

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

J. Mohn et al.

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We are grateful to Reviewer #2 for taking time to comment on the manuscript. His suggestions resulted in a clearer and better revised version of the original manuscript. The comments have been addressed individually.

General comments

1. Comment: Please state in the title and abstract that the described QCLAS method is not feasible to measure the 18O/16O ratio of nitrous oxide (because of technical limitations of the laser system (limited wavelength range and "measurement channels"
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of the used equipment)).

Reply: The title as well as the abstract already contains this information by using the terminology of isotopomer. The isotopic species of N₂O containing the oxygen isotope would already be named as isotopologues. Nevertheless, the authors agree that with the current QC laser simultaneous d18O-N₂O measurements are not feasible as there are no suitable 14N14N18O rotational lines in the laser scanning range. However, there are no general restrictions in this aspect, and d18O-N₂O could be accomplished at 2105 cm⁻¹ for example. To clarify the issue the following sentence was added to section 4 Conclusions p. 3114, l. 25: Expected spectroscopic improvements, e.g. using continuous wave (cw) lasers and/or spectral ratio methods will provide enhanced precision without significant modifications in the instrumental setup. Additionally, d18O-N₂O measurements would be feasible by selecting a QC laser with an appropriate scanning range.

2. Comment: p. 3101, l. 29: NO⁺ and N₂O⁺ are molecule and fragment ions of nitrous oxide

Reply: Changed

3. Comment: p. 3102 1st paragraph: The authors listed advantages of their system vs. the IRMS method. Please give here additional numbers on measurement time of the QCL system. Also the amount of nitrous oxide (air sample volumina) needed for measurement of QCL in comparison to IRMS would be nice. See e.g. in below mentioned IRMS papers (appendix)

Reply: Information about measurement time and air sample volume are given in the introduction p. 3103, l. 8: ... temporal resolution of approx. 30 min. and in the conclusions p. 3114, l. 15 ... from 10 l of ambient air ... and l. 22-23: ... with a temporal resolution of less than 30 min. However, the authors agree that this information should also be included in the abstract and added the following sentence to p. 3100, l. 9: ... based spectrometer. During standard operation 10 l of ambient air are preconcentrated

on a HayeSep D trap and desorbed in 50 ml of synthetic air within 30 min. Rigorous tests were . . .

4. Comment: p. 3103, l. 16: Please replace "for other trace gases and their isotopes" by something like "measurement of mixing ratios and isotope ratios of other trace gases . . ."

Reply: Changed

5. Comment: p. 3104, l. 1-17: Can you give an exact value of the freezing temp.? Please include here or somewhere else the freezing point temp. of N₂O.

Reply: The authors agree to this comment and changed the following sentence on p. 3105, l. 9: .. release of N₂O (boiling point: -88.5°C) can be observed . . .

6. Comment: p. 3104, l. 26: Please give information on purity of the gases, e.g. N₂ 5.0

Reply: Changed

Specific comments

7. Comment: p. 3109 last paragraph: medical N₂O → For a publication it is highly recommended to calibrate the working and "reference gases" used by Mohn et al.! This can be done by controlled "thermal decomposition" of NH₄NO₃ with specific ¹⁵N labelling as already described by Friedman and Bigeleisen (1950): J Chem Phys 18, 1325ff. Perhaps the exchange of gas mixtures of N₂O in air with specialized IRMS labs also would fulfil this calibration. Although there is obviously some dispute on correct calibration results, please see the articles by Griffith et al. (2009): Anal. Chem. 81, 2227ff and Westley et al. (2007): RCMS 21, 391ff. The former authors even claim to be able to perform an "absolute calibration of the intramolecular site preference of ¹⁵N fractionation . . .".

Reply: The authors agree to include an absolute calibration of the isotopic composition

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of the N₂O reference gases applied in the present study. N₂O reference gases were analysed by Sakae Toyoda in the laboratory of Prof. Naohiro Yoshida at the Tokyo Institute of Technology. Details on the corrections in the text are given in reply to comment 2 of Reviewer #1.

Appendix

8. Comment: Additionally, it should be noted that also for Isotope Ratio Mass Spectrometry (IRMS) measurement a pre-concentration step for the N₂O is needed. This is usually done by freezing followed by an isolation of N₂O from other components by preparative gas chromatography and passing of an Ascarite trap (see e.g. Brandt et al., 1995 Isot. Env. Health Stud. 31, 277ff; or Roeckmann et al. (2003): RCMS 17, 1897ff, also discussing the possible influence of interfering substances especially on the NO⁺ measurement).

Reply: The authors acknowledge this comment and change p. 3101, l. 25-27 as mentioned in reply to comment 15 of Reviewer #1 to: In the past the only technique for high precision isotopic analysis was laboratory-based isotope-ratio mass-spectrometry (IRMS) in combination with flask sampling and cryogenic preconcentration.

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

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