

Interactive comment on “A liquid nitrogen-free preconcentration unit for measurements of ambient N₂O isotopomers by QCLAS” by J. Mohn et al.

Anonymous Referee #1

Received and published: 9 January 2010

General comments:

The paper presents adaption and testing of an existing preconcentration device (MEDUSA) for isotopic analysis of nitrous oxide at ambient atmospheric mixing ratios. The main advantage of the present approach over existing cryogenic N₂O preconcentration devices is that liquid nitrogen is not required. Quantitative trapping is achieved by a commercial chiller combined with a chemical absorbent (HayeSep D).

The final goal of the authors is to develop an optical method for position-specific nitrogen isotope analysis in N₂O. The present work is all but a first step to this goal. I would

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have normally expected that such minor development steps appear as a section of a proper method paper. As such, I am surprised that this work has been published as a stand-alone publication. However, in terms of scientific and technical quality, there are no major flaws with this paper.

Specific comments:

The "enriched" N₂O (15N/14N 25.4 ‰ enriched vs. "medical" N₂O) has not been described. Also, an independent verification of this value using established techniques (i.e. isotope ratio mass spectrometry) should be included.

Isotopic fractionation of "medical" and "enriched" N₂O should be tested independently to check whether the preconcentration method suffers from any scale compression.

Technical corrections:

p. 3100:

l. 4: Please replace "isotope ratios" by "relative isotope ratio differences" or "delta values".

l. 18: Replace "greenhouse warming potential" by "radiative forcing among long-lived greenhouse gases".

l. 19: Replace "concentrations" by "mixing ratios".

l. 20: Replace "parts per billion, 10–9 molar" by "parts per billion = 10⁻⁹".

l. 21: Replace "yr-1" by the international symbol "a-1".

l. 21/22: Change to "on a global a scale are microbial production in agricultural and natural soils as well as rivers, estuaries, coastal areas and oceans". Fossil fuel and biomass burning are actually minor sources.

l. 24: Add "individual" before "sources".

p. 3101:

I. 12: The value of 7.0 ‰ is too high and was later corrected to 6.5 ‰ (Toyoda S, Yoshida N, Urabe T, Nakayama Y, Suzuki T, Tsuji K, Shibuya K, Aoki S, Nakazawa T, Ishidoya S, Ishijima K, Sugawara S, Machida T, Hashida G, Morimoto S, Honda H (2004) Temporal and latitudinal distributions of stratospheric N₂O isotopomers. *J Geophys Res* 109, D08308, doi:10.1029/2003JD004316) in recognition of interlaboratory comparisons. Kaiser et al. (2003) reported (6.72 ± 0.12) ‰ (Kaiser J, Röckmann T, Brenninkmeijer CAM (2003) Complete and accurate mass-spectrometric isotope analysis of tropospheric nitrous oxide. *J Geophys Res* 108, 4476, doi:10.1029/2003JD003613). Park et al. (2004) found (6.3 ± 0.3) ‰ (Park S, Atlas EL, Boering KA (2004) Measurements of N₂O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotope fluxes to the troposphere. *J Geophys Res* 109, D01305, doi:10.1029/2003JD003731).

I. 12 & I. 13: Please include errors with these numbers.

I. 17: Values up to 140 ‰ have been reported by Kaiser et al. (2006) (Kaiser J, Engel A, Borchers R, Röckmann T (2006) Probing stratospheric transport and chemistry with new balloon and aircraft observations of the meridional and vertical N₂O isotope distribution. *Atmos Chem Phys* 6, 3535-3556).

I. 19: The upper stratospheric N₂O mixing ratio is essentially 0.

I. 19: Replace "Isotopomer ratios" by "Isotopic signatures". Please note the difference between isotopologues (molecules with different isotopic composition) and isotopomers (molecules with the same isotopic composition, but different arrangement of the isotopes).

I. 27: There are also optical techniques such as laser spectroscopy (Uehara K, Yamamoto K, Kikugawa T, Yoshida N (2003) Site-selective nitrogen isotopic ratio measurement of nitrous oxide using 2 μ m diode lasers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 59, 957-962) and FTIR techniques (Esler MB, Griffith DWT, Turatti F, Wilson SR, Rahn T, Zhang H (2000) N₂O concentration

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and flux measurements and complete isotopic analysis by FTIR spectroscopy. Chemosphere: Global Change Science 2, 445-454). Note that GC-IRMS measurements of N₂O isotopologues do not occur at ambient concentrations, but rely on cryogenic pre-concentration and GC separation.

I. 25 to p. 3102, I. 20: Please reformulate these paragraphs to more accurately reflect what can be and what has been done in terms of IRMS and optical N₂O isotopomer measurements.

p. 3104:

I. 3: "Redy" should not be hyphenated

I. 17 and elsewhere: Please change the "proportional to" sign (tilde) to an "approximately equal" sign (two wavy lines arranged like an "equal" sign (=)). The use of the tilde sign to indicate approximation is a bad habit that presumably originates from limitations of typewriters.

I. 25 and elsewhere: "sccm" should be written as "cm³ (STP)" and STP (standard temperature and pressure) should be defined because its meaning (temperature and pressure) varies

p. 3107:

I. 1: delta values are not ratios (see above)

I. 18: 25.4 ‰ - calibrated how?

p. 3108:

I. 8: Delete "molar" (amount (of substance) is always measured in mol).

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3099, 2009.

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