

Interactive comment on “The importance of cylinder passivation chemistry for preparation and long-term stability of multicomponent monoterpene primary reference materials” by Nicholas D. C. Allen et al.

Anonymous Referee #1

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The manuscript entitled "The importance of passivation chemistry for preparation and long-term stability of multicomponent monoterpene primary reference materials" describes an investigation into the stability of monoterpenes in different gas cylinders and sample containers at nmol/mol levels.

The authors present evidence that several monoterpenes can be stored long-term in a particular type of cylinder. They also show that in other cylinders, with a different internal passivation treatment, the monoterpenes degraded considerably, and underwent oxidation or other conversion to different species. This is useful information and will help

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inform researchers on choices of cylinder types for reference materials. The authors also show that reference materials containing monoterpenes can be sub-sampled, or transferred, to certain passivated stainless steel containers, which implies that these containers are useful for storing air samples or sub-sampling from high-pressure cylinders.

General Comments

The manuscript does not really address "chemistry" of passivation: I suggest removing "chemistry" from the title.

The citation format is annoying. Why are there two authors listed in many of the citations? This is not consistent with AMT style.

Section 2.7 could be moved to the supplement. The derivation of uncertainty is not critical to the manuscript.

The manuscript could use some minor editing for grammar. I've included some suggestions.

Specific Comments

P1, L40: Nicklaus et al. 2013 not found in reference list.

P2, L67: I would argue that accurate measurement is dependent on PRMs (Rhoderick 2010) AND analytical methods (Helmig et al. 2013).

P2, L79: Where does "better than 1%" come from? Is there a citation you can add? One might argue that a factor of 4 is required, the $5\%/4 = 1.25\%$.

P2, L97: Move explanation of passivation to first use of the term (previous paragraph).

P3, L114: Subject/verb agreement. Suggest splitting this sentence into two. "PRMs containing the four monoterpenes, α -pinene (both the minus and plus optical isomers), 3-carene, R-limonene and 1,8-cineole were prepared independently in a balance of

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high purity dry nitrogen (BIP+, Air Products) in accordance with ISO 6142 (ISO 2015). N-Octane was also added and used as an internal standard."

P 3, L 122: Were both hydrocarbons and water removed to < 1 nmol/mol, or just water?

P4, Table 1: Please explain what the "verification process" is.

P4 4, L 164: Again, consider two sentences. "... a flow of 50 mL/min could not be achieved. Consequently, the flowrate across the trap was recorded using a mass flowmeter, "

P5, L195: "value" or "amount fraction" instead of "valve". And is it really "certified"?

P7, L246: Please clarify if this applies to dry samples or natural air samples, for which some humidity can improve storage.

P7, L272: Suggest section 2.7 be moved to Supplement

P10, L346: This sentence should be re-arranged: "To investigate potential degradation components, a sample of a monoterpene mixture in an internally treated SPECTRA-SEAL cylinder was loaded onto a sets of Chromasorb-106 and Tenax sorbent tubes (both packed in-house) and analysed on a Thermal-Desorption Gas Chromatograph Mass Spectrometer (TD-GC-MS)."

P10, L351: "Five additional peaks were consistently observed"

P11. L352: "The additional peaks"

P12, L382: replace "run" with "analyzed"

P13, L413: In Table 2, it was confusion at first that the two columns represent two different days. Why not just show one column of data, representing the average and standard deviation over 2 days. Otherwise it seems to the reader that there is something significant about the differences between the two days.

P14, L427: suggest: "were compared after 1, 8, and 83 days."

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P14, L440: This needs more explanation. What was it about the sample flow: too little flow, too little pressure to flush tubing?

P15, L452: An introductory sentence is needed here. This paragraph should begin with the objective: comparing gravimetric PRMs to an SI-traceable dilution method.

P15, L462: semi-colon after NIST

P15, L466: poor grammar here.

P16, L506: This percentage difference should be stated in the previous section.

Also, if there were additional complications with the dilution system, the uncertainty assigned is probably too low.

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