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Comparison of nitrous oxide (N₂O) analyzers for high-precision measurements of atmospheric mole fractions

**B. Lebegue¹, M. Schmidt², M. Ramonet¹, B. Wastine¹, C. Yver Kwok¹,
O. Laurent¹, S. Belviso¹, A. Guemri¹, C. Philippon¹, J. Smith³, S. Conil⁴,
H. J. Jost⁵, and E. R. Crosson⁶**

¹Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), UMR
CEA-CNRS-UVSQ, Gif-sur-Yvette, France

²Institut für Umweltphysik, University Heidelberg, Heidelberg, Germany

³Thünen Institut für Agrarklimaschutz, Braunschweig, Germany

⁴Observatoire Pérenne de l'Environnement, ANDRA, Bure, France

⁵Thermo Fischer Scientific, Reinach, Switzerland

⁶Picarro, Inc., Sunnyvale, CA 94085, USA

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Correspondence to: B. Lebegue (benjamin.lebegue@lsce.ipsl.fr)

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Abstract

Over the last few decades, in-situ measurements of atmospheric N₂O mole fractions have been performed using gas chromatographs (GCs) equipped with electron capture detectors (ECDs). When trying to meet the World Meteorological Organization's (WMO) quality goal, this technique becomes very challenging as the detectors are highly non-linear and the GCs at remote stations require a considerable amount of maintenance by qualified technicians to maintain good short-term and long-term repeatability. With more robust optical spectrometers being now available for N₂O measurements, we aim to identify a robust and stable analyzer that can be integrated into atmospheric monitoring networks, such as the Integrated Carbon Observation System (ICOS). In this study, we tested seven analyzers that were developed and commercialized from five different companies and compared the results with established techniques. Each instrument was characterized during a time period of approximately eight weeks. The test protocols included the characterization of the short-term and long-term repeatability, drift, temperature dependence, linearity and sensitivity to water vapor. During the test period, ambient air measurements were compared under field conditions at the Gif-sur-Yvette station. All of the analyzers showed a standard deviation better than 0.1 ppb for the 10 min averages. Some analyzers would benefit from improvements in temperature stability to reduce the instrument drift, which could then help in reducing the frequency of calibrations. For most instruments, the water vapor correction algorithms applied by companies are not sufficient for high-precision atmospheric measurements, which results in the need to dry the ambient air prior to analysis.

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1 Introduction

Nitrous oxide (N₂O) is a greenhouse gas with an atmospheric life-time of 131 years and a global warming potential that is approximately 300 times that of CO₂ at a 100 year time horizon (Prather et al., 2012). At present, the N₂O emissions are the most important factor for stratospheric ozone depletion, and they are expected to remain the largest factor for this century (Ravishankara et al., 2009; Wuebbles, 2009).

Overall, gradients over the continent or between maritime and continental air are small (0.1–0.2 % of background mixing ratio) and need to be measured precisely. Global observations of the atmospheric N₂O mole fraction from networks such as Advanced Global Atmospheric Gas Experiment (AGAGE), National Oceanic and Atmospheric Administration's Earth System Research Laboratory (NOAA/ESRL), and Réseau Atmosphérique de Mesure des Composés à Effet de Serre (RAMCES) showed a mean value of approximately 328 ppb for the Northern Hemisphere and 326.5 ppb for the Southern Hemisphere in 2014 (Lopez et al., 2012; Schmidt et al., 2014; Thompson et al., 2013). The amplitude of the seasonal cycle is smaller in the Southern than in the Northern Hemisphere, with a value of approximately 0.4 ppb at Cape Grim, Tasmania, compared with 0.89 ppb at Mace Head, Ireland (Nevison et al., 2007). The N₂O growth rate in the atmosphere over the last five years is, on average, 0.75–0.78 ppb year⁻¹.

Even closer to the sources, at European semi-rural stations, only slight variations in atmospheric N₂O were found on the timescale of days. Lopez et al. (2012) showed that the diurnal cycle at the semi-urban station Gif-sur-Yvette (France, measurements 7 m a.g.l.) has an amplitude of 0.96 ppb, whereas at Trainou tall tower (rural area, measurements up to 180 m a.g.l.), the mean amplitude is only 0.32 ppb. Accordingly, the World Meteorological Organization (WMO) Expert group on CO₂ and other GHGs recommended an N₂O inter-laboratory comparability goal of ±0.1 ppb at the 17th WMO/IAEA Meeting, 10–13 June 2013, in Beijing (http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_213_web.pdf). This ambitious goal has not yet been reached, as shown recently by Bergamaschi et al. (2015), who found biases between

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in situ GC measurements and flask sampling at different European stations of up to 0.7 ppb. These biases, even when corrected, limit the precision of N₂O emission estimates by inverse models.

High-precision atmospheric N₂O measurements in flask measurement networks and at in-situ stations are traditionally measured by gas chromatography using an Electron Capture Detector (ECD). With this setup, a typical short-term repeatability of 0.1–0.3 ppb was reached for instruments that were set up since 1995 (Lopez et al., 2012; Nevison et al., 2011; Popa et al., 2010; Schmidt et al., 2001). Over the last few years, new analytical techniques became commercially available for obtaining high-precision measurements of atmospheric N₂O. Hammer et al. (2013) described the Fourier Transform Infrared (FTIR) absorption, which can reach a long-term repeatability for N₂O of 0.04 ppb over a 10 month period. More recently, laser-based systems, e.g., cavity-enhanced off-axis Integrated Cavity Output Spectroscopy (ICOS), Cavity Ring-Down Spectroscopy (CRDS), Quantum Cascade Tunable Infrared Laser Differential Absorption Spectroscopy (QC-TILDAS) and Difference Frequency Generation (DFG)-based systems, were developed and commercialized by different companies. In this study, we present the first assessment of the performance of seven N₂O analyzers and compare these techniques to routine instruments, including a GC analyzer (Lopez et al., 2012) that is used at LSCE (Laboratoire des Sciences du Climat et de l'Environnement) for ambient air measurements since 2001 and a FTIR that has been running since 2012. All of the tested instruments have been characterized for repeatability, long-term stability, linearity, temperature dependency and spectroscopic cross interferences with water vapor. The instrument evaluations were all performed at the Integrated Carbon Observation System (ICOS) Atmospheric Thematic Center Metrology Laboratory (ATC MLab) hosted at LSCE in Gif-sur-Yvette, but not all of the instruments were tested at the same time. Because the ATC MLab was in its creation phase, there has been evolution toward the best practices in the test protocol, which will be detailed below. The evaluations have been performed between October 2012 and January 2014 over 3 periods: November–December 2012, May–June 2013 and December 2013–January 2014.

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2 Instrument descriptions

2.1 Gas Chromatograph instrument (GC)

The LSCE laboratory at Gif-sur-Yvette is equipped with an automated gas chromatograph (GC) system (HP-6890, Agilent coupled to a PP1, Peak Performer Laboratories up to May 2013; since then, HP-7890A was used with the same PP1 and similar specificities and performances) to analyze the CO₂, CH₄, N₂O, SF₆, CO and H₂ mole fractions. This instrument has been contributing to the RAMCES monitoring network since 2001 and is used to obtain in-situ measurements at Gif-sur-Yvette station for the analysis of flask samples and the calibration of working standards. It also serves as a reference instrument for international comparison programs, such as the WMO Round Robin or the European Cucumber ICP program (<http://cucumbers.uea.ac.uk/>). Detailed descriptions of the GC system for N₂O analysis is given by Lopez et al. (2012). The GC is equipped with a flame ionization detector (FID) and a nickel catalyst to determine the CH₄ and CO₂ and with an electron capture detector (ECD) for N₂O and SF₆ analysis. We use a 10 mL sample loop, two Haysep-Q columns and Ar/CH₄ as a carrier gas to separate N₂O and SF₆ from the other compounds of air. Each analysis takes less than 6 min and allows two to six measurements of air samples on a hourly basis. For the small range of N₂O mole fractions in the ambient air (324–334 ppb), the ECD can be considered linear, and we apply a two-point calibration strategy with two working standards (322 and 338 ppb). A calibration frequency of 30 to 45 min was chosen to reach a N₂O repeatability of 0.2 ppb. Lopez et al. (2012) described an interference between SF₆ and N₂O measurements when SF₆ mole fraction exceeds 15 ppt. Therefore, during the comparison period, all of the N₂O measurements made by our routine GC are flagged as not valid when SF₆ exceeds 15 ppt. The standard deviation of the quality control gas (i.e., the “target” gas), which was injected every 2 h, was 0.3 ppb over the comparison period (October 2012–January 2014). The GC is used in this study as the routine reference instrument to compare the instruments’ perfor-

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mance regarding continuous measurement repeatability and drift assessments and for ambient air comparisons.

2.2 Spectronus trace gas and isotope system, ecotech (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is based on the absorption of infrared radiation (Beer–Lambert Law). A polychromatic infrared beam from an infrared source first passes through a Michelson interferometer, and this modulated beam then traverses the sample cell. The resulting time-modulated signal is converted into an infrared spectrum through Fourier transformation. The spectra obtained are analyzed using a method comparing the measured data with data obtained from a model using the HITRAN database (Rothman et al., 2009, 2005). One of the main advantages of an FTIR analyzer is its ability to record a spectrum over a broad IR range, thereby offering the possibility to measure a large number of species simultaneously. Spectra are stored and can be analyzed at a later date with a different method to obtain better data or study new species. The spectral range of the FTIR extends from 1800 to 7500 cm^{-1} with a resolution of 1 cm^{-1} .

Here, we briefly describe the instrument configuration used during the comparison. The LSCE purchased this analyzer (built by Ecotech, Australia) in 2011 from the University of Wollongong (Australia). Detailed descriptions of similar analyzers used in the atmospheric community are presented by Griffith et al. (2012) and Hammer et al. (2013). The instrument used in our laboratory consists of a commercially available FTIR interferometer (IRcube, Bruker Optics, Germany) with a 1 cm^{-1} resolution coupled to a 3.5 L multi-pass glass cell with a 24 m optical path length (PA-24, Infrared Analysis, USA). The cell and the interferometer are assembled on an optical bench inside a temperature controlled chamber. An in-situ J-type thermocouple, to monitor the cell temperature, and a pressure sensor (HPM-760s, Teledyne Hastings, USA) are included in the multi-pass cell. Initially, we used nitrogen 4.5 purity (99.995 Vol %) to slowly purge the interferometer housing and the transfer-optics between the cell and the interferometer. In 2014, we observed an improvement for the CO stability of the FTIR when using nitro-

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gen 6.0 (99.9999 Vol %). Since September 2014, we systematically use N_2 6.0, which had no influence on the N_2O measurements. A drying system composed of a 24 inch counter-flow Nafion dryer (Permapure, Toms River, USA) followed by a chemical dryer ($\text{Mg}(\text{ClO}_4)_2$) is installed upstream of the cell. The flow is provided by a pump (MV2NT, Vacuubrand, Germany). The pressure of the cell is controlled using a built-in mass flow controller mounted at the outlet of the cell, and the flow is controlled by a mass flow controller installed upstream of the cell and downstream of the drying system. Our instrument analyzes and saves the absorption bands located between 0 and 7999 cm^{-1} . Four windows are exploited. One of them, between 2097 and 2242 cm^{-1} , provides the mole fraction of N_2O and CO. A calibration with 5 working standards is carried out every two weeks, and a quality control gas is analyzed every 5 h for 40 min. Due to its size, it takes five to ten minutes to empty and flush the cell, when changing the type of sample. The sample flow rate was regulated at $1 \pm 0.05 \text{ L min}^{-1}$ and the cell pressure and temperature were regulated at $1100 \pm 0.02 \text{ hPa}$ ($1.1 \times 10^5 \pm 2 \text{ Pa}$) and $32 \pm 0.03^\circ\text{C}$, respectively. The sample measurement intervals for the target and air measurements are one and three minutes, respectively. The quality control gas showed a N_2O standard deviation of 0.08 ppb during the first and third periods of the comparison (December 2012 and January 2014) and a standard deviation of 0.12 ppb during the second period (May 2013).

2.3 CRDS-QCL instruments G5101-I Picarro (CRDS)

The two Cavity Ring Down Spectrometer (CRDS) instruments tested in this study were a loaned prototype, tested from November to December 2012, and the commercialized model of the G5101-i unit from Picarro (Picarro Inc., CA, USA) bought by the LSCE in May 2014. The thermal regulation was not yet fully optimized for the prototype, and it did not possess a water vapor correction. The CRDS system made by Picarro uses a Quantum Cascade Laser (QCL) as a source to measure N_2O , $\delta^{15}\text{N}_\alpha$, $\delta^{15}\text{N}_\beta$ and H_2O in the mid infrared region (4.55 μm). The CRDS technique uses an optical cell (48 mL) with 3 highly reflective mirrors (Crosson, 2008). Light is injected into the cavity

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at the required wavelength from the QCL through a highly reflective mirror and is measured by a photodetector through a second highly reflective mirror. The path length inside the cell is about 8 km. The intensity of the light inside the cell builds up over time by resonance due to a third mirror mounted on a piezoelectric device, which allows for inter-mirror distance adjustment. Then, the laser is switched off, and the time constant of the light intensity decrease is measured. From this cavity decay time, the concentration is retrieved when knowing the absorption cross-section of the species at the laser wavelength. A measurement interval of less than 10 s is obtained. During the comparison campaign at LSCE, the sample flow rate is approximately 50 mL min^{-1} . The cell pressure is regulated at $100 \pm 0.001 \text{ Torr}$ ($1.33 \times 10^4 \pm 0.13 \text{ Pa}$), and the cell temperature is set at $40 \pm 0.001 \text{ }^\circ\text{C}$. A calibration with four working standards is performed every ten days, and a quality control gas is analyzed every 5 h for 30 min.

2.4 IRIS 4600, ThermoFischer Scientific (DFG)

The Thermo IRIS 4600 was lent by Thermo Fisher Scientific for our test campaign from November to December 2012. The instrument measures N_2O and water vapor. It uses Difference Frequency Generation (DFG) laser technology, which consists of combining two near-infrared telecom lasers into a non-linear frequency conversion crystal to reach the mid infrared region. The laser continuously sweeps in the frequency through the absorption bandwidth at a rate of 500 Hz (Scherer et al., 2013). This spectrometer measures in the $4.6 \mu\text{m}$ N_2O and H_2O bands, each sweep provides a near instantaneous measurement of the two gases. The measurement interval is adjustable between 0.1 and 10 s. The cell is 40 cm long for a cell size of approximately 80 mL, which provides an optical path length of 5 m. The sample flow rate through the cell is 300 mL min^{-1} . The cell pressure and temperature are regulated at $175 \pm 0.002 \text{ mbar}$ ($1.75 \times 10^4 \pm 0.2 \text{ Pa}$) and $37.5 \pm 0.002 \text{ }^\circ\text{C}$ respectively. A calibration with four standard gases is performed every week, and a quality control gas is measured every 5 h for 30 min.

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2.5 ICOS-QCL instruments Los Gatos Research (ICOS)

Three Off-Axis Integrated Cavity Output Spectroscopes with Quantum Cascade Lasers (OA-ICOS-QCL) made by Los Gatos Research (LGR, USA) were provided to us by the French National Radioactive Waste Management Agency (ANDRA) for a performance assessment. These three instruments measure N_2O , CO and H_2O in the $4.6 \mu\text{m}$ region. Instruments based on off-axis ICOS use a tunable laser and an optical cavity (408 mL). However, unlike other cavity methods such as CRDS, this technique is based on directing the laser beam off axis through the cavity, which, when combined with highly reflective mirrors, provides a long effective optical path that spatially sweeps the cavity volume due to spatially separated multi-reflections within the cavity before the reentrant condition of the optical beam is fulfilled. Moreover, in contrast to CRDS, the laser beam is not locked on each cavity mode but is swept over the gas absorption line. The mole fraction can then be obtained from the measured spectra integrated over the entire absorption feature, the cell pressure and temperature, the effective optical path length and the absorption line parameters for each species. These instruments have a measurement rate of up to 1 Hz with the internal pump and up to 10 Hz with an optional pump.

One instrument is the standard model of the analyzer, referred to here as ICOS-SD. The two others are Enhanced Performance models that incorporate an improved temperature control of the cavity, referred to here as ICOS-EP38 and ICOS-EP40. The sample flow rate is set for the three analyzers at 300 mL min^{-1} . The cell is regulated at $85 \pm 0.007 \text{ Torr}$ ($1.13 \times 10^4 \pm 0.93 \text{ Pa}$) and $27 \pm 0.2 \text{ }^\circ\text{C}$ for the standard model and $45 \pm 0.005 \text{ }^\circ\text{C}$ for the enhanced models. For the ICOS-SD, a calibration is conducted once a week. For the two enhanced models, the calibration frequency occurs every two weeks. For all instruments, a quality control gas is analyzed every 5 h for 30 min for the ICOS-SD and every 6 h for 30 min for the two ICOS-EP models.

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2.6 QCL Mini Monitor, Aerodyne (QC-TILDAS)

The tested Aerodyne's Quantum Cascade Laser Mini Monitor (Aerodyne Research Inc., USA) was provided by the Thünen Institut für Agrarklimaschutz (Braunschweig, Germany) for our test campaign. This instrument is currently used for Eddy covariance measurements.

The instrument uses a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectroscopy technique and is referred to here as QC-TILDAS for the remainder of the discussion. One QC Laser beam is sent through a Herriott astigmatic multi-pass cavity (0.5 L) with a fixed optical path length of 76 m. Then, the light is received by a thermoelectrically cooled infrared detector. This instrument works in the mid-infrared domain (4.54 μm). The instrument performs an advanced type of wavelength sweep integration before dropping the laser current below a threshold to determine the voltage of the detector for zero light. The instrument can then determine concentrations by fitting the measured spectrum with the HITRAN database using the cell temperature and pressure. The instrument can run periodically an auto-background, which consists of acquiring a spectrum with the sample cell filled with dry nitrogen and is used to normalize future spectra. This option was not used during this campaign. The instrument tested had no active control of the cell pressure. During the tests in our laboratory, we set the sample flow rate at 1 L min^{-1} and the pressure at 33 ± 0.2 Torr ($4.4 \times 10^3 \pm 27$ Pa) by using a valve at the outlet of the cavity and a needle valve at the inlet. The cell's temperature is regulated at 22 ± 0.03 °C. A calibration is conducted every two weeks, and a quality control gas is measured every 5 h.

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3 Instrument tests

3.1 Laboratory description

All tests were performed at the ICOS ATC MLab located at Gif-sur-Yvette, 20 km southwest of Paris. The MLab purpose is to test and validate atmospheric analyzers, instrumental setups and related components and consumables. The laboratory is air conditioned and equipped with calibration scales, target gases and inlet lines coupled with drying systems for ambient air comparisons. Two CRDS reference analyzers are used for the ambient air comparisons of CO_2 , CH_4 and CO mole fractions. The water dependency, which was first tested using the droplet test, is now evaluated with a dedicated humidifier bench. The ambient air inlet is located on the roof of the laboratory, 7 m a.g.l.

For ambient air comparisons, the air is dehumidified, by passing through 335 mL glass traps cooled in an ethanol bath using a cryogenic cooler (Thermo Neslab CC-65 or HAAKE EK 90). The cooling traps are filled with glass beads to increase the surface area for water vapor condensation. Depending on the weather conditions, the cooling traps are typically changed once or twice per week. This setup dries the air sample down to less than 15 ppm of water.

In total, we use four sets of calibration cylinders (laboratory standards) to calibrate all of the N_2O analyzers presented in this study. For the GC measurements, we use two calibration cylinders (Luxfer aluminum cylinders) filled by Deuste Steininger (Mühlhausen, Germany) in a synthetic matrix of N_2 , O_2 and Ar. These cylinders have been calibrated against laboratory primary standards purchased from NOAA/CMDL and are reported for N_2O on the NOAA-2006a scale. For all optical instruments, three other sets of calibration cylinders are used during the comparison with a certified concentration of N_2O (Table 1) among others gases such as CO , CH_4 or CO_2 . The first calibration set consists of five aluminum cylinders (Luxfer), which were filled with ambient air, spiked and calibrated with a GC-ECD by the Max Planck Institute of Jena, Germany, on the NOAA-2006a scale (Hall et al., 2007) spanning a range from 320 to 345 ppb N_2O . Because this scale has been routinely used by the FTIR and to test other

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analyzers in the MLab, this scale was not always available during the second test period and had to be replaced by another scale. This second set consists of six aluminum cylinders filled with a synthetic matrix of N_2 , O_2 and Ar (Deuste Steininger) and calibrated by our FTIR against the Max Planck Institute calibration scale. This set spans a range from 320 to 360 ppb N_2O . When the Aerodyne was tested, a third calibration set was performed once by the instrument. This set consists of four aluminum cylinders, spanning a range from 335 to 355 ppb N_2O , filled with a synthetic matrix of N_2 , O_2 and Ar (Deuste Steininger) and calibrated by our FTIR against the MPI calibration scale. These sets were analyzed at least every two weeks on each analyzer. Calibration sequences were made by measuring each cylinder for at least 15 min, including 10 min for flushing the inlet line and instrument cell. The whole calibration set was analyzed at least three times, with the first run systematically rejected to ensure a proper flushing of the system. The target cylinders used for various tests are filled with dry ambient air, using an oil free compressor (RIX) and coalescent filters associated with magnesium perchlorate drying cartridges. These cylinders are analyzed prior and after use by the GC system. All calibration and test cylinders are equipped with the same type of two-stage nickel-plated brass pressure regulators (Model 14, Scott Specialty Gases, Breda, the Netherlands).

All of the tests were performed in a temperature controlled room ($22 \pm 1^\circ C$), except for the temperature dependence tests, for which the laboratory temperature was deliberately modified. In general, all analyzers were tested using similar procedures and during the same time span. We would have preferred to test all of the instruments at the same time, but due to constraints in their availability, tests were spread over time from October 2012 to January 2014. During this time span, the test procedures were improved towards the ICOS standard test protocol, which is now used to test new instruments in the MLab for the European ICOS atmospheric measurement network. In some cases, the time period was just too short to perform all tests. In the paragraphs below, we describe the test procedures in detail and state when an individual test or

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analysis diverged from the standard protocol. Most of the tests presented in the following sections have been already described by Yver Kwok et al. (2015).

3.2 Continuous measurement repeatability (CMR) and drift assessment

To determine the continuous measurement repeatability (CMR, often called precision by the manufacturer) of the instruments, a single target gas tank filled at the MLab with dry natural air is measured continuously over a time period of at least 30 h. The raw data measurement interval of the analyzers tested varied from 5 min for the GC to 1 s for the QC-TILDAS analyzer (Table 2). We calculate the standard deviations of 30 h of continuous measurements of a target gas. Table 2 presents these values for the raw data at the frequency given by all instruments for 1 min averaged data (when available), 10 min averaged data and 1 h averaged data. During this 30 h sequence of target gas measurement, no calibrations were performed, and no drift correction was applied, except for the GC, which automatically corrects the data with calibration cylinders every 45 min.

From this experiment, we also calculate the drift for each instrument (Table 2). The drift is calculated using a linear regression with the data from the 30 h test. The slope of the regression represents the drift of the instrument (in $ppb h^{-1}$, which has been converted to $ppb d^{-1}$) over this 30 h period.

For high-frequency measurements (1–2 s), the ICOS-EP and QC-TILDAS analyzers show the best CMR (0.08–0.10 ppb). For 1 min averaged data, the QC-TILDAS, CRDS and ICOS-EP models show very similar standard deviations of approximately 0.05–0.07 ppb, whereas the standard deviations of the ICOS-SD, DFG and FTIR are between 0.12 and 0.16 ppb. For the 1 h averaging data, the GC, FTIR and CRDS are the most precise, with the two ICOS-EP models and QC-TILDAS two times less precise and the ICOS-SD and DFG five times less precise. Apart from the GC, whose drift is corrected with the working standards, the FTIR has the smallest drift, with the CRDS and QC-TILDAS drifts being slightly higher. The other instruments present a significant

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drift of 0.1 ppb d^{-1} or more. For these instruments, a standard gas measured several times a day could be used to correct this drift.

The optimal averaging time can be estimated by using Allan standard deviation plots. These plots can also be used, with long-term repeatability assessment, to estimate the stability of an instrument and decide on a calibration strategy. Figure 1 shows the time series of the 30 h target test for each instrument (two upper panels), and the Allan deviation plotted against the averaging times using a logarithmic scale (lower panel). With the Allan standard deviation assessment, we can define two main categories. First is the category of instruments with a high precision for high-frequency measurements (ICOS-SD, ICOS-EPs or QC-TILDAS instruments). They present their best averaging time for intervals shorter than five minutes and higher variability over longer averaging times. The other category regroups the instruments with better stability over longer averaging intervals; the best averaging time is from 10 min to 1 h or higher (CRDS, FTIR, DFG and ICOS-EP38). Some instruments, such as the ICOS-EP38, have strong performances in both categories: high precision for high frequencies and good stability. These two types of performances will interest different research communities: the high precision for high frequencies will interest anyone working on short time phenomena ($< 1 \text{ min}$), such as eddy covariance studies. The second category will interest communities working on typically 10 min to hourly averaged data, which is the case of atmospheric background monitoring stations, such as the ICOS atmospheric network. It should be noted that all of the instruments tested at the MLab for this study achieved the CMR specifications given by the manufacturers (often called precision in their technical documents).

3.3 Short-term repeatability (STR) assessment

Because the CMR test is an assessment of the precision of the instrument over continuous measurements, the short-term repeatability (STR) assessment quantifies the ability of one instrument to always reach the same value for a target gas when alter-

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nated with a different sample. For this test, a target gas is measured 10 times for 15 to 20 min alternating with dry ambient air measurements for 5 min. Similar to the CMR assessment, no calibration or drift corrections are applied. A N_2O mean value is then calculated for each injection of the target by taking the last 5 min of each analysis. The repeatability is expressed as the dispersion (1σ) of the ten injections, and the results are presented in Table 3.

The STR is approximately the same for all instruments ($\approx 0.02 \text{ ppb}$). Only the FTIR and DFG instruments show higher STR of 0.09 and 0.17 ppb, respectively. Part of the difference between the FTIR and DFG and the other instruments can be explained with the CMR, as the FTIR and DFG are the least precise instruments for small averaging time (1 to 5 min). As a consequence, when measuring calibration scales or standard gas, FTIR and DFG owners would need to increase the measurement time to 20 to 30 min and then keep the last 10 min to reach a better STR.

3.4 Long-term repeatability (LTR)

The long-term repeatability (LTR) assessment tests quantify the stability of an analyzer over periods of several days. For each instrument, a target gas was measured regularly (at least twice a day) alternating with ambient air for several days. Depending on the instrument type and the test period, the target measurements were performed for a period of 20 min for the instruments that were compared during the first campaign, 30 min for the second and third campaigns, and 40 min for the FTIR due to its cell size, which needs more time for the stabilization of the physical parameters. For all instruments, a mean value was calculated over the last 5 min of each analysis. A calibration was performed every week or 14 days and was applied as a drift correction, with a linear interpolation between the bracketing calibrations. Table 4 shows the standard deviation (1σ) over 30 measurements for all tested instruments.

The two instruments showing the best LTR are the FTIR and CRDS with a dispersion of 0.07 ppb. They are the only two instruments that can reach the compatibility goal recommended by the WMO. The QC-TILDAS, with a precision of 0.14 ppb, is just

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above the recommendations, but the instrument tested had no pressure control and its pressure needed regular adjustment during this test. We can expect an improvement of the LTR for the QC-TILDAS when using a pressure controller. The three ICOS-QCL instruments and the DFG instrument present a LTR between 0.2 and 0.4 ppb. To meet the WMO recommendations, the calibration frequency may need to be increased to one to several calibrations per week. To test this point, the ICOS-EP40 was re-tested from November to December 2014. During this period, a sequence of analysis of one hour of air alternated with 15 min of a target gas was used. The target gas measurements were separated into two datasets. One was used as a target gas, and the other was used as a calibration gas, which was used to correct the first dataset as a one-point calibration. Different LTRs were calculated by choosing different frequencies for the calibration dataset. Without any calibrations, the LTR was 0.85 ppb (over three weeks), and with a calibration every 2 days, the LTR was 0.28 ppb. For every 12 h, the LTR decreased to 0.07 ppb, and for every two and a half hours (one target gas alternated with one calibration gas), the LTR reached 0.03 ppb. Thus, to reach a LTR better than 0.1 ppb for the ICOS-EP40, a calibration frequency of twice a day is necessary.

3.5 Linearity assessment

For each instrument, linearity assessments were made using calibration tanks with known N₂O mole fractions. As explained in Sect. 3.1, three calibration sets of four to six different tanks were used during the campaigns. The mole fraction measured by the instrument compared with the assigned mole fraction was used to assess the linearity of the instrument. The linearity assessment for each instrument is displayed in Fig. 2.

All of the analyzers show a linear response curve, which can be described by a linear fit using several calibration cylinders. To reduce the errors in the assessment of the calibration cylinders, we recommend the use of at least 3 calibration gases, spanning the full atmospheric range. During our linearity assessment, we looked at the deviation of individual tanks from the fit curve (Fig. 2, lower panel for each instrument), and used this as a measure of the linearity of an analyzer. We found typical residuals of up to

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± 0.15 ppb for the FTIR, ICOS-QCL, and DFG and ± 0.05 for the CRDS and QC-TILDAS analyzers.

The linear fit of the differences between assigned values minus measured values plotted against the assigned value (upper panel) show different slopes, depending on the instrument. Even with the same analyzer model, such as the ICOS-EP38 and ICOS-EP40, the slopes differ considerably. From the time evolution of the linear fit function, we can extract further information about the long-term stability and calibration frequency needed. We extract the mean and maximum drift observed between two calibrations and normalize it to a time span of 10 days for all analyzers (Table 5). Overall, this study confirms the results from the much shorter 30 h test presented in Table 2. The FTIR, CRDS and QC-TILDAS show a mean drift of approximately $0.1 \text{ ppb} (10 \text{ d})^{-1}$, which justifies a calibration frequency of 10–14 days. The ICOS-SD, ICOS-EPs and DFG show a mean drift over 10 days between 0.3 and 1 ppb, which suggests that they should be calibrated at least every three days or daily to obtain an equivalent correction of the drift.

3.6 Stabilization time

Another important parameter is the time necessary for the instrument to reach a stable value when changing the sample analyzed. This test is made by using the calibration runs. The calibration sets the N₂O mole fraction differences between the different samples ranging from 3 to 16 ppb. For each analysis of a calibration cylinder, the raw data are first averaged over one-minute intervals, and the final values are calculated by averaging the last five minutes of a 15–20 min sequence. We estimated the stabilization time by examining the time from which all the one-minute averaged data stay within ± 0.1 or $\pm 2\sigma$ ppb (see CMR test for one min averaged data, Table 2) of the final value. The stabilization time is a function of the cell volume, dead volume and sample flow rate. Because we used the same inlet system (e.g., pressure regulators, inlet valve, tubing lengths) for all of the analyzers tested, this result is only valid for our setup and for the sample flow rates that were considered. Other inlet systems need to be tested

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individually. We used the flow rates recommended by the constructors, which are documented in Table 1. The amplitude of the concentration change compared to the sample analyzed previously could also influence the stabilization time, but despite concentration changes ranging from 3 to 16 ppb, no correlation was found between the two. The values in Table 6 are the stabilization times of all the instruments obtained by averaging the stabilization times calculated for at least 24 cylinder runs.

When choosing 0.1 ppb as the criterion for reaching stabilization, the instruments can be classified into two categories: in the first category, the stabilization is reached after one to two minutes (ICOS and QC-TILDAS), and in the second category, the stabilization is reached later or never completely reached (FTIR, CRDS and DFG). These last results can be easily explained by the CMR test (Table 2) because for some instruments, the ± 0.1 ppb criterion cannot be reached for one-minute averaged data. To make a meaningful comparison, a criterion of $\pm 2\sigma$ ppb of the final value was chosen. In this case, the ICOS, DFG and QC-TILDAS instruments rapidly reach the final values (under three minutes), but the FTIR and CRDS instruments require much more time to achieve stabilization (more than ten minutes). As a consequence, instrument owners should be mindful of the time required to reach stabilization to keep only the relevant data.

3.7 Temperature dependence

All tests and measurements described previously were performed in a laboratory with temperature variations of less than $\pm 1^\circ\text{C}$. However, the working conditions at stations where the analyzers will be installed might not always be as stable. Temperature dependence tests were conducted to characterize the sensitivity of the instruments to room temperature variations. While continuously measuring a target tank, the temperature of the laboratory was changed. From the laboratory working conditions ($22 \pm 1^\circ\text{C}$), the temperature was varied between a low temperature ($15\text{--}20^\circ\text{C}$) and a high temperature ($28\text{--}35^\circ\text{C}$) before returning to the normal working temperature. The low and high temperatures were maintained for several hours to allow for stabilization. Depending

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on the season or time period when the instrument was tested, the span of the variation differs between 10 and 17°C . Due to the high gas consumption of the FTIR, for this instrument, the target tank measurements were not analyzed continuously, but every 6 h at different temperatures for 3 days, and the last 7 min of each measurement were kept for this test.

In Fig. 3, a two-panel plot for each instrument is presented to describe the N_2O response to the room temperature changes. Table 7 summarizes these results with the room temperature change applied to the instrument, the type of temperature dependence and its slope when a linear dependence was found.

Most of the instruments show a significant sensitivity to room temperature variations. Only the QC-TILDAS instrument and the ICOS-EP38 do not show significant temperature dependence for N_2O , with variation below 0.1 ppb for five degree variations. The FTIR and CRDS instruments show a linear dependence to the temperature of -0.04 and $0.05 \text{ ppb } ^\circ\text{C}^{-1}$, respectively. The CRDS instrument tested was a prototype, and thus, no correction for temperature was applied at this stage. Such correction is now built in the commercialized version, and in May 2014, we had the opportunity to test a newly purchased CRDS analyzer with temperature correction in the MLab. It shows an improved behavior to room temperature changes, with a sensitivity to temperature of less than $0.02 \text{ ppb of } \text{N}_2\text{O } ^\circ\text{C}^{-1}$. The DFG instrument presents a dependence that is not significant compared with the relatively large noise. A larger temperature dependence was found for the ICOS-SD with approximately 2 ppb N_2O changes (peak-to-peak), but the nonlinear relationship makes it difficult to apply a correction. The ICOS-EP model does improve the temperature control compared with the standard model, but it is important to highlight the difference between the instruments: although instrument ICOS-EP38 presents no significant temperature influence, instrument ICOS-EP40 shows a temperature dependence of $0.07 \text{ ppb } \text{N}_2\text{O } ^\circ\text{C}^{-1}$. To reach the best attainable performance, most instruments need a temperature-controlled environment, especially the FTIR and ICOS-SD. If an instrument presents a linear dependence, it is also possible for the user to add an instrumental specific correction that could be applied to the final

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data. In this case, the room temperature needs to be monitored precisely, and a regular verification of the temperature dependence is required.

3.8 Water vapor correction

Water vapor in the atmosphere can vary from a few ppm to several percent of volume.

Usually, the N_2O measurements are presented as a dry mole fraction, and a drying system is needed for ambient air measurement. Several of the instruments tested provide water vapor measurements and a correction function to transfer wet ambient air measurements to the dry mole fraction. This correction accounts for dilution and spectroscopic effects such as pressure broadening (Chen et al., 2013). In this study, we test the water vapor correction applied by the manufacturer of the different instruments. This test was not performed for the FTIR and GC because the FTIR has its own built-in drying system, which removes the water vapor to 2–4 ppm and because the GC is required to measure dry air only.

This test consists of measuring a high-pressure tank filled with dry natural air and then injecting a droplet of Milli-Q water (0.2 mL) on a hygroscopic filter (M&C LB1SS) to humidify the stream. This water droplet humidifies the gas at approximately 3 vol % of water depending of the room temperature and sample pressure. After this, the dry natural air from the high pressure tank dries slowly the filter (droplet evaporation). With this method, the tanks of dry ambient air were humidified at varying levels, up to 2–3 vol % of water vapor. However, this method, even though easy to implement, does not offer a steady drying rate over all the H_2O range, resulting in few measurement data over part of the H_2O range. In order to get a better statistical weight on these H_2O range parts, the method is repeated at least three times for all of the instruments. The assessment of the water vapor correction is made by comparing the values of the wet target found by the instrument to its dry value. When the QC-TILDAS and the commercialized model of the CRDS were tested, a new method to characterize the water vapor correction had been implemented by the MLab. A humidifying bench is composed of one thermal Mass Flow Controller (F-201CV, Bronkhorst), to regulate the

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flow of a tank filled with dry natural air, one Liquid Mass flow Controller (Mini Cori-Flow M12, Bronkhorst), to regulate the quantity of Milli-Q water injected in the sample line, and one Controlled Evaporator Mixer (Bronkhorst) to humidify the target gas by evaporating the water at 40 °C while mixing it with the gas. This setup enables a precise control of the water vapor percentage in the sample analyzed. The target gas can now be humidified at different H_2O levels (up to 5 vol % of water vapor) with a suitable stability (H_2O standard deviation of 100 ppm) as long as required, allowing long data set averaging and thus improving the representativeness of the results, especially for noisy analyzers.

The manufacturers Picarro, Los Gatos, ThermoFischer and Aerodyne provided a water vapor correction for their instruments. The correction was not yet implemented in the CRDS prototype tested; therefore, we did not include the results for this instrument. Figure 4 shows the difference between water vapor corrected and the dry N_2O mole fraction against the concentration of H_2O for each instrument. All data were averaged in 30 s intervals.

This test demonstrates the difficulty of most analyzers to provide a correct water vapor correction when measuring wet air. Of all of the instruments, only the QC-TILDAS supplies an accurate water vapor correction: its corrected wet measurements of N_2O did not exceed 0.1 ppb compared with the dry mole fraction. The ICOS-SD supplies a correction that results in a N_2O difference to the dry value below 0.2 ppb for H_2O not exceeding 1–1.5 vol %. For higher H_2O values, the correction shows larger differences of up to 2 ppb. The two ICOS-EP corrections are not sufficient, with a N_2O difference to the dry value of up to 0.5 ppb for high water vapor concentrations. The DFG instrument correction is clearly not suitable, with a difference in the N_2O 's dry/wet values between –1.0 and +2.0 ppb. Finally, the commercialized version of the CRDS supplies a correction that results, similar to the ICOS-SD, in a N_2O difference to the dry value below 0.2 ppb for H_2O not exceeding 1 vol %. However, for higher values of water vapor, the N_2O difference increases to 1.5 ppb. As a result, to achieve the best performances for high-precision atmospheric N_2O measurements, most instruments will need a drying

system prior to the inlet or a careful evaluation of the water vapor dependence, with the exception of the QC-TILDAS analyzer and the FTIR, which has a built-in drying system.

Here, we can only recommend using a drying system for high precision N₂O measurements with all of the instruments tested. Some stations or laboratories might be sufficiently equipped to make their own instrument specific water vapor dependency test on a regular basis and apply this correction during the processing phase.

3.9 Air comparison

All of the instruments that were tested measured at least 100 h of ambient air during the testing period. The measurements were made at the MLab, as described in Sect. 3.1. Pumps were used to reduce the residence time in the air line to avoid time differences between the measurements of the different instruments. For all instruments, the measurements were hourly averaged to allow for meaningful comparisons and to reduce the influence of short time variations. For the three test periods, the GC and the FTIR were the only instruments that were always present. Figure 5 presents the comparison between these instruments over the three periods. It can be observed that although the N₂O mole fraction ranged from 325 to 338 ppb, most of the peaks were less than 2 to 3 ppb in height. Although the mean difference between the instruments is different in each period (−0.21 ppb for the first, 0.01 ppb for the second and 0.14 ppb for the third), it was constant during each period, with a standard deviation between 0.26 and 0.4 ppb. Because the FTIR is the instrument with the smallest dispersion, it was chosen as the reference instrument for the comparison with all of the other instruments.

During the first test period (CRDS, ICOS-SD and DFG), a water trap was used to dry the air (see Sect. 3.1), and the dry air measurements were then compared. During the second period (ICOS-EP38 and ICOS-EP40), there was not enough common dry air data for the ICOS-EP and the FTIR to conduct the comparison. Therefore, we were only able to compare the wet air measurements, which were corrected for the water vapor by the correction algorithms provided by the manufacturers. For the third

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period (QC-TILDAS), the instrument only measured wet air, so the comparison was conducted on the values of the QC-TILDAS with the manufacturer's water vapor corrections applied (1 % of water vapor or less during the period). For all comparisons, the 100 h periods were chosen among the most stable consecutive data available (see Fig. 5 for the period chosen for each instrument). For all instruments measuring wet air, we attempted to apply the corrections obtained from the water vapor test to the dry air values (Sect. 3.8); however, it either had no effect (QC-TILDAS), or it did not improve the comparison (ICOS-EP). Thus, for all of these instruments, the air comparison was performed with the dry values given by the instrument.

Figure 6 presents the relative difference histograms for each instrument compared with the FTIR. Of the six instruments that were compared with the FTIR, the ICOS-SD, the ICOS-EP40 and the QC-TILDAS show an offset of the mean difference with the FTIR of more than 0.25 ppb, whereas the other three instruments show an offset smaller than 0.05 ppb. However, as observed previously, there is an offset between the FTIR and GC for the first and third period (0.2 and 0.1 ppb). When conducting the comparison with the GC, the offset with Aerodyne improved to 0.15 ppb, but compared with the ICOS-SD, CRDS and DFG, the offset increased to 0.2 to 0.4 ppb. As discussed in Sect. 3.5, increasing the frequency of the calibrations should decrease the offset for the DFG and the ICOS-EP38. For the QC-TILDAS, the calibration frequency was once every month, which should be increased to once every week or two weeks for the QC-TILDAS, as indicated by the small drift time (see Sect. 3.5).

Table 8 summarizes the parameters of the linear regressions made between the FTIR and all of the other instruments. As observed with the different coefficients of determination and the different standard deviations in Fig. 6, the CRDS and the two ICOS-EPs are the instruments that show the best correlation with the FTIR. For the comparison with the QC-TILDAS, the standard deviation of 0.16 ppb cannot be explained by the drift (only 0.05 ppb for 100 h). The lack of good pressure control is probably what caused this dispersion. Finally, for the DFG and the ICOS-SD, the standard deviations are the highest of all instruments, particularly with an R^2 less than 0.9 for

the DFG. This is easily explained by the high variability these instruments have shown, and a calibration every 8–9 days is clearly not sufficient. Once again, we see the importance of choosing a calibration frequency adapted to each instrument and its absolute necessity when trying to compare air measurements from different instruments or, on a larger scale, networks.

4 Summary

Here, we briefly summarize the most important findings of the different tests performed to specify the performance of N₂O analyzers for atmospheric measurements.

CMR: the raw data measurement interval varies between 1 s for the QC-TILDAS and 1 min for the FTIR. For atmospheric measurements at a tower, a typical averaging time between 1 to 10 min is used. The CRDS shows the best CMR for a 10 min average with a 1 sigma standard deviation of 0.026 ppb. The CMR for the ICOS-EP and QC-TILDAS is approximately 0.07 ppb (10 min average), whereas that of the FTIR is 0.055 ppb. DFG and ICOS-SD are less appropriate for tower measurements, as the 10 min averages have a CMR greater than 0.1 ppb. For 1 min or less averaged data, the ICOS-EP and QC-TILDAS show the best CMR (0.1 ppb).

Stabilization/Flushing time: due to different cell/cavity volumes, geometry and flow rates, the flushing and stabilization time after a sample change (with contrasted level of N₂O) is different for all analyzers. In our tests, we used the same inlet system for all analyzers and the flow rate recommended by the manufacturer for each instrument. These tests need to be performed at the field station prior to routine measurements because the flushing time also depends on the inlet system and the related dead volumes and flow rate used. To reach a stable N₂O value, which corresponds to $\pm 2\sigma$ ppb of the final values, the CRDS and FTIR analyzers have a relatively long flushing time of more than 10 min. The ICOS and DFG analyzers varied from 2 to 3 min, whereas the QC-TILDAS, which is widely used for eddy covariance measurements needs the shortest flushing time with less than 1 min after the change of a sample.

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Temperature dependency: temperature dependency of the instrument response is a major issue for stations and laboratories without air conditioning or with poor air conditioning. Daily room temperature changes can easily be 5°C or more if the measurements are performed in a container. Most of the tested instruments show temperature dependent drifts. For most instruments, the dependency is linear, ranging from less than 0.02 ppb °C⁻¹, for the QC-TILDAS and ICOS-EP38, to 0.07 ppb °C⁻¹, for the ICOS-EP40, and can be easily corrected by the user. Only the ICOS-SD presents an important nonlinear temperature dependency and should be used in environments with fine control of the temperature.

Linearity and calibration strategy: all of the instruments showed response curves that can be fitted with linear curves. Using four calibration cylinders, the residuals differ between 0.06 and 0.1 ppb N₂O for the different instruments. 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.

Water vapor: wet ambient air measurements are influenced by dilution and interferences with atmospheric water vapor. The FTIR has an inbuilt drying system, whereas other manufacturers provide a H₂O correction algorithm with H₂O measurements. In this study, we tested the correction algorithms built-in by the manufacturers for water vapor concentrations ranging from 0 to 3 %. Nearly all of the correction algorithms showed large deviations of 0.5–1 ppb from the dry air value and are not suitable for our application. Only the QC-TILDAS instrument had a sufficient correction algorithm and showed differences smaller than 0.1 ppb.

5 Conclusions

A new standardized protocol to evaluate the performances of trace gases analyzers was implemented at the ICOS/ATC metrological laboratory in Gif-sur-Yvette. Yver Kwok

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et al. (2015) described the different tests performed for each instrument and showed examples for 47 CO₂ analyzers. Because our study, which was dedicated to the evaluation of N₂O analyzers for high precision atmospheric measurement, was conducted between October 2012 and December 2014, the experimental protocols were not fully finalized and have since been continuously improved due to gains in experience. Though not all of the analyzers were tested in the exact same way, the tests performed do not differ sufficiently to make meaningful conclusions impossible.

Most of the analyzers showed a clear dependency to the room temperature. This needs further investigation and technical improvements by the manufacturers. As long as the room temperature is still an issue, the N₂O analyzers should be used in an air-conditioned environment, and the room temperature should be monitored to correct for dependency. All of the tests demonstrated that the water vapor correction functions provided by the manufacturer are not sufficient to analyze wet ambient air. Therefore, we recommend that for high-precision atmospheric measurements, ambient air should be dried prior to the analysis.

During our initial tests, the calibration strategy was too much driven from our experiences from CO₂ and CH₄ analyzers and the wish to have a similar performance for N₂O. With a calibration performed only every 14–21 days (Yver Kwok et al., 2015), some of the tested N₂O analyzers show a significant drift, which cannot be corrected. In the case of the ICOS-EP40, we tested for possible improvement when adding a 5th reference cylinder, which is used to correct for short-term drift. In our case, an injection frequency of 11 h for a reference gas led to an improvement of the short-term repeatability of the target gas from 0.85 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.

This study of seven analyzers shows that new optical techniques have the potential to replace the gas chromatographic techniques, which were widely used over the past 20 years for atmospheric measurements of N₂O. These new techniques require much less maintenance at the stations and have lower operational costs because they do

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not need consumables, such as carrier gas. Achieving the WMO recommendation for N₂O network compatibility of 0.1 ppb is still challenging but is absolutely needed to characterize the small variability at continental or coastal stations. This can only be reached at the moment if the above described recommendations are followed.

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Table 1. The time period during which the tests were performed for all instruments and working specificities. Most instruments used two sets of calibration cylinders; here, we indicate the most frequently used Max Planck Institute (MPI), or Deuste Steiningger (DS).

Instrument	Test period	Cell size (mL)	Cell Flow Rate (mL min ⁻¹)	Cell Temperature (°C)	Cell Pressure (Pa)	Main calibration scale
FTIR	Oct 2012–Jan 2014	3500	1000 ± 50	32 ± 0.03	1.1 × 10 ⁵ ± 2	MPI
CRDS	Nov 2012–Dec 2012	48	< 50	40 ± 0.001	1.33 × 10 ⁴ ± 0.13	MPI
DFG	Nov 2012–Dec 2012	80	300	37.5 ± 0.002	1.75 × 10 ⁴ ± 0.2	MPI
ICOS-SD	Nov 2012–Dec 2012	408	300	27 ± 0.2	1.13 × 10 ⁴ ± 0.93	MPI
ICOS-EP38	May 2013–Jun 2013	408	300	45 ± 0.005	1.13 × 10 ⁴ ± 0.93	DS
ICOS-EP40	May 2013–Jun 2013	408	300	45 ± 0.005	1.13 × 10 ⁴ ± 0.93	DS
QC-TILDAS	Dec 2013–Jan 2014	500	1000	22 ± 0.03	4.4 × 10 ³ ± 667	MPI

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Table 2. Continuous measurement repeatability calculated as one standard deviation over more than 30 h for different averaging times (raw data, 1, 10 min and 1 h averaging). The short term drift is estimated with a linear regression over 30 h.

Instrument	1σ (ppb, Raw)	1σ (ppb, 1 min)	1σ (ppb, 10 min)	1σ (ppb, 1 h)	Drift (ppb d ⁻¹)
GC	0.16 (5 min)	–	0.113	0.016	0.0001
FTIR	0.15 (1 min)	0.149	0.055	0.026	0.017
CRDS	0.17 (4 s)	0.055	0.026	0.023	–0.034
DFG	0.66 (2 s)	0.159	0.107	0.097	–0.108
ICOS-SD	0.14 (2 s)	0.124	0.114	0.106	–0.185
ICOS-EP38	0.08 (2 s)	0.064	0.062	0.061	0.151
ICOS-EP40	0.10 (2 s)	0.068	0.060	0.054	0.070
QC-TILDAS	0.09 (1 s)	0.075	0.070	0.066	0.046

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Table 3. Short-term repeatability assessment. A target tank is measured 10 times for 15 to 20 min (30 min for the FTIR) alternating with ambient air (for 5 min). A N_2O mean value is calculated by taking the last 5 min of each analysis. The repeatability is expressed as the dispersion (1σ) of these ten injections.

Instrument	Repeatability (ppb, $N = 10$)	Peak to peak (ppb)
FTIR	0.09	0.26
CRDS	0.03	0.11
DFG	0.17	0.55
ICOS-SD	0.02	0.04
ICOS-EP38	0.02	0.06
ICOS-EP40	0.02	0.06
QC-TILDAS	0.02	0.05

10969

Table 4. Long-term repeatability computed from the standard deviation (1σ) of the mean values over the last 5 min of 30 target measurements (N). The calibration frequency gives the mean time between two calibrations. The calibrations were applied as drift corrections.

Instrument	N	Period (min)	1σ (ppb)	Peak to peak (ppb)	Mean calibration frequency
GC	1 year		0.29		30–45 min
FTIR	30 (7 days)	40	0.07	0.27	20 days
CRDS	30 (12 days)	20	0.07	0.28	11 days
DFG	30 (12 days)	20	0.21	0.86	8 days
ICOS-SD	30 (7 days)	20	0.32	1	9 days
ICOS-EP38	30 (7 days)	30	0.25	0.7	13 days
ICOS-EP40	30 (7 days)	30	0.29	0.6	13 days
QC-TILDAS	27 (6 days)	30	0.14	0.44	30 days

10970

Table 5. Long term drift. The drifts between two consecutive calibrations from the same scale are normalized over a time span of ten days. The drifts from all consecutive calibrations are then averaged to obtain a mean drift for all analyzers.

Instrument	Mean drift for 10 days (ppb)	Highest drift (ppb)
FTIR	0.12	0.23
CRDS	0.07	0.19
DFG	1.02	2.53
ICOS-SD	0.30	0.71
ICOS-EP38	0.76	1.62
ICOS-EP40	0.31	1.08
QC-TILDAS	0.12	0.16

10971

Table 6. Stabilization time. Time necessary to reach the final value (calculated over the last 5 min of an analysis) at either ± 0.1 or 2σ (from CMR test) ppb of the final value. The stabilization time is averaged over at least 24 injections of cylinders from calibration sets.

Instrument	± 0.1 ppb of final value		$\pm 2\sigma$ of final value	
	Stab. Time (min)	Not reached* (%)	2σ (ppb)	Stab. Time (min)
FTIR	–	70	0.298	10 ± 7
CRDS	11 ± 5	6	0.11	10 ± 6
DFG	17 ± 2	9	0.318	2 ± 3
ICOS-SD	2 ± 1	0	0.248	1 ± 1
ICOS-EP38	2 ± 2	0	0.128	2 ± 2
ICOS-EP40	2 ± 1	0	0.136	2 ± 0
QC-TILDAS	1 ± 1	0	0.125	1 ± 0

* The “not reached” value is the percent of runs that did not reach ± 0.1 ppb of the final value.

10972

Table 7. Influence of room temperature on N₂O.

Instrument	Temperature dependence	Temperature range (°C)	Temperature dependence (ppb °C ⁻¹)	Peak to peak (ppb)
FTIR	Linear	17–34	–0.04	0.84
CRDS	Linear	20–31	+0.05	0.73
DFG	Linear	17–30	–0.02	1.33
ICOS-SD	No linear dependence	18–28	NA*	2.70
ICOS-EP38	No significant dependence	17.5–32	NA*	0.60
ICOS-EP40	Linear	17.5–32	+0.07	1.11
QC-TILDAS	No significant dependence	15–30	NA*	1.19

* denotes cases where it was not possible to give a value because either there was no dependence or it was not linear.

10973

Table 8. Results of the linear regression analysis of the ambient air measurement difference between the FTIR and the others techniques. R^2 is the coefficient of determination and N is the number of air measurement points (1 h averaged).

Instrument	Intercept (ppb)	Slope	R^2	N
CRDS	– 8.48	1.0261	0.9962	100
DFG	– 40.56	1.1242	0.8758	100
ICOS-SD	– 27.08	1.0823	0.9544	100
ICOS-EP38	10.06	0.9692	0.9825	100
ICOS-EP40	8.73	0.9740	0.9880	100
QC-TILDAS	–23.71	1.0715	0.9626	100

10974

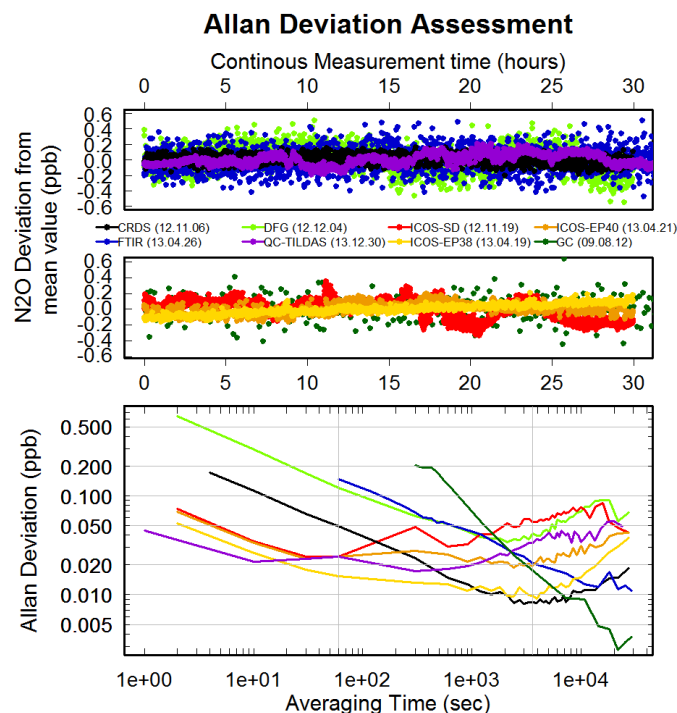


Figure 1. Allan deviation assessment for all instruments. The two upper panels present the times series for the eight instruments over at least 30 h. The lower panel presents the Allan deviation for all instruments from 1 to $3 \cdot 10^4$ s (logarithmic scale). The color codes for the instruments and the test periods are given in the legend.

10975

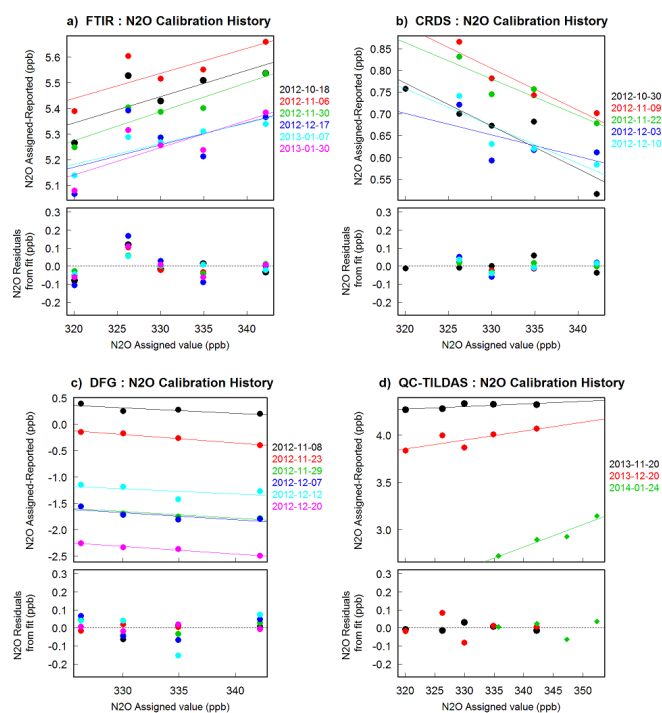


Figure 2. Linearity tests for each instrument are plotted in individual graphs. The upper panel presents the difference between the certified values of the calibration scale and the values measured for all the calibrations made during the tests. The cylinders from the MPI scale are represented with circles, and those from the DS scale are represented by triangles. Squares for the fourth calibration set are only used once by the QC-TILDAS. The lower panel presents the residuals from the fit. The color code for the calibration dates is given in the legend.

10976

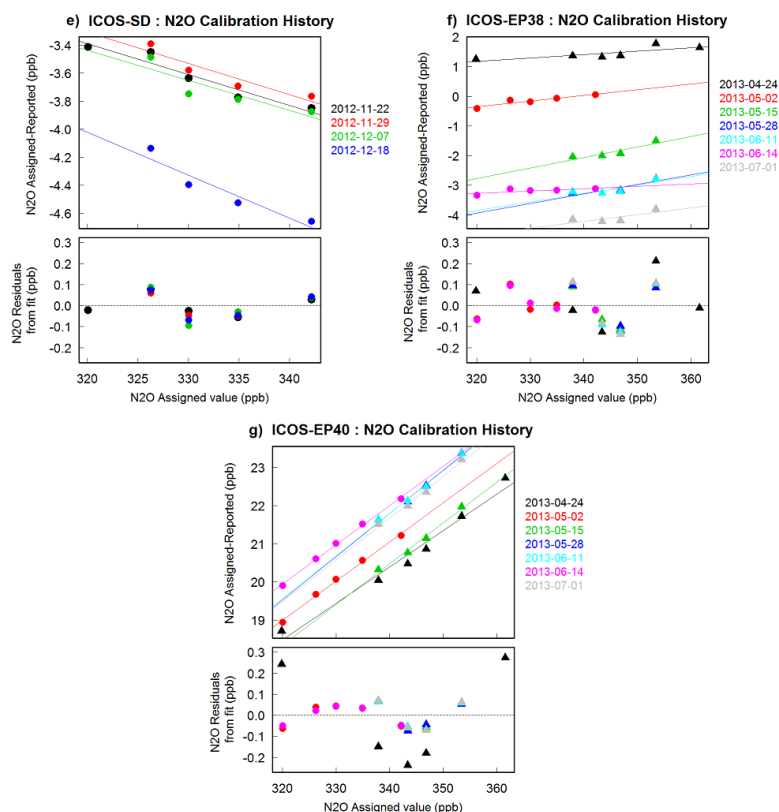


Figure 2. Continued.

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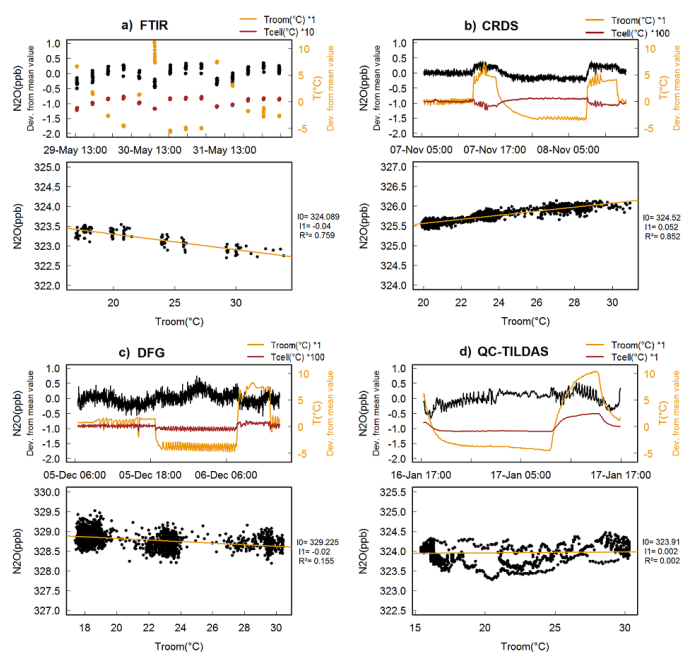


Figure 3. The results of the temperature dependence test for each instrument tested. The top panel presents the time series of concentration (black), the room temperature in the laboratory (orange) and the temperature in the cell (red). For some instruments, the temperature in the cell was multiplied by either 10 or 100 to make the variations visible on the same scale as the room temperature (right axis). The concentration of N₂O is plotted against the room temperature in the lower panel. On the right of the lower panel, I1 is the slope, I0 is the intercept and R² is the coefficient of determination of the linear regression.

10978

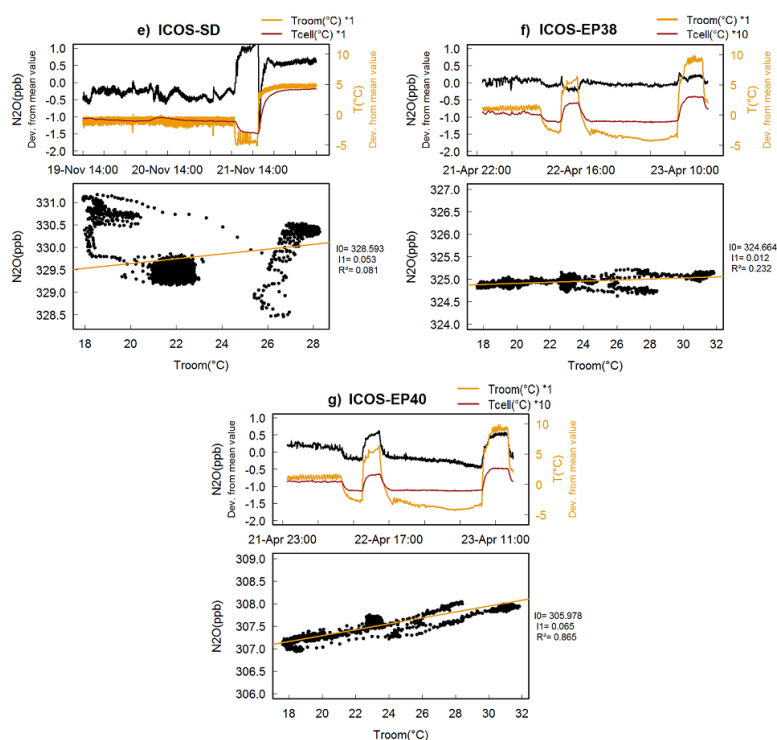


Figure 3. Continued.

10979

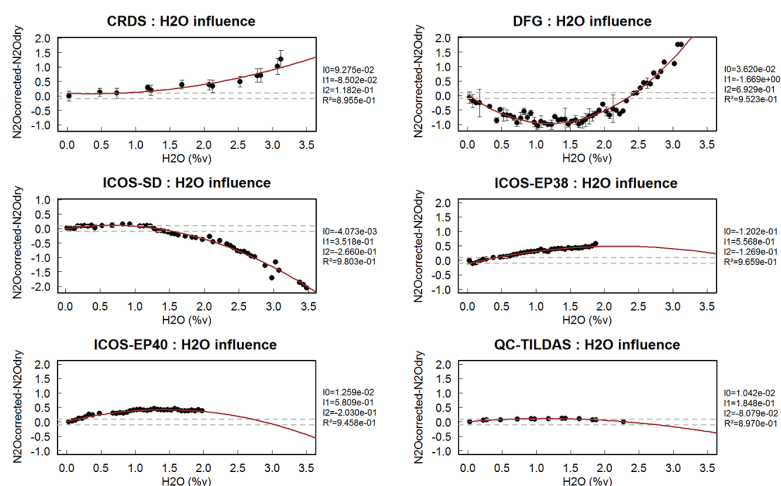


Figure 4. Water vapor correction for all instruments except the FTIR. All the data were averaged over 30 s and separated into bins of 0.05 vol % of H₂O. The dashed lines represent ± 0.1 ppb of the dry value. On the right hand of the panels, I₀, I₁ and I₂ are the coefficients, R², and the coefficient of determination of the polynomial regression, respectively.

10980

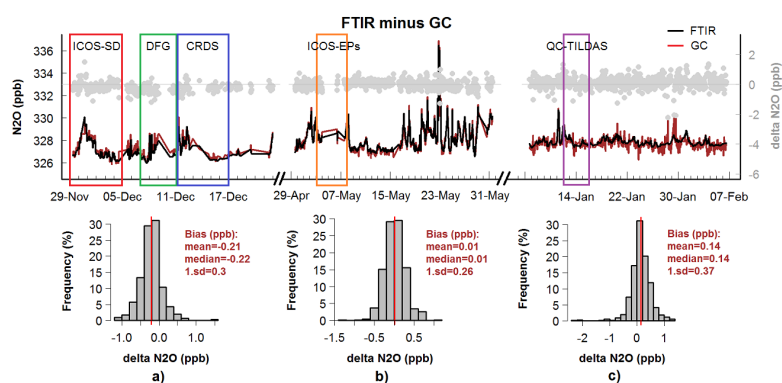


Figure 5. Air comparison between the FTIR and the GC (1 h averaged data) during the time when the air comparison tests were performed with the other instruments. The top panel presents the times series of the GC (red) and the FTIR (black) for the three periods (December 2012, May 2013 and January 2014). In grey is the difference between the instruments. The colored frames show the time periods chosen to conduct the air comparison between the FTIR and the other instruments (see Fig. 6). In the lower panel, three histograms give the difference for the two instruments for the (a) first test period, (b) second test period and (c) third test period.

10981

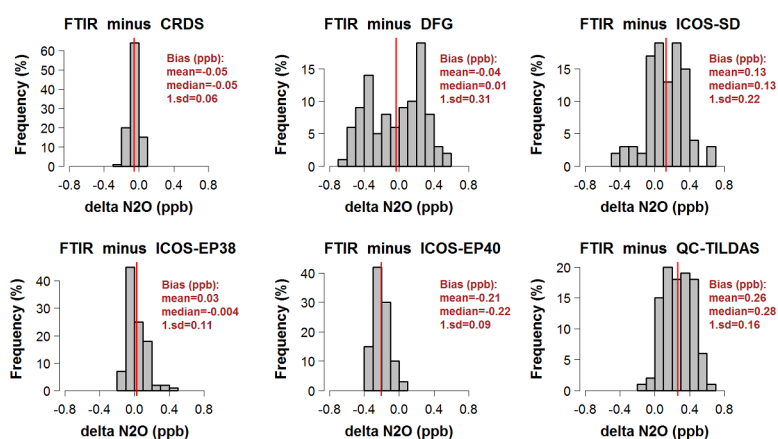


Figure 6. Comparison between the FTIR and the other instruments: CRDS, DFG, ICOS-SD, ICOS-EP38, ICOS-EP40 and QC-TILDAS (1 h averaged data). All comparisons were conducted using 100 continuous hour averaged air measurements.

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