

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

Anonymous Referee #2

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The paper presents a method for intramolecular (position-specific) stable isotope measurements on N₂O from atmosphere with QCLAS. Because of the low concentration of nitrous oxide in air (<400 ppb) no state-of-the-art QCL system is feasible to measure isotope ratios of atmospheric nitrous oxide without pre-concentration. The description of the system is accurate and covers all important factors. Only a calibration of their working and reference gases is highly recommended (see below) to enable a comparison of the new setup with existing techniques. The described elegant pre-concentration method is based on the MEDUSA system published by Miller et al. (2008), but several adaptations and specific testing for the N₂O freezing have been performed and de-

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scribed by Mohn et al. The manuscript itself is in first line methodologically orientated with some basic background on nitrous oxide and its isotopomers.

General comments

- 1) 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" of the used equipment)).
- 2) p. 3101 line 29: NO⁺ and N₂O⁺ are molecule and fragment ions of nitrous oxide
- 3) 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)
- 4) p. 3103 line 16: please replace "for other trace gases and their isotopes" by something like "measurement of mixing ratios and isotope ratios of other trace gases. . ."
- 5) p. 3104 line 1/line 17: can you give an exact value of the freezing temp.? Please include here or somewhere else the freezing point temp. of N₂O.
- 6) p. 3104 line 26 please give information on purity of the gases, e.g. N₂ 5.0

Specific comments

- 7) 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 labeling 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 fulfill this calibration. Although there is obviously some dispute on correct calibration results,

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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 a “absolute calibration of the intramolecular site preference of ^{15}N fractionation . . .”.

Appendix

Additionally, it should be noted that also for Isotope Ratio Mass Spectrometry (IRMS) measurement a pre-concentration step for the N_2O is needed. This is usually done by freezing followed by an isolation of N_2O 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).

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