Monoterpane Gas Standard Developments at NIST

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5th WMO/GAW-VOC Expert Workshop on Volatile Organic Compounds
KRISS, Daejeon, Republic of Korea
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Recap of 4th WMO/GAW-VOC meeting in York, UK, 2012

- Air Products aluminum w/ Experis treatment very promising
  - Nickel plate steel cylinders show degradation, but at a much slower rate than Aculifed aluminum

- Results indicated stable mixtures of α-pinene, β-pinene, 3-carene, p-cymene, R-limonene, and camphene (300+ days)
  - 1,8-cineole at 70+ days

- Based on discussions and request at York meeting, NIST submitted proposal to become WMO CCL for monoterpenes in Dec 2012

- NIST became official WMO CCL for Monoterpenes in Feb 2013
Continued Stability Study of Monoterpene Standard D646508


- Error bars are expanded uncertainties ($U$) based on standard deviations ($sd$) of the average response of replicate measurements ($n$) of the individual terpene and benzene, where $n = 3$ to $5$; $U = [\sqrt{sd^2_{\text{terpene}} + sd^2_{\text{benzene}}} * 2] * \text{Ratio}$
Monoterpene Standards Preparation Timeline

APE1082180
225 ppb
α-pinene
3-carene
limonene
1,8-cineole
n-hexane (IS)
prepared 21/8/2013

APE1135902
225 ppb
α-pinene
3-carene
limonene
1,8-cineole
n-octane (IS)
prepared 16/04/2014

APE1135917
225 ppb
β-pinene
camphene
α-terpinene
p-cymene
n-octane (IS)
prepared 23/07/2014

APE1135913
2 ppb
prepared 25/09/2013

APE1135915
2 ppb
prepared 30/01/2014

APE1135894
225 ppb
β-pinene
camphene
α-terpinene
p-cymene
n-octane (IS)
prepared 15/09/2014

Impurities/Purity of Starting Monoterpenes

Error bars are combined uncertainties, $k=1$. 
Tracking Stability in APE1082180; 250 nmol mol^{-1}

**α-Pinene and 3-Carene in APE1082180**

- Ratios (monoterpene/n-hexane peak areas) over time from preparation date
- Error bars are standard deviations (sd) of replicate measurements (n) of the individual terpene and n-hexane, where n = 3 to 5; $u = \sqrt{sd_{\text{terpene}}^2 + sd_{\text{n-hexane}}^2} \times Ratio$
Tracking Stability in APE1082180; 250 nmol mol\(^{-1}\)

**Limonene and 1,8-Cineole in APE1082180**

- **Ratio to n-Hexane**
- **Days from Preparation**

- **Limonene** (red dots)
- **1,8-Cineole** (blue dots)
Stability Determined vs. New Standard

APE1082180 analyzed vs. new standard APE1135902

- Original standard APE1082180 prepared August 21, 2013
- New standard APE1135902 prepared April 16, 2014
- Error bars are expanded uncertainties, 95% confidence interval
Tracking Stability in APE1135913; 2 nmol mol\(^{-1}\)

- Ratio of monoterpenes to n-hexane over time from preparation date

![Graph showing the ratio of monoterpenes to n-hexane over time. The graph includes data points for \(\alpha\)-pinene and 3-carene, with error bars indicating variability. The x-axis represents days from preparation, ranging from 0 to 300, and the y-axis represents the ratio to n-hexane, ranging from 1.52 to 1.68.]
Tracking Stability in APE1135913; 2 nmol mol\(^{-1}\)

- Ratio of monoterpenes to n-hexane over time from preparation date
NIST Determinations of NPL Standard D910392

- Error bars are expanded uncertainties, 95% confidence interval
Tracking Stability in APE1135917; 225 nmol mol$^{-1}$

![Graph showing stability over time for different components]

- Camphene
- $\beta$-Pinene
- p-Cymene
- $\alpha$-Terpinene
Future Work/Collaborations with other NMIs

• Continue comparisons of monoterpenes with other National Metrology Institutes

• Continue stability studies

• Further development of “2nd Group” of monoterpenes standards at 2 ppb
  • β-pinene, camphene, α-terpinene, p-cymene

• Planned CCQM/GAWG key comparison (K-121) on monoterpenes at 2 ppb level
  • NIST coordinating; participants include NPL, NIM, KRISS
  • Underway with participant analyses of samples planned for 2015
  • α-pinene, 3-carene, limonene, 1,8-cineole
NIST PSM and Reference Materials Development to Support Measurements of Atmospheric and Air Pollution Species

- PSMs developed for:
  - greenhouse gases CO₂, CH₄, N₂O, CO, SF₆
  - halocarbons including CFC-12, CFC-11, CFC-113, HCFC-22, HCFC-142b, HFC-134a, CFC-114, HCFC-141b, HFC-152a, HFC-143a
  - VOCs: 80+ light & heavy hydrocarbons, aromatics, chloro/fluoro species
  - monoterpenes: α-pinene, 3-carene, limonene, 1,8-cineole, β-pinene, camphene, terpinene, p-cymene (others being studied)
  - oxygenates methanol, ethanol, acetone
  - developing methods for ammonia, HCHO, HCl

- SRMs completed or near completion:
  - 1718 N₂O in Synthetic Air at 1000 ppb
  - 1720 Northern Continental Air (Dry) and 1721 Southern Oceanic Air with CO₂, CH₄, N₂O certified; informational values for O₂, Ar, CO, ¹³C-CO₂ and ¹⁸O
  - SRM 1722 Halocarbons in Air (Northern Continental)