

Reply to the reviewer #2

Reviewer's comment is typed in blue, authors' response is typed in black, and the change in the revised text is highlighted with red.

General comments:

The manuscript of Sakae Toyoda and Naohiro Yoshida with the title “Development of automated preparation system for isotopocule analysis of N₂O in various air samples” describes the development, optimization and automation of a preparation system for subsequent analysis of N₂O isotopocules from ambient air by isotope-ratio massspectrometry. The manuscript gives technical details on the instrumentation and compares the final performance to state-of-the art instrumentation applied by other research groups. The research area of N₂O isotope analysis is very active and the presented work is therefore of interest for a number of readers and potential future users of this technique. The manuscript is well-structured and written and is sufficiently detailed. Therefore, I suggest publication in Atmospheric Measurement Techniques with minor revisions, as detailed below.

We appreciated the reviewer for his/her many constructive comments. We have revised the manuscript according to his/her suggestions.

Specific comments:

Page 1 Line 15: The term “... for gas samples with various amounts and various N₂O concentrations.” might be replaced by “... which offers flexibility with respect to the available gas volume, pressure and N₂O concentration.”

The sentence has been revised accordingly.

Page 1 Line 25 - 27: The correct definition for “N₂O concentration and units” should be given when used for the first time and both sentences could be combined: “Its globally averaged concentration, given as mole fraction, was about 324 nmol mol⁻¹ (10⁻⁹ moles per mole of dry air) in 2011 (Hartmann et al., 2013) and increases by 0.73 nmol mol⁻¹ a⁻¹ (Ciais et al., 2013).

Revised as suggested.

Page 1 Line 29: The word “but” could be deleted.

Corrected.

Page 2 Line 4 - 5: The term “compounds” could be replaced by “substrates” or “educts”.

We replaced "compounds" with "substrates".

Page 2 Line 8: The following phrase could be added “... causes a progressive decrease in the ¹⁵N/¹⁴N isotope ratio of tropospheric N₂O.”

Revised as suggested.

Page 2 Line 17 – 18: The reasoning for this argumentation might be added; e.g. higher precision for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, lower sample volume required.

We have revised the sentence as follows:

... mass spectrometry combined with flask sampling still holds advantages for high-precision isotopic monitoring at polar regions or remote areas and flight observation using a balloon or an airplane because of smaller sample volume requirements.

Page 2 Line 26: A statement might be added, which gases are not separated sufficiently.

We have revised the sentence as follows:

This low precision is partly caused by incomplete separation of interfering components such as CO_2 and fluorinated hydrocarbons, or by imprecise manual handling during sample preparation.

Page 2 Line 33: The term "... an automated sample preparation-mid-infrared quantum cascade laser spectroscopy system ..." is rather bulky and might be replaced by "... an automated sample preparation system has been reported, which can be coupled to a quantum cascade laser absorption spectrometer ...".

Revised as suggested.

Page 3 Line 3: The term "atmospheric" might be replaced by "ambient or subambient".

Revised as suggested.

Page 3 Line 3 – 5: As the flow and adsorption time of MFC based systems can be adjusted quite flexibly these systems can be applied for high concentrations as well, so this sentence might be deleted. In addition, the presented system is not suitable for concentrations above $10 \mu\text{mol mol}^{-1}$.

The sentence has been deleted.

Page 3 Line 6 – 8: The last section might be rephrased to: "... system that offers enhanced flexibility in terms of sample gas pressure and N_2O concentration. The novel system encloses a ...".

Revised as suggested.

Page 3 Line 12: The correct wording might be "... with wheels attached, and is connected to a gas ...".

Revised as suggested.

Page Line 26: The term "flask inner pressure" might be replaced by "sample gas pressure in the flask".

Revised as suggested.

Page 4 Line 7 – 9: The reader would benefit from information on the amounts of $\text{Mg}(\text{ClO}_4)_2$ and Ascarite in the chemical trap and how often (after which sample gas volume) you renew it.

Since the development of the system, we have not replaced the chemical trap for more than 10 months without any analytical problems. We will further check how often it should be renewed. As for the amounts

of adsorbents, we have modified the sentence as follows:

The chemical trap is a glass tube (9 mm inner diameter, 20 cm long) packed with Mg(ClO₄)₂ (8–24 mesh; Wako Pure Chemical Industries Ltd., Osaka, Japan), NaOH on support (Ascarite, 20–30 mesh; Thomas Scientific), and Mg(ClO₄)₂ (20–48 mesh) in series **with approximately equal length**.

Page 4 Line 28: The term “electric sheated heater” is unclear might be reformulated.

Not "sheated", but "sheathed" heater. It is a heater with electrically-insulated outer sheath. It can be applied both to the contact heating of metals and the immersion heating of liquids. We reorganized the words as "sheathed electric heater".

Page 5 Line 9: The word “was” might be replaced by “is”.

Revised as suggested.

Page 5 Line 25: The word “respectively” might be placed at the end of the sentence.

Revised as suggested.

Page 6 Line 6: The sentence might be rephrased to “... to adapt the sampling procedure to the prevailing sample pressure and N₂O concentration”

Revised as suggested.

Page 6 Line 8: The term “inner” should be replaced by “sample gas”.

Revised as suggested.

Page 6 Line 17: The term “sample” might be replaced by “sample volume”.

Revised as suggested.

Page 6 Line 20: The term “becomes greater” might be replaced by “increases”.

Revised as suggested.

Page 6 Line 21: The wording “using another flask” might be deleted.

We have deleted the phrase.

Page 6 Line 24 – 25: The sentence might be rephrased to “... to ensure quantitative recovery of N₂O and thus also minimize contamination of subsequent analyses (blank values).”

Revised as suggested.

Page 7 Line 4: What is the meaning of “It was not complete even at 50°C ...”, was the separation not complete or the elution, please rephrase.

The separation was not complete. We revised the text.

Page 7 Line 16: Please rephrase to "... To achieve a quantitative N₂O recovery the timing of the cryofocussing step was optimized to trap the eluent from the first column only while N₂O was released." or similar.

Revised as suggested.

Page 11 Table 1: Please compare the performance additionally to the work of Wolf et al. (2015) doi:10.5194/bg-12-2517-2015.

Sample size: 8000 mL of ambient air; $\delta^{15}\text{N}_{\text{bulk}}$, $\delta^{15}\text{N}_{\alpha}$, $\delta^{15}\text{N}_{\beta}$, SP, $\delta^{18}\text{O}$: 0.12, 0.20, 0.12, 0.22, 0.10 ‰; analytical time ca. 30 minutes, fully automated system with QCLAS (n = 331).

Thank you for the information on the latest publication. We have added this paper in the table.

Page 11 Table 1: The term "precision (1s)" might be replaced by "precision (1 standard deviation)" as 1s is often used for 1 second.

Corrected.