cineole		1.84	6.1	4

Measurement No. 4 (optional)	Date	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene				
3-Carene				
R-Limonene				
1,8-Cineole				

Measurement No. 5 (optional)	Date	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene 3-Carene R-Limonene 1,8-Cineole				

Measurement No. 6 (optional)	Date	Result (nmol mol ⁻¹)	Stand. deviation (% relative)	# of sub-measurements
α -Pinene 3-Carene R-Limonene 1,8-Cineole				

Summary Results:

Gas Mixture Component	Result (assigned value) (nmol mol ⁻¹)	Coverage factor	Assigned expanded uncertainty (nmol mol ⁻¹)
α -Pinene	2.36	1	0.47
3-Carene	2.54	1	0.51
R-Limonene	2.12	1	0.42
1,8-Cineole	1.89	1	0.38

Reference Method:

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

Air sampling on Tenax-tubes followed by thermal desorption and gas chromatography / mass spectrometry (ISO 16000-6),

Equipment: Agilent GC/MS (6890/5973) with Gerstel TDS 3 (thermal desorption)

Calibration Standards:

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

10 mg of pure standard substances were solved in methanol. A mixture of the standards was prepared and dilutions were made to get concentrations from 2 to 17 ng/ μ l.

Instrument Calibration:

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

For the calibration 6 levels in the range from 2 ng/μl to 17 ng/μl were spiked (1 μl) onto Tenax tubes which were analyzed in one measurement sequence together with the samples.

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.)?

The cylinder was placed upright all time in a place for gas cylinders at room temperature. The gas was transferred in two different bags (tedlar bag with a volume of 5 liters and nalophan bag with a volume of 20 liters). From each bag air sampling was done onto two Tenax tubes by sampling a volume of one liter.

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.

a) Uncertainty table:

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Sampling volume			3 %		
Purity of standards			1 %		
Standard mixture			3 %		
Complete analysis			20 %		

Coverage factor: 1
Expanded uncertainty: 20 %

Optional

You may provide additional data, such as raw measurement data, information on your measurement procedure, etc.

Appendix B

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	8 Sept 2015	2.521	0.015	3
3-Carene		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	9 Sept 2015	2.527	0.010	3
3-Carene		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	10 Sept 2015	2.524	0.012	3
3-Carene		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) N₂. 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 N₂, 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 N₂ balance gas then filled with N₂ 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 N₂ 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 N₂ balance gas was considered as a collective lot of one Ar concentration (17.72 ± 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 \pm 0.017	2.180 \pm 0.018	2.100 \pm 0.017	2.248 \pm 0.018	2.308 \pm 0.018
APE1145326	2.518 \pm 0.022	2.600 \pm 0.023	2.504 \pm 0.022	2.681 \pm 0.023	2.752 \pm 0.024
APE1145327	3.411 \pm 0.029	3.522 \pm 0.030	3.392 \pm 0.028	3.632 \pm 0.030	3.728 \pm 0.031
APE1145334	1.576 \pm 0.019	1.538 \pm 0.019	1.591 \pm 0.020	1.561 \pm 0.019	1.546 \pm 0.019
APE1145336	3.093 \pm 0.021	3.020 \pm 0.020	3.122 \pm 0.021	3.063 \pm 0.021	3.035 \pm 0.020

^aExpanded uncertainties are shown with a confidence interval of approximately 95 %.

^bInt 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.