U.S. Department of Commerce
National Institute of Standards and Technology
Material Measurement Laboratory
Chemical Sciences Division
Gaithersburg, Maryland 20899

REPORT OF ANALYSIS

March 15, 2024

SUBMITTED TO: Anja Claude
Deutscher Wetterdienst (DWD)
Meteorologisches Observatorium Hohenpeissenberg
Albin-Schwaiger-Weg 10
82383 Hohenpeissenberg
Germany

AUTHORS: Christina E. Cecelski

TITLE: Preparation of a 2 nmol mol^{-1} Monoterpene Mixture for Deutscher Wetterdienst

CONSTITUENTS: Monoterpenes (α-Pinene, Camphene, β-Pinene, 3-Carene, α-Terpinene, *R*-Limonene, 1,8-Cineole, *p*-Cymene), *n*-Hexane, *n*-Octane, Nitrogen

METHOD: Gas Chromatography/Flame Ionization Detection with Cryogenic Preconcentration

COPIES TO:

BACKGROUND:

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Preparation of a 2 nmol mol^{-1} Monoterpene Mixture for Deutscher Wetterdienst

Submitted to:

Anja Claude
Deutscher Wetterdienst
Meteorologisches Observatorium Hohenpeissenberg
Albin-Schwaiger-Weg 10
82383 Hohenpeissenberg
Germany

Job #: 23024

Introduction

One compressed gas mixture containing "Group 1" (*α*-pinene, 3-carene, *R*-limonene, and 1,8-cineole) and "Group 2" (camphene, *β*-pinene, *α*-terpinene, and *p*-cymene) monoterpenes in a balance of nitrogen (N_2) was prepared for the German Meteorological Service (Deutscher Wetterdienst, DWD) located at the Hohenpeissenberg meteorological observatory. The mixture was prepared by dilution of aliquots of previously prepared monoterpene mixtures. All work was performed in accordance with the Gas Sensing Metrology Group Quality System (QMIII-646.03) Technical Procedure 646.03.08: Preparation of Primary Gas Mixtures Containing Volatile Organic Compounds by Gravimetry. The certified amount fractions assigned to this mixture are included below.

Component	Amount Fraction (nmol mol^{-1})	Expiration Date
α-Pinene	2.036 ± 0.128	15 March 2027
Camphene	2.481 ± 0.068	15 March 2027
β-Pinene	2.022 ± 0.233	15 March 2027
3-Carene	2.093 ± 0.086	15 March 2027
α-Terpinene	1.051 ± 0.062	15 March 2027
R-Limonene	2.094 ± 0.229	15 March 2027
1,8-Cineole	2.152 ± 0.088	15 March 2027
p-Cymene	2.583 ± 0.120	15 March 2027
n-Hexane	3.556 ± 0.078	15 March 2027
n-Octane	2.209 ± 0.049	15 March 2027

Uncertainties expressed at approximately 95 % confidence (k = 2).

Mixture Preparation

Cylinder Evacuation

The mixture was prepared in a new, 20 L aluminum gas cylinder (APE1214770), equipped with a DIN-1 stainless steel valve and pretreated with Experis (proprietary process) by Air Products, Belgium. The cylinder was connected to a fill manifold (Manifold # 2) and its contents (3 bar helium) were vented and evacuated to a pressure of approximately 3 mTorr.

Mass measurements were determined for the evacuated cylinder using a Mettler SR64001 single-pan balance (NIST # 619572), with a capacity of 64 kg and a sensitivity of 0.1 g. The cylinder was weighed a total of 10 times, and the balance was zeroed between each weighing.

Minor Component Additions

The cylinder was connected to the fill manifold along with the first parent mixture, APE1228483 [1] (Table 1). The manifold was purged and vented a minimum of three times with at least 100 psig of the parent mixture, then evacuated to approximately 3 mTorr. The cylinder was filled to a predetermined pressure with the parent mixture and set aside to equilibrate for approximately 3 h. Ten mass measurements of the cylinder were taken after the addition of the first parent mixture.

The cylinder was reconnected to the fill manifold along with the second parent mixture, APE1135902 [2] (Table 2). The manifold was purged and vented a minimum of three times with at least 100 psig of the parent mixture, then evacuated to approximately 3 mTorr. The cylinder was filled to a predetermined pressure with the parent mixture and set aside overnight to equilibrate. Ten mass measurements of the cylinder were taken after the addition of the second parent mixture.

Table 1. Amount fractions in the "Group 2" parent mixture, APE1228483, with associated uncertainties for 95 % confidence ($k = 2$).

Component	Amount Fraction (nmol mol^{-1})	Weight Fraction ($\times 10^{-6}$)
Camphene	334.12 ± 10.18	1.6248
β-Pinene	294.75 ± 9.46	1.4333
α-Terpinene	141.56 ± 5.07	0.6884
p-Cymene	347.78 ± 8.26	1.6662
n-Hexane	478.8 ± 7.16	1.4728

Table 2. Amount fractions in the "Group 1" parent mixture, APE1135902, with associated uncertainties for 95 % confidence ($k = 2$).

Component	Amount Fraction (nmol mol^{-1})	Weight Fraction ($\times 10^{-6}$)
α-Pinene	222.53 ± 0.39	1.0822
3-Carene	229.83 ± 0.51	1.1177
R-Limonene	221.35 ± 0.33	1.0765
1,8-Cineole	236.97 ± 0.37	1.3048
n-Octane	243.24 ± 0.32	0.9918

Major Component Addition

The cylinder was then connected to the fill manifold along with Airgas ALPHAGAZ Nano N_2 (with integrated purifier), which was previously analyzed for hydrocarbon impurities. The manifold was purged and vented a minimum of five times with at least 100 psig of N_2, evacuated to approximately (4 to 6) mTorr, then purged an additional five times. The cylinder was filled with N_2 to a predetermined pressure over the course of two days, and allowed to equilibrate after each addition.

Ten mass measurements were taken after the final addition of the balance gas. After the final weighing, the cylinder was rolled for approximately 2 hours using a Fredlov cylinder roller (NIST # 611935). Cylinder rolling is performed to ensure proper mixing of the cylinder contents.

Instrumentation

The mixture was analyzed using an Agilent 7890A gas chromatograph with flame ionization detection (GC/FID) [NIST # 632012] coupled to a Nutech 3351DS preconcentrator [NIST # 632008]. The components were separated using a 60 m x 0.32 mm capillary column with 0.25 µm of AT-WAX at the following temperature program: hold at 50 °C for 12 min; increase at 4 °C min^{-1} to 110 °C; hold for 1 min. The FID was set to 250 °C, with a fuel gas mixture of 30 mL min^{-1} hydrogen and 400 mL min^{-1} air. The preconcentrator was used to cryogenically trap 200 mL of sample. A representative chromatogram using this method is shown in Figure 1.

The chosen chromatographic method does not baseline-separate *R*-limonene and 1,8-cineole. Baseline separation can be achieved using a different coated capillary column. However, NIST is also tracking long-term stability of other mixtures containing many monoterpenes. The column used in these measurements baseline-separates nearly 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 results of any long-term stability data. NIST has used the same column and dedicated instrument to maintain stability for all of its measurements, to better understand the behavior of monoterpene mixtures over time.

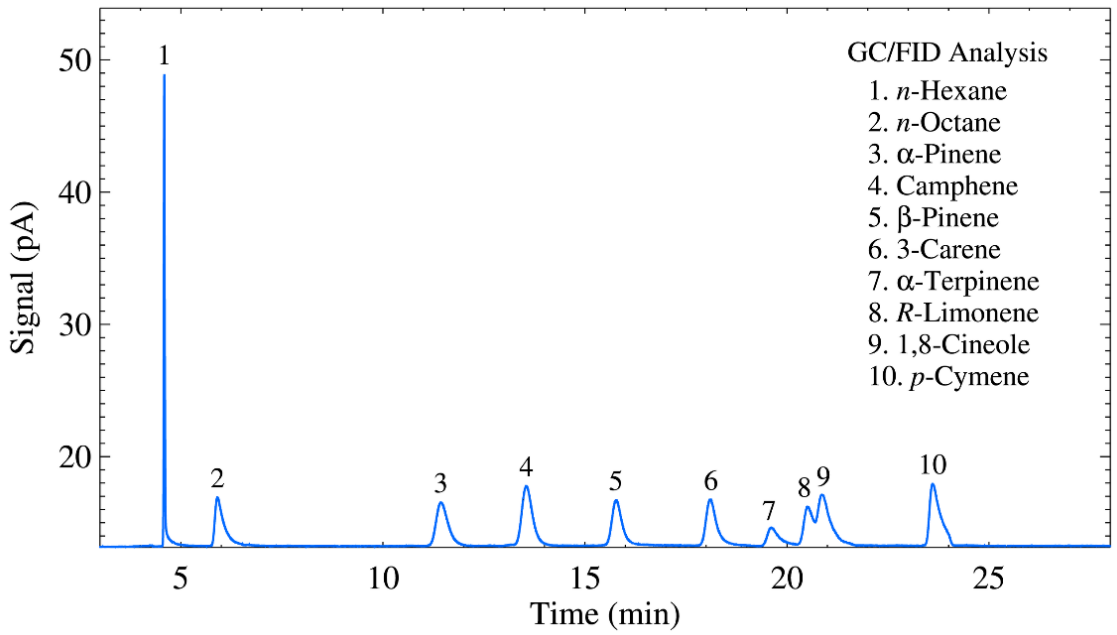

Figure 1. Sample chromatogram of monoterpene mixture APE1214770.

Verification

The amount fractions of this mixture were verified against five NIST primary standard mixtures (PSMs) [3,4], whose gravimetric values are listed in Table 3. The results of the analysis are summarized in Figure 2. α-Terpinene was not included in the verification because there were no standards available at a similar nominal amount fraction. For all other components analyzed, the measured value agreed with the gravimetric value within the associated uncertainties. Nonetheless, all of the certified uncertainties were increased to include the uncertainties from both the gravimetric calculations and the verification analysis.

Table 3. Amount fractions of NIST PSMs used to verify mixture APE1214770. All values are expressed in nmol mol^{-1}, with associated uncertainties for 95 % confidence (k = 2). Values shown in bold have been corrected for long-term stability changes.

Component	APE1161693	APE1228492	APE1145330	APE1145315	APE1145331
n-Hexane		4.067 ± 0.029			
n-Octane	2.308 ± 0.018	4.315 ± 0.025	1.918 ± 0.022	2.766 ± 0.035	2.772 ± 0.020
α-Pinene	2.111 ± 0.017	4.154 ± 0.030		2.531 ± 0.032	2.536 ± 0.018
Camphene		3.918 ± 0.023	1.742 ± 0.019		
β-Pinene		4.358 ± 0.026	1.937 ± 0.022		
3-Carene	2.181 ± 0.018	4.056 ± 0.029		2.614 ± 0.034	2.619 ± 0.019
R-Limonene	***1.542 ± 0.090***	***5.016 ± 0.283***			
1,8-Cineole	2.248 ± 0.018	***3.965 ± 0.138***		2.695 ± 0.034	2.701 ± 0.019
p-Cymene		4.647 ± 0.028	2.066 ± 0.023		

Stability

The mixture was monitored for stability for approximately three months after preparation, using *n*-hexane as an internal standard. Response ratios were determined by dividing the GC peak area of each monoterpene by the peak area of *n*-hexane. A consistent response ratio over time demonstrates that the mixture is stable.

The stability data for APE1214770, as shown in Figure 3, indicate that α-pinene, camphene, 3-carene, α-terpinene, and *n*-octane have remained stable. No significant long-term trending or variability in their response ratios has been observed. Although their stability data are included in the combined uncertainty of the final certified value, the overall contribution is small relative to the uncertainties based on gravimetry and verification.

R-Limonene and 1,8-cineole appear to be drifting, a behavior that has been observed in previous monoterpene stability studies [5,6]. In these studies, the responses for *R*-limonene and 1,8-cineole were highly varied and inversely proportional, but no long-term decay or growth was observed for either component. It is likely that this mixture is behaving similarly, and that the observed drift is related to variations in the peak-to-baseline integration, rather than instability of the mixture. This is also supported by the stability data for the combined peaks, as seen in the plot labeled "*R*-limonene+1,8-cineole". Nonetheless, the certified uncertainties for these components have been increased to account for such variations over time.

There also appears to be some variability in the response ratio for *p*-cymene, as observed in the first two months of stability data. Although the most recent measurements give little indication of any long-term trending, the certified uncertainty has been increased to cover these variations.

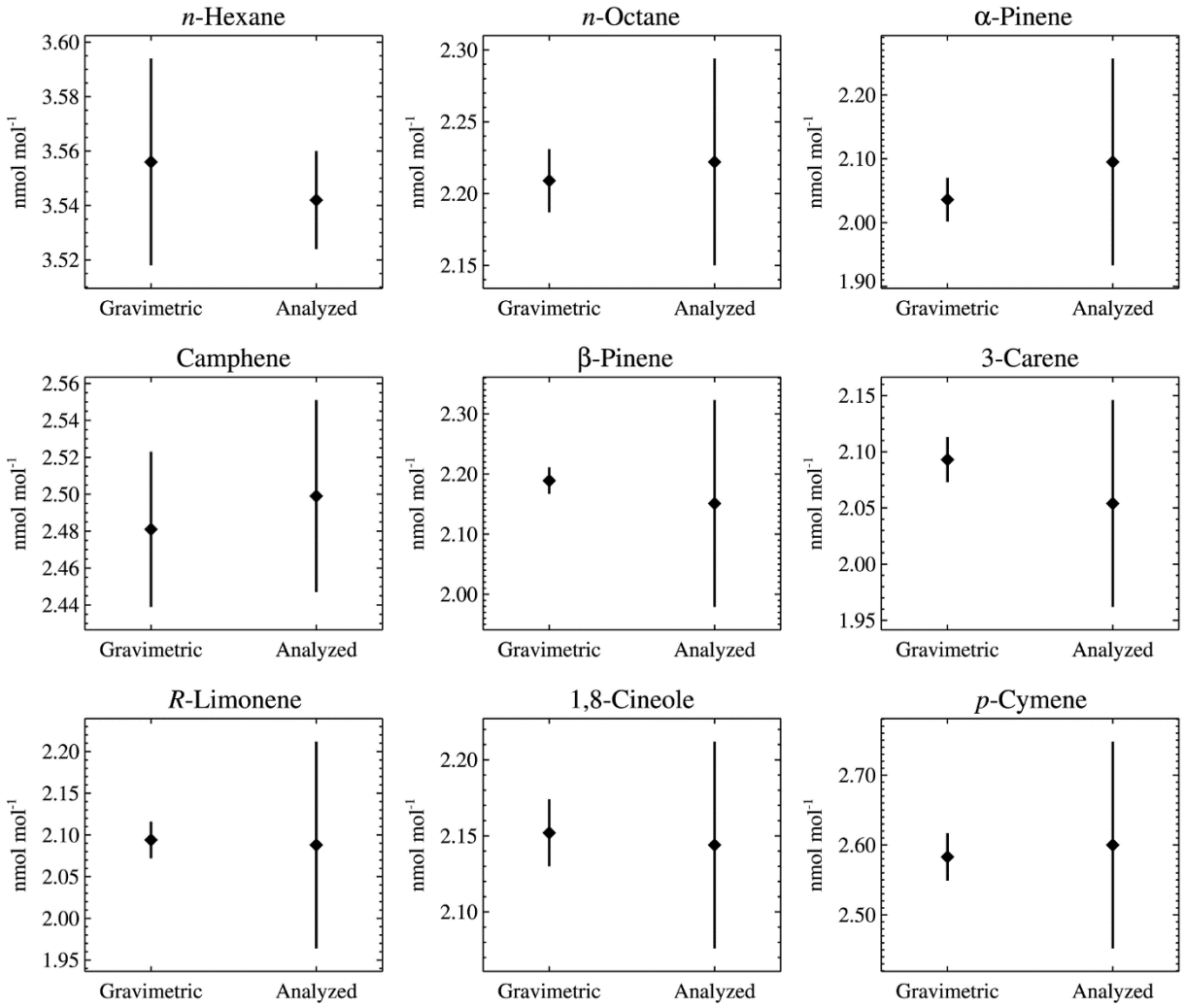

Figure 2. Monoterpene amount fractions in APE1214770, as determined gravimetrically and as analyzed using NIST PSMs. Error bars represent expanded (k = 2) uncertainties.

Finally, there is clear evidence of a consistent, downward trend in β-pinene, indicating that this component is not stable. Based on the stability data, it is assumed that β-pinene will continue to decay over time. As a result, the certified amount fraction has been corrected, to the most recent expected value at the time of this report, and the uncertainty has been increased to cover both the original gravimetric value and any further decay anticipated over the course of the period of validity.

It is highly recommended that the user, upon receiving this mixture, establish their own "baseline" monoterpene/*n*-hexane ratios using their own chromatographic method. The user should then monitor the stability of this mixture, by tracking these ratios over time, in a similar manner as described above. Any significant stability changes should be reported to NIST for further evaluation.

Based on the observed stability of previous monoterpene mixtures of similar nominal composition, and the expected stability of this mixture, all components in APE1214770 have been assigned a period of validity of 3 years, during which the certified values will be supported. At the end of this period, if there is adequate evidence to demonstrate that this mixture has remained stable, then its period of validity may be extended, and the expiration date stated in this document updated.

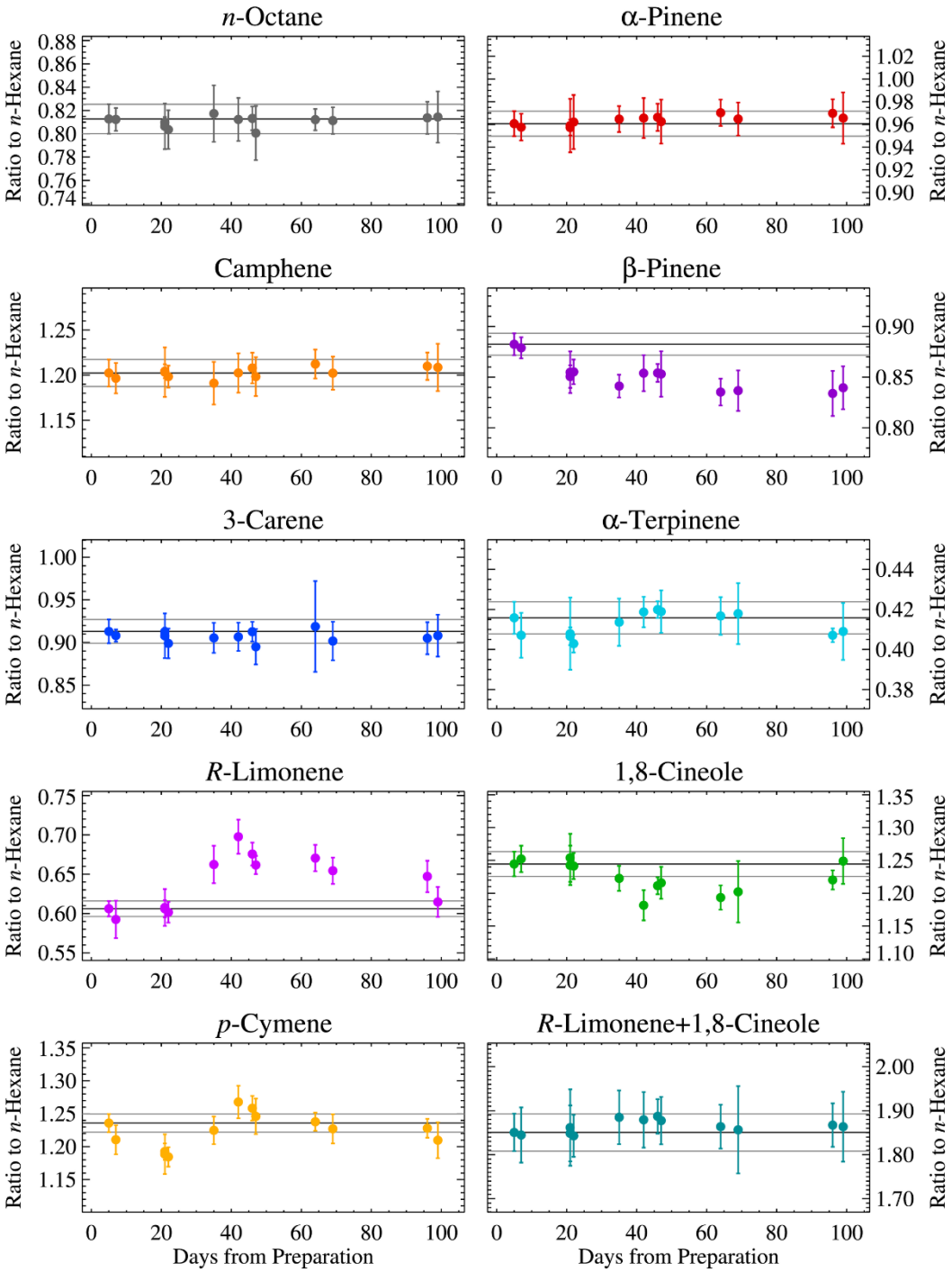

Figure 3. Stability testing of APE1214770 over time from the date of mixture preparation. Individual data points represent response ratios of each monoterpene to the internal standard, *n*-hexane. Error bars represent expanded (k = 2) uncertainties. The dark and light gray lines represent, for each component, the initial response ratio and associated expanded uncertainty (k = 2).

Amount Fraction Values

The gravimetric and certified amount fractions for this mixture are listed in Table 4. The gravimetric values were determined from the masses and purities of the added gases. For nearly all components, the gravimetric amount fraction will serve as the certified value for this mixture. The exception to this is β-pinene, which has been adjusted according to the stability data in Figure 3.

Table 3. Gravimetric and certified amount fractions in mixture APE1214770, with associated uncertainties for 95 % confidence (k = 2).

Component	Gravimetric Amount Fraction (nmol mol^{-1})	Certified Amount Fraction (nmol mol^{-1})
α-Pinene	2.036 ± 0.034	2.036 ± 0.128
Camphene	2.481 ± 0.042	2.481 ± 0.068
β-Pinene	2.189 ± 0.023	2.022 ± 0.233
3-Carene	2.093 ± 0.021	2.093 ± 0.086
α-Terpinene	1.051 ± 0.039	1.051 ± 0.062
R-Limonene	2.094 ± 0.022	2.094 ± 0.229
1,8-Cineole	2.152 ± 0.022	2.152 ± 0.088
p-Cymene	2.583 ± 0.033	2.583 ± 0.120
n-Hexane	3.556 ± 0.037	3.556 ± 0.078
n-Octane	2.209 ± 0.022	2.209 ± 0.049

Uncertainty Calculations

The stated total uncertainty was determined, for each component in the mixture, from the uncertainties in the gravimetric preparation (u_{grav}), verification (u_{ver}), and stability testing (u_{stab}), using Equation 1.

$$u_c = \sqrt{u_{\mathrm{grav}}^2 + u_{\mathrm{ver}}^2 + u_{\mathrm{stab}}^2} \tag{1}$$

The final uncertainty is expressed as an expanded uncertainty, $U = ku_c$, where the coverage factor k = 2. The true value for each component is therefore asserted to lie in the interval defined by the certified amount fraction ± U, with a level of confidence of approximately 95 % [7].

References

[1] NIST Report of Analysis 646.03-22-72, Preparation of a Group 2 Monoterpene in Nitrogen Primary Standard Mixture (24 May 2022).

[2] NIST Report of Analysis 646.03-15-030a, Preparation of a Monoterpene in Nitrogen Primary Standard Mixture (16 Oct 2015).

[3] NIST Report of Analysis 646.03-15-054a, Preparation of a Five Monoterpene-in-Nitrogen Primary Standard Mixtures at 1.5 to 3.5 nmol mol^{-1} (16 Oct 2015).

[4] NIST Report of Analysis 646.03-15-088a, Preparation of Monoterpene-in-Nitrogen Samples for the CCQM-K121 Comparison (16 Oct 2015).

[5] C. Liaskos, G. Rhoderick, J. Hodges, A. Possolo, C. Goodman, Y. D. Kim, D. H. Kim, S. Lee, N. Allen, M. Corbel. D. Worton, R. Brown, P. Brewer, CCQM-K121 – Monoterpenes in Nitrogen at 2.5 nmol mol^{-1} Final Report, *Metrologia*, 55(1A), 08019, doi:10.1088/0026-1394/55/1A/08019 (2018).

[6] Rhoderick, G. C., et al., Stability of gaseous volatile organic compounds contained in gas cylinders with different internal wall treatments, *Elem Sci Anth*, 7(28), doi:10.1525/elementa.366 (2019).

[7] JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (Gum 1995 with minor corrections), Joint Committee for Guides in Metrology, BIPM, Sèvres, France (2008).

Notebook References: Research Gas Mixtures # 1 [CSD # 3781], pp. 9–12; 69–74
Terpene Research # 3 [CSD # 3722], pp. 33–35

Prepared by:

Christina E. Cecelski
Physical Scientist

Reviewed by:

JENNIFER CARNEY
Digitally signed by JENNIFER CARNEY
Date: 2024.06.04 11:04:10 -04'00'

Jennifer Carney
Leader, Gas Sensing Metrology Group

Gonzalez, Carlos A. (Fed)
Digitally signed by Gonzalez, Carlos A. (Fed)
Date: 2024.06.05 10:05:02 -04'00'

Carlos A. Gonzalez
Chief, Chemical Sciences Division