

Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry and climate. They contribute to photochemical processes that produce tropospheric ozone and chemical smog, they act as a sink to hydroxyl radicals that oxidize methane and other greenhouse gases, and they form secondary organic aerosols (SOAs) that serve as cloud condensation nuclei. Considerable interest in ambient VOC measurements has led to the need for reliable calibration standards.

Objective

The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) has proposed the need for a manageable VOC measurement program, with the primary objective of having a single source of international measurement standards for VOCs.

GLOBAL ATMOSPHERE WATCH NIST serves as the WMO Central Calibration Laboratory (CCL) for monoterpenes, providing compressed gas monoterpene standards to the WMO World Calibration Center, as well as other atmospheric laboratories, for the calibration of their measurement systems.

In support of WMO/GAW, NIST is developing several multi-component, lowlevel (nominal 1 to 5 nmol mol⁻¹) monoterpene gas standards (see Table 1). Typically, these mixtures are prepared
Table 1: Monoterpene mixture groups for
 in a balance of nitrogen; however, in WMO/GAW standards development. an effort to improve the consistency in matrix composition between gas calibration standards and ambient measurement samples, NIST is also developing low-level monoterpene gas standards in a balance of air.



Stability data for monoterpene-in-air mixture APE1145335 yield encouraging results, with α -pinene, camphene, β -pinene, 3-carene and p-cymene exhibiting stability for over 200 days. Drifts in α -terpinene, R-limonene and 1,8-cineole, however, indicate a potential stability problem with these components. More data is needed to determine whether these drifts are due to mixture instability or to limitations of the current GC method. Continued developments of monoterpene mixtures in air and in nitrogen, along with improvements in the current analytical method, will help establish the cause of the observed ratio drift and direct the need for further research.

Disclaimer: Certain commercial equipment, instruments, or materials are identified in this poster in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Developments in hydrocarbon gas standards at NIST: Supporting the World Meteorological Organization measurement infrastructure Christina E. Liaskos and George C. Rhoderick National Institute of Standards and Technology, Gaithersburg, MD 21113

Group 1	Group 2	Group 3
α-pinene	β-pinene	myrcene
3-carene	camphene	cis-ocimene
R-limonene	α-terpinene	γ-terpinene
1,8-cineole	p-cymene	phellandrene

R-Limone

R-Limonene

Monoterpene mixture APE1145335 was prepared via dilution of aliquots of parent mixtures APE1082180 and APE1135917 (see Table 2) to a nominal concentration of 2 nmol mol⁻¹. Each parent was added to the cylinder using a fill manifold, after which the cylinder was filled with a balance of synthetic air.

4. Stability tracking of APE1145335 Stability is monitored by observing the response ratio of each monoterpene to that of the internal standard over time (right).



Method

1. Monoterpene purity analysis α -Pinene (99.430 ± 0.064 %) β-Pinene (99.423 ± 0.034 %)



3. Preparation of APE1145335





2. Preparation and analysis of parent mixtures

Parent mixtures were prepared via vaporization and transfer of pure monoterpenes from sealed capillary tubes into an evacuated gas cylinder, and were then analyzed over time for stability (see below).





Table 2: Parent mixtures used to prepare monoterpene-in-air mixture APE1145335.

Parent Cylinder # 1: Preparation date Nominal concentrati Components Parent Cylinder # 2: Preparation date Nominal concentrati Components ^aInternal standard, inclu

Dedicated Agilent 7890 GC/FID

- Capillary column
 - 60 m × 0.32 mm ID
 - 0.25 µm film AT-WAX™ (polyethylene glycol)
- Oven temperature program
 - Hold 50 °C for 12 min
 - Ramp 4 °C min⁻¹ to 110 °C
 - Hold 110 °C for 1 min
- FID temperature set to 250 °C

Nutech 3551 Preconcentrator

- Cryogenically traps sample
 - 50 mL for 200 nmol mol⁻¹
 - $-200 \text{ mL for } 2 \text{ nmol mol}^{-1}$

- Low-level mixtures prepared in a 1-step process
- Mixtures made gravimetrically (i.e., traceable to the gram)
- Cylinders filled with a balance gas of nitrogen after addition of monoterpenes

APE1082180		
	August 2013	
ion	225 nmol mol ⁻¹	
	α-pinene, 3-carene, R-limonene, 1,8-cineole; n-hexane ^a	
APE1135917		
	July 2014	
ion	240 nmol mol ⁻¹	
	camphene, β-pinene, α-terpinene, p-cymene; n-octane ^a	
uded	in mixture for stability monitoring	
	Stability of Monoterpenes Cylinder # APE1145335	

