Interactive comment on “Comparison of nitrous oxide (N2O) analyzers for high-precision measurements of atmospheric mole fractions” by B. Lebegue et al.

Anonymous Referee #4

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This paper is a timely assessment of new measurement technology, available for the precise determination of N2O in the atmosphere. Many of the tests presented in the paper follow on from similar tests described in Yver Kwok et al. (2015). The testing procedure is appropriate for the type of measurements being made, unfortunately the tests were obviously carried out at different times and the testing procedure/protocol tended to vary somewhat over time. I am sure that if all of the instruments were to be retested the results would differ a little from those presented.

We would like to thank the reviewer for having reviewed this paper and formulated helpful comments. We answer each of them hereafter and add when needed modifications in the revised manuscript.

Little is said within the paper about N2O isotopes and how the different analysers behave with regards to these. This is important with regards to measuring atmospheric mole fractions and the standards used for calibration, especially as the former GC systems aren’t isotopically sensitive. It might be good to mention something about the optical instruments being sensitive to isotopes in the conclusions and recommend that users bare this in mind when acquiring calibration standards and for these instruments.
We understand the interest for studying the N_2O isotopes or other isotopologues and species measured by the various instruments. In this paper we chose to compare different analyzers measuring the same species. As the isotopes of N_2O are measured by only one instrument, comparisons and study of interferences are impossible.

A sentence will be added in the conclusion to remind the reader of the possible influence of N_2O isotopes
P10964 L1 It should be noted that, while here we only studied N_2O, all these new optical techniques are sensitive to isotopes and users should keep this in mind until further study is made on this subject.

Finally, the only recommendations given are for the drying of air samples prior to analysis due to the poor manufacturer water vapour corrections. The atmospheric community would probably welcome more recommendations based on the results presented in this paper, such as calibration frequency, etc. Some recommendations may be difficult due to the inclusion of certain manufacturers as authors of the manuscript.
We also give recommendations to use the analyzers in temperature controlled environments. The calibration frequency is different for each tested analyzer and depends also on the station environment like temperature variation in the laboratory. In paragraph 2.5 and in the summary, we give information concerning the calibration frequency.
“The calibration strategy chosen for the test with a 14-day frequency is only acceptable for the CRDS, FTIR and QC-TILDAS. For the other instruments, a more frequent calibration strategy needs to be developed. The results showed that for an ICOS-EP, a calibration

frequency of twice a day is necessary to reduce the LTR below the WMO recommendations."
In addition we have more information concerning the ICOS-EP in the conclusion:
"In our case, an injection frequency of 11 hours for a reference gas led to an improvement of the short-term repeatability of the target gas from 0.85 ppb to 0.07 ppb. Thus, prior to the use of an analyzer, the calibration strategy should be studied and optimized for the instrument and station conditions."
Some recommendations were given about the different analyzers depending on their stability and performances, some instruments are better at high frequencies and other are useful for their good stability over time.

The two co-authors who are also instrument vendors have decided to withdraw from the co-author list as their contribution, apart from lending us their instrument, was minimal. The acknowledgment will be rewritten in order to acknowledge all the contributions from the various instruments.

Specific comments: - The Abstract states part of the drive to replace gas chromatography-electron capture detectors with optical methods are that ECDs are highly non-linear. However, page 10942, line 19 it is stated that the ECD used is linear over the ambient mole fraction range. These two statements do not concur, and I believe it is highly unlikely that the ECD is linear, although the correction for non-linearity over this range will be small. Some evidence on linearity of non-linearity should be presented.
We will clarify the sentence on page 10942, line19 to:
For the small range of N_2O mole fractions in the ambient air (324-334 ppb), the ECD can be corrected for its non-linear response by applying a two-point calibration strategy with two working standards (322 and 338 ppb).

It is also indicated that the short-term repeatability of an GC-ECD system is in the order of 0.1-0.3ppb (p10941), however the short-term precision detailed in Table 1 shows a repeatability of 0.016 ppb for a 1 hour average, better that some of the optical instruments? –
Actually the 0.1 – 0.3 ppb is the CMR for raw data (5 min measurements). Short-term precision will be changed to continuous measurement precision p10941 L6.
It is however possible for the GC to have a better 1hour CMR than some other instruments

- ICOS is defined as two different things - integrated carbon observation system (p10939) and integrated cavity output – spectroscopy (P10941), this could cause some confusion.
Off-Axis Integrated Cavity Output Spectroscopes will now be shortened to OA-ICOS.

Line 11 of section 2.1 – the acronym ICP is not defined.
We will replace ICP by inter comparison

- Section 3.1 - the make up of the synthetic air is not presented, nor a mention of the isotopic matrix.
The content of the synthetic air matrix will be added but no information was available on the isotopic matrix.
P10949 L3 and L7: …filled with a synthetic matrix of 21.00 Vol.-% ± 1 % of O_2, 0.93 Vol.-% ± 1 % of Ar and a balance of N_2 (Deuste Steininger)…

- Section 3.2, it is a bit misleading to provide a drift value for the GC in Table 2, since the GC data was drift corrected (as described in the text).

The drift value for the GC will be removed.

- Section 3.4 – the 2 ICOS-QCL instruments and the DFG instrument actually show a LTR of between 0.21 and 0.32

The values will be changed.

- Section 3.6 - There is no description of the inlet system used during the tests, just that the same system was used for all analysers.

The description of the inlet system will be added and its non-influence on the stabilization time will be highlighted. The lines from P10954 L25 to P10955 L2 will be changed:

P10954 L25 For all instruments, the inlet system consisted in pressure regulators (SCOTT MODEL 14 M-14C, nickel-plated brass) installed on each cylinder, connected to a Valco multi-port valve (VICI) using two to four meter length of either ¼" OD Synflex 1300 (EATON) tubing for the FTIR and QC-TILDAS or 1/16" OD stainless steel tubing for the other instruments. A short length of similar tubing was used to connect the Valco valve to the inlet of the instruments. It should be noted that such an inlet system did not impact the time of stabilization as there are nearly no dead volumes and the volume to flush (mainly the tubing) is neither significant in regard of the flow rates (short residence time). The stabilization time is a function of the cell volume and design, dead volume and sample flow rate. The results found in this study are only valid for the sample flow rates that were considered and for our inlet systems. Other inlet systems should be mindful of any possible dead volumes or the influence of the tubing length.

- Section 3.7 – Fig 3e – it is difficult to conclude that this instrument shows a measurable temp dependence.

The mole fraction to temperature relationship look unusual – perhaps this text needs to be re-evaluated for this instrument? –

No parameters other than the temperature have been changed for this test. For the ICOS-SD (Fig 3e), in the section 3.7 we say that there was a large temperature dependence. It is shown that the instrument somehow reacts on temperature changes, but it cannot easily be translated to an equation. We will modify the term "dependence" to "sensitivity".

Section 3.9 and Figure 6. The author states that in comparison to the FTIR, the ICOS SD, ICOS 40 and QC-TILDAS show and offset of the mean difference of more than 0.25 ppb. However, the data presented in Figure 6 indicates that a value of 0.13 ppb for the ICOS SD and 0.21 ppb for the ICOS 40?

P10960 L13, the value of 0.25 ppb has been changed to 0.1 ppb, the WMO recommendation for intercomparison.

All values will be verified and corrected.

- Throughout the text precisions are reported with varying numbers of significant figures – be consistent.

All numbers in the text, tables and figures have been verified and will be adjusted to be consistent.

- Nomenclature - swap between using Aerodyne and QC-TILDAS. Try to be consistent throughout the manuscript.

We verified it throughout the manuscript and this occurrence of "Aerodyne" will be changed to "QC-TILDAS".

- Table 1 - not clear about calibration scales. DS and MPI aren't calibration scales for N2O but places where analysed. Should state that on WMO-X2006a and place where calibrated.

We will change the legend of Table 1:

P10967 Most instruments used two sets of calibration cylinders; here, we indicate the most frequently used: the set filled and calibrated by Max Planck Institute (MPI), spanning a range from 320 to 360 ppb of N_2O, or the set filled by Deuste Steininger and calibrated with our FTIR (DS), ranging from 320 to 345 ppb N_2O.

- Tables 3 and 4 – Peak to peak need explaining in the table captions.

We will add to Table 3:

The peak to peak value is the difference between the lowest and the highest values of the 10 analysis.

We will add to Table 4:

The peak to peak value is the difference between the lowest and the highest values of the N target measurements.

- Table 5 - normalisation process needs explaining both in table 5 and section 3.5.

We will clarify in the legend:

P10954 L8 For each calibration cylinder, we measure the drift between the consecutive calibration runs. Then these drifts per day are normalized to drifts per ten days. Finally we average the drifts from all calibration cylinders to extract the mean and maximum drift (Table 5).