Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., author comment AC1
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Reply on RC1

Ruth E. Hill-Pearce et al.

Author comment on "Characterisation of gas reference materials for underpinning atmospheric measurements of stable isotopes of nitrous oxide" by Ruth E. Hill-Pearce et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-45-AC1, 2021

- The introduction section can be improved. There are quite some equations and definitions and their need is not always clear (e.g. site-specific distribution expressed by SP in equation 4).

This has been addressed throughout the introduction text. The equation for site preference and bulk $\delta^{15}N$ has been removed from the introduction.

- A table with an uncertainty budget for the developed standards can help the reader get a quick overview of the main uncertainty contributions. From the current text this is more difficult to grasp.

Please see the added table at line 247 which contains the sources of gravimetric uncertainty which replaces the description in the text.

- line 115 'to inhibit adsorption of target components' Is there any evidence in literature that N2O at these amount fractions adsorbs on aluminium? Regarding the other components in the mixtures (except for CO2 for which adsorption has been demonstrated) is there some evidence that they adsorb?

To the best of the authors' knowledge there is no published evidence that N_2O adsorbs on aluminium or passivated surfaces. We expect to provide N_2O reference materials in combination with other greenhouse gases and, as such, appropriate passivation chemistry to reduce adsorption of e.g. CO_2 should be selected and tested for use with N_2O.

- 'Figure 5: For some symbols only a cap but no error bar is shown.

The formatting of the error bars has been updated in figure 5 so that they are clearer to see.

- Line 125: '± 0.3 mg' and Line 129: '± 3 mg' Please give some explanation.

Line 116: '± 0.3 mg' and Line 121: '± 3 mg'. This describes the mass uncertainty on the two balances we use during the preparation of our gaseous reference materials. 0.3 mg is the mass uncertainty on the balance we use to weigh the transfer vessels used for indirect transfer vessel additions. The 3 mg is the mass uncertainty for the balance we use to weigh 10 litre gas cylinders between direct gas additions.

- line 262 'providing independence' Rephrase as within one lab often parent mixtures do have some dependencies (e.g. prepared using the same instruments, or purity analysis of the pure gases using the same analytical instruments and reference gases)

We have rephrased as follows;

line 252: "The amount fraction of N_2O in a prepared mixture was validated through comparison to NPL in-house PRMs. The PRMs used for validation were derived from different parent mixtures which are, where possible, produced by different operators in order to provide a greater degree of independence from errors in amount fraction of a parent mixture."

- Line 27 '(WMO, 2020)' seems to be missing from the list of references.

Updated in the references, it was previously listed with just the website address.

- A few typos, e.g. line 366 'vales', line 395 'measured of 10 minutes', figure 3 'of Certified amount'

The spelling errors have been corrected in the text. See lines 366 (values), line 392 (10 minute repetitions) and figure 3 axis (certified amount).

9. In equation 8, where does 'c' refers to?

In equation 8 (now 6 with updates to introduction), 'c' refers to the amount fraction of N2O, in nmol mol-1. The term '8.13e-4' refers to the combined uncertainty from the NOAA scale and pressure changes. The term '0.06 nmol mol-1' refers to the combined uncertainty from scale propagation and analyser drift. A description of the terms has been added to the text. See line 421.

10. In figure 8, there seems to be a clear trend in the assigned values of NPL - Empa as a function of the Empa assigned amount fraction. Please comment on this.

The following text was added;

Line 397: Reference materials with amount fractions within the range 295- 345 nmol mol^{-1} verified within the experimental extended combined standard uncertainty (k=2) for NPL certified amount fraction. A trend was observed with lower NPL amount fractions certifying lower and higher NPL amount fractions certifying higher.

11. Lines 250-254: Mismatch between the number of significant digits for the mass uncertainty ('0.3 mg', '3 mg') and the contributions to the percentage of the combined uncertainty ('73.07 %' '17.87 %').

The number of significant figures for the percentage contributions in table 1 has been reduced to align with the significant figures in the mass uncertainties.

12. Correct the author list of reference 'BIPM et al., 2008'.

The author list has been updated to include all of the institutions.

13. Line 148-150. It is mentioned that N2O was determined in the matrix gas but no data

are presented. Please provide these data including the corresponding uncertainty.

The N_2O in the synthetic air matrix was determined as 0.75 ± 0.09 nmol mol^{-1}. This value, corresponding uncertainty and a reference to the method of determination have been added to the text, see line 142. There is ongoing research to improve the accuracy of the quantification which may form the basis of a future publication.