

CCQM-K68.2019, Nitrous Oxide (N₂O) in air, Ambient level Final Report

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Summary

The key comparison CCQM-K68.2019 was aimed at evaluating the level of comparability of laboratories' capabilities for preparing nitrous oxide in air primary reference mixtures at ambient amount fractions, in the range 320 nmol mol⁻¹ to 350 nmol mol⁻¹.

The comparison was coordinated by the BIPM and the KRISS. It consisted in the simultaneous comparison of a suite of $2n$ primary gas standards, two standards to be prepared by each of the n participating laboratories. Two independent analytical methods were used by the BIPM to analyse the amount fraction of N₂O in air, namely Gas Chromatography with an Electron Capture Detector (GC-ECD) and Quantum Cascade Laser Absorption Spectroscopy (QCLAS).

Since the circulation of the Draft A report in April 2021, four meetings took place with participants to discuss the mathematical treatment of the comparisons results, and several models were proposed. The model chosen by participants is the Bayesian Errors-In-Variables regression with shades of dark uncertainty. In this final report, the Key Comparison Reference Values were obtained with this model, with calculations performed by B. Toman and A. Possolo.

The key comparison CCQM-K68.2019 is considered to present an analytical challenge and therefore classified as Track C comparison in the CCQM nomenclature.

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2 Rational for the comparison

Nitrous oxide (N₂O) is an important greenhouse gas with a strong radiative forcing, which is of great interest to National Metrology Institutes (NMI) and Designated Institutes (DI) producing reference materials to support climate observation measurements. It has already been the subject of a CCQM-GAWG comparison organised by the KRISS in 2008, CCQM-K68 [1]. In the 2008 comparison, each of the seven 7 participants received one standard of N₂O in synthetic air prepared by the KRISS, targeting the mean tropospheric amount fraction at that time, 320 nmol mol⁻¹. It was therefore designed as a so-called model 1 comparison in the CCQM-GAWG classification, aimed at comparing laboratories' abilities to assign the N₂O amount fraction in the travelling standard using their in-house capabilities and standards.

This comparison, CCQM-K68.2019, followed model 2 in which each of the 9 participants was to prepare N₂O in air reference mixtures at ambient amount fractions, and the coordinating laboratory BIPM was to compare all mixtures using analytical instruments maintained under repeatability conditions. Participants were asked to prepare two standards, and the nominal N₂O amount fractions in the standards was chosen so that the 18 values would cover a range from 320 nmol mol⁻¹ to 350 nmol mol⁻¹, to encompass the mean tropospheric amount fraction observed in 2018, around 330 nmol mol⁻¹, and its expected increase of about 1 nmol mol⁻¹ per year.

The 2008 comparison included the Earth System Research Laboratory of the National Oceanic and Atmospheric Administration (NOAA/ESRL), which has been the Central Calibration Laboratory (CCL) for the Global Atmosphere Watch (GAW) programme of the World Meteorological Organisation (WMO) since 2000 [2], to also examine its agreement with NMIs. Since then, WMO signed the CIPM-MRA in 2010 and NOAA/ESRL was designated for CO₂, CH₄, N₂O, SF₆ and CO measurements. The laboratory took part in the 2019 comparison as well, with two standards of N₂O in whole dried air traceable to the NOAA-2006A scale. Additionally, this comparison was the occasion to invite Scripps Institution of Oceanography of the University of California San Diego (SIO/UCSD) as guest laboratory, for their long experience in this field, and for their role as calibration laboratory in the Advanced Global Atmospheric Gases Experiment (AGAGE) global measurement network. The laboratory has developed a unique independent method which differs from gravimetry. The comparison with SIO was the Pilot Study CCQM-P206 and its results are published in a separate report [3].

For N₂O in air standards to be valuable in supporting atmospheric observations, one of the constraints is that they should be as close as possible from real air. In this comparison, standards were required in a matrix of dry air, with tight limits imposed on the composition of this matrix (see section 6.3). This was also the warranty that measurements performed by the coordinator using Quantum Cascade Laser Absorption Spectroscopy (QCLAS) would not be biased due to pressure broadening effects observed when the nitrogen amount fraction in air is modified.

Preparation of N₂O in dry air at ambient amount fractions and in the matrix imposed by this protocol is considered to represent an analytical challenge. Therefore CCQM-K68.2019 is classified as a Track C comparison in the terminology of CCQM comparisons.

3 Measurand, quantities and Units

The measurand was the amount fraction of nitrous oxide in air, with measurement results being expressed in mol mol^{-1} (or one of its multiples mmol mol^{-1} , $\mu\text{mol mol}^{-1}$ or nmol mol^{-1}).

4 Participants

The comparison included 9 participants listed below:

- Finnish Meteorological Institute (FMI)
- Korea Research Institute of Standards and Science (KRISS)
- National Institute of Metrology (NIM)
- National Institute of Standards and Technology (NIST)
- National Metrology Institute of South Africa (NMISA)
- National Oceanic and Atmospheric Administration, Earth System Research Laboratory (abbreviated as NOAA)
- National Physical Laboratory (NPL)
- Dutch Metrology Institute (VSL)
- D.I.Mendeleyev Institute for Metrology (VNIIM)

5 Comparison schedule

The comparison was organised by the BIPM following the schedule (updated after the comparison) displayed in Table 1. Meetings organised to discuss the comparisons results are also indicated in this table to reflect the different steps achieved by the group of participants, which eventually lead to the choice of the final model applied to calculate the reference values.

Table 1: schedule of events in CCQM-K68.2019 organisation

Due Date	Event
30 April 2019	Registration
31 July 2019	Shipment of standards to BIPM
28 Feb. 2020	Measurements at BIPM
31 July 2020	Collection of standards by participants
31 Jan. 2021	Second analysis (optional) and submission of result forms
29 Mar. 2021	Draft A report distributed to participants – 1 st model proposed based on Error-In-Variable (EIV) regression and selection of a consistent calibration set.
11 May 2021	1 st Draft A discussion meeting followed by requests of additional information on the purity of the matrix gas.
11 June 2021	2 nd Draft A discussion meeting followed by proposal of a 2 nd model to include a dark uncertainty component in the KCRV
11 Nov. 2021	3 rd Draft A discussion meeting – decision to compare 3 models: conventional EIV regression, Bayesian EIV regression with dark uncertainty, and a variation of the second with shades of dark uncertainty
7 Feb. 2022	Questionnaire circulated to participants to gather their preferred option
22 March 2022	4 th Draft A discussion meeting – decision to use the EIV regression with shades of dark uncertainty to calculate the KCRVs

6 Standards prepared by participants

6.1 Preparation technique

Participants were asked to prepare two standards using their usual technique. As displayed in Table 3, gravimetry with all components added separately was employed by all participants except two: FMI and NOAA.

FMI chose two cylinders filled with dried air from the arctic as transfer standards. In their case the N₂O amount fraction was therefore assigned by Off-Axis Cavity Enhanced Absorption Spectroscopy (OA-CEAS) measurements calibrated with one standard of higher N₂O amount fraction (40.15 μmol mol⁻¹) from the VSL, diluted to match the amount fraction in the transfer standards.

NOAA sent two cylinders considered at “level 3” on their traceability hierarchy, prepared by blending dried natural air with N₂O-free air, or spiking natural air with a small aliquot of N₂O in synthetic air. Amount fractions were assigned by GC-ECD calibrated using “level 2” standards which are traceable to “level 1” standards prepared gravimetrically in a matrix of synthetic air (O₂, N₂).

6.2 Nominal N₂O amount fraction

Each participant was required to provide two standards of N₂O in air at nominal amount fractions provided by the coordinating laboratory upon registration. The repartition of nominal values was organised such as to reach most equal weights in the regression analysis performed to calculate the reference values of the comparison. Figure 1 below shows the distribution of the nominal N₂O amount fraction, which was reported by participants when they sent the standards. This value was within a 5 nmol mol⁻¹ range requested by the coordinating laboratory. It was close but not equal to the value measured by the participant. Its purpose was to allow the coordinating laboratory to organise the measurements in two sequences, corresponding to one first batch of 10 standards below the median (337 nmol mol⁻¹) and a second batch of 11 standards above this median.

It should be noted that FMI could not send standards prepared at specific N₂O amount fractions, because their cylinders were filled with ambient air only, without addition of pure N₂O to adjust its concentration. Therefore, their two standards fall in the lower part of the distribution, with amount fractions below 330 nmol mol⁻¹.

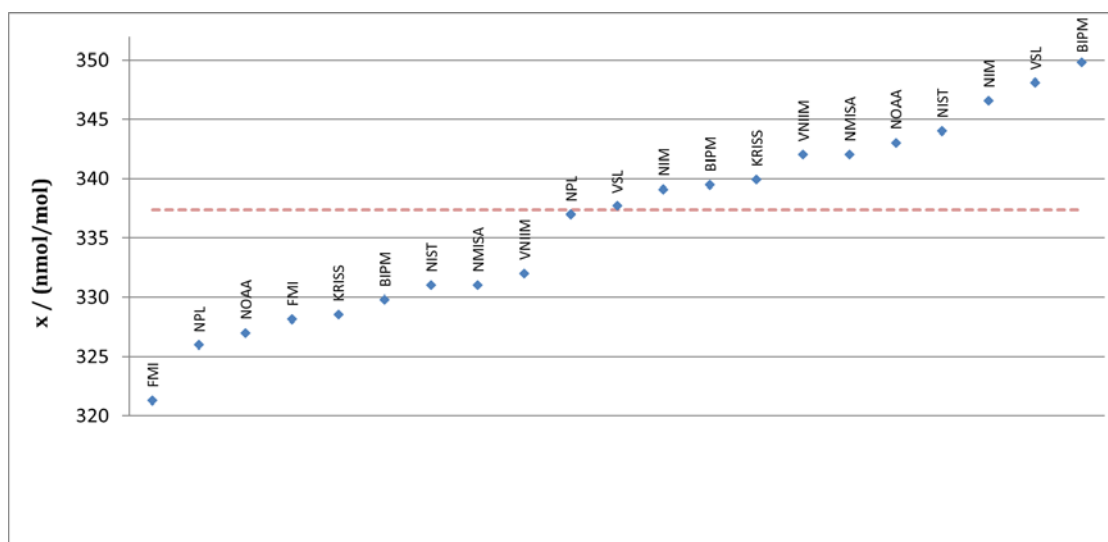


Figure 1: nominal N₂O amount fraction in standards prepared by participants and in the three BIPM cylinders analysed with them. The dash pink line indicates the median of the 21 values.

6.3 Matrix composition

The comparison protocol required that the matrix gas be dry air, either *scrubbed real air* or *synthetic air* (blended from pure gases). The matrix was to contain the major constituents of air (nitrogen, oxygen, argon) and could contain the other two major greenhouse gases (carbon dioxide and methane) at ambient mole fractions. To avoid known biases in spectroscopic analyzers due to differences in the matrix composition [4], limits of the amount fraction of the major constituents were provided in the protocol as reported in Table 2.

Table 2: Matrix composition limits

Species	'Ambient' level mole fraction	Unit	Min mole fraction	Unit	Max mole fraction	Unit
N ₂	0.780876	mol mol ⁻¹	0.7804	mol mol ⁻¹	0.7814	mol mol ⁻¹
O ₂	0.2093335	mol mol ⁻¹	0.2088	mol mol ⁻¹	0.2098	mol mol ⁻¹
Ar	0.0093332	mol mol ⁻¹	0.0089	mol mol ⁻¹	0.0097	mol mol ⁻¹
CO ₂	380	μmol mol ⁻¹	0	μmol mol ⁻¹	400	μmol mol ⁻¹
CH ₄	1900	nmol mol ⁻¹	0	nmol mol ⁻¹	2000	nmol mol ⁻¹

All standards sent by participants conformed with the above requirements as detailed in participants' reports. NIST reported nitrogen amount fractions which are slightly above the maximum value, and the difference is not expected to cause a measurable bias. Table 3 indicates the matrices chosen by participants, being scrubbed air or synthetic air. For synthetic air, it is indicated if CO₂ and/or CH₄ were added to match ambient levels. This was the case only for KRIS who added CO₂, and for NMISA who added CO₂ and CH₄ but at lower levels (around 190 μmol mol⁻¹ and 1040 nmol mol⁻¹ respectively).

Other compounds which could influence measurements of N₂O in air by GC-ECD were not mentioned by the protocol of the comparison. The main interfering compound is SF₆ [5], and it was the responsibility of the coordinating laboratory to ensure it was separated from N₂O during their analysis (see 7.1). Presence of SF₆ in the transfer standards would only be an issue for those participants using scrubbed real air as matrix and GC-ECD as analytical technique. NOAA is the only laboratory in this case, and their measurement report clearly clarified the efficiency of their separation technique.

Table 3: Information on participants' standards: the preparation technique (gravimetry or scrubbed air), the date of preparation, the matrix composition, the analytical technique used for the verification (or calibration), and the N₂O amount fraction reported in the matrix gas x_{bkd} .

Lab	Preparation	Date	Matrix	Analysis	x_{bkd} / ppb
FMI	scrubbed air	01/01/2016	scrubbed air	OA-CEAS	N.A.
KRIS	gravimetry	15/08/2018	N ₂ -O ₂ -Ar-CO ₂	GC-μECD	0.1
NIM	gravimetry	25/09/2019	N ₂ -O ₂ -Ar	CRDS	0.1
NIST	gravimetry	04/12/2014	N ₂ -O ₂ -Ar	OA-CEAS	0.19
NMISA	gravimetry	10/07/2019	N ₂ -O ₂ -Ar-CO ₂ -CH ₄	CRDS	0.2
NOAA	Scrubbed air		scrubbed air	GC-ECD	0.1-0.5
NPL	gravimetry	15/08/2019	N ₂ -O ₂ -Ar	CRDS	0.37
VNIIM	gravimetry	16/09/2019	N ₂ -O ₂ -Ar	GC-ECD + GC-MS	< 1
VSL	gravimetry	05/08/2019	N ₂ -O ₂ -Ar	QCLAS	0.07

6.4 N₂O in the matrix gas

A purity table of the matrix gas was required to be reported by participants. Particular attention was to be paid to traces of N₂O present in the nitrogen or synthetic air used to dilute pure N₂O, as the amount fraction can easily be of the same order as the final

combined uncertainty of the total N₂O amount fraction. The N₂O amount fractions in the matrix gas reported by participants are included in Table 3. This value was unknown for FMI as the standard was not prepared by adding pure components.

This subject became the core of discussions during the first meeting of participants, and additional information was requested to them, compared to the comparison protocol. The replies are compiled together with the participants results forms and added in annex to this report. The main issue was that N₂O should be considered as *critical impurity* in the matrix gas, in the sense of the normative document ISO 19229 [6]. Following this observation, the question of N₂O being potentially a *significant impurity* was raised, and if a complete purity analysis with results that are traceable was required. Alternatively, if N₂O was not considered significant, participants were asked to justify this statement by showing that the uncertainty on N₂O as impurity contributed for less than 10% to the overall measurement uncertainty.

After presentations of the methods employed by participants, it appeared that three of them were compliant with ISO 19229 recommendations: NIM, NPL and VSL:

- NIM and NPL considered N₂O as significant impurity in the matrix gas. They both measured its amount fraction by the standard addition method, consisting of gradually adding known amounts (by volume) of pure N₂O in the matrix and constructing a response curve with an appropriate analyser, calibrated with in-house reference materials. The value in the matrix was then deduced by extrapolation.
- VSL considered that N₂O was not significant, because the uncertainty of its measurement in synthetic air by CRDS was not a major contribution to the final uncertainty, which was dominated by the verification uncertainty.

6.5 Analytical techniques for verification (or calibration)

All except two (FMI and NOAA) of the participants used an analytical technique to verify the N₂O amount fraction in the prepared standards by comparison to other sets of their standards. FMI and NOAA did use analytical techniques as well, with the difference that the purpose of the measurement was to value assign the N₂O amount fraction in the standards. For FMI, this was done against one standard of VSL. For NOAA, the calibration set consisted of in-house secondary standards, which are traceable to the NOAA-2006A scale [2].

The analytical technique used by participants for this step is also indicated in Table 3, showing two main groups of instruments: three participants used GC-ECDs, while six used analysers based on light absorption, namely three Cavity Ring-Down Spectroscopy (CRDS) analysers, two OA-CEAS analysers, and one custom-built infrared spectrometer based on Quantum Cascade Laser Absorption Spectroscopy (QCLAS).

6.6 N₂O amount fraction and uncertainties reported by participants

After being analysed at the BIPM, cylinders were shipped back to participants, and the protocol gave the possibility for them to verify the mixtures another time. Following this, participants were asked to report a final value of the N₂O amount fraction and associated uncertainty, considering any instabilities. Only three participants, NOAA, NIST and VSL, reported that they analysed the mixtures again. Other participants either estimated their mixtures to be stable or estimated a stability component uncertainty based on past measurements of the same mixtures or of similar mixtures. All values reported are

displayed in Table 4, together with the pressure inside the cylinders measured by the BIPM upon arrival and before their departure.

Table 4 shows quite a spread in standard uncertainties reported by participants, with the lowest value reported by NIST equal to $0.065 \text{ nmol mol}^{-1}$, and the highest value reported by FMI equal to $2.52 \text{ nmol mol}^{-1}$. Looking at analytical techniques chosen by participants for the verification as reported in Table 3, there seem to be a trend that lowest uncertainties were reported by those who used laser spectroscopy rather than GC-ECD. FMI did use OA-CEAS like NIST, but their uncertainties are dominated by their calibration method, which relies on dilution from a more concentrated reference cylinder. More details regarding the sources of uncertainties estimated by participants can be found in their reports in the annex.

Table 4: participant's name (Lab), cylinder reference (REF), amount fraction of N₂O assigned by participants (x), associated standard uncertainty (u), pressure measured on arrival of the cylinder (P_1) and before its departure from the BIPM (P_2).

Lab	REF	x (nmol mol ⁻¹)	u (nmol mol ⁻¹)	P_1 (bar)	P_2 (bar)
FMI	D232761	320.41	2.46	68.6	64.0
FMI	D232760	327.60	2.52	158.2	154.0
KRISS	D641445	328.54	0.33	86.3	82.9
KRISS	D641669	338.93	0.34	82.9	79.1
NIM	FB03830	339.07	0.26	92.3	86.3
NIM	FB03840	346.55	0.26	87.5	82.1
NIST	FF22145	331.13	0.07	84.4	78.3
NIST	FF22146	344.38	0.07	86.0	82.3
NMISA	D732200	331.49	0.11	96.9	91.9
NMISA	D679627	342.38	0.24	99.8	96.4
NOAA	FF57617	326.81	0.31	93.6	85.7
NOAA	FF57625	342.87	0.30	86.9	78.8
NPL	2731	326.50	0.55	121.1	117.6
NPL	2864	337.70	0.55	122.3	117.4
VNIIM	D648613	332.40	1.60	104.6	97.2
VNIIM	D648616	342.50	1.50	101.8	94.8
VSL	D791189	337.80	0.75	115.4	109.8
VSL	D791188	348.20	0.75	118.2	105.9

6.7 Issues encountered with the standards

Because of the measures adopted by various countries in 2020 in response to the Covid-19 pandemic, many standards encountered delays in the shipment from BIPM to the

participants. Delays were also encountered in participants' laboratories, resulting in an increased duration between standard preparation and second verification, or the impossibility to perform the second verification in some cases. It should be emphasised that the impact on the comparisons results appears very limited, as expected with these gaseous mixtures which are generally considered stable.

6.8 Other information

In addition to the above summary information, participants were asked to report the following details on the standards, in report forms annexed to this document (see Annex 2 – Participants reports):

- The uncertainty budget used to calculate the uncertainty associated with the measurement of the nitrous oxide amount fraction.
- A description of the measurements performed for the validation of values obtained from the preparation.
- An outline of the dilution series undertaken to produce the final mixtures.
- A purity table for each of the final mixtures, including gravimetric uncertainties.
- An outline of the verification procedure applied to the final mixtures.
- A description of any stability testing of the mixtures between the time they were prepared and the time they were analysed again after return from BIPM. This final verification was proposed as an option in the protocol.

Unlike the comparison CCQM-K120 on CO₂ in air standards, which was very similar in its organisation and analytical instruments employed by the coordinator [7], there was no consideration in this exercise relative to the isotopic composition of N₂O in the standards. The reason was that commercial sources of pure N₂O available to prepare synthetic mixtures are known to cover a limited range of isotopic composition, which actually constitutes a limitation in calibration of isotope ratio measurements [8]. At present, there is no evidence of absence of commutability between N₂O reference materials and real air samples due to a mismatch in isotopic composition [9].

7 BIPM comparison facility

In this comparison, the BIPM measurement facilities acted as comparators of all standards, meaning that all standards were analysed with the same techniques maintained under repeatability conditions and considered a priori as a valid calibration set.

The BIPM used two instruments to perform two distinct series of comparison measurements in which all standards were analysed in similar sequences, as reported below. The two instruments had been chosen for their very different principles to detect technique-specific biases: one chromatographic technique on one side (GC-ECD), and laser spectroscopy on the other side (QCLAS). With both instruments, a method was developed prior to the comparison to optimise the repeatability, correct for drifts and demonstrate linearity of the measured values versus N₂O amount fractions, or estimate non-linearities when observed. For this purpose, two series of standards produced by the KRISSE were used, as well as three standards from NOAA already used for the validation of the key comparison CCQM-K120 [7]. The N₂O amount fraction range covered was from 320 nmol mol⁻¹ to 365 nmol mol⁻¹. To detect possible interferences with the QCLAS instrument, some standards included CO₂ at ambient levels, some did not.

Likewise, to detect possible issues in the separation of N₂O from SF₆ with the GC-ECD, some standards included SF₆ and some did not.

7.1 Gas Chromatography - Electron Capture Detector (GC-ECD)

7.1.1 Analyser description and samples injection method

A first series of analysis was performed with a GC-ECD analyser customised from an Agilent system series 7890A by SRA Instruments, equipped with a micro-electron capture detector. The input of the analyser was connected to the output of the autosampler described in section 8.1. 2 ml samples were injected in a first column (PPQ 3m) maintained at 60°C temperature. To avoid contact between oxygen and the ECD, a valve placed just after the column allowed rejection of all components separated by the column and eluting before N₂O. Three minutes after injection of the sample, the valve was switched to let N₂O in the carrier gas (nitrogen BIP) flowing through the detector via an inert short line. Pure CO₂ was added to the flow as make-up gas just before reaching the detector. The detector was maintained at 390°C during the analysis. Outside analysis periods, the detector was maintained under a constant flow of dry nitrogen.

7.1.2 Measurement method and performances

The injection method tested with cylinders from NOAA demonstrated a good separation of the N₂O and SF₆ peaks. The N₂O peak was always clear and an automatic method of integration with a short window (width of 0.5 minutes on the chromatogram) was defined for the analysis of all chromatograms recorded during the comparisons.

Several sequences were tested to optimise the repeatability (i.e. minimise the variance). The best performances were obtained with five successive injections of each sample, followed by five injections from a control cylinder before moving to the next sample. When all samples (typically 10 per batch) were analysed, the series was repeated seven more times. The average peak area obtained with 5 injections of the sample was ratioed to the average peak area obtained with 5 injections of the control cylinder, interpolated between two measurements at the measurement time of the sample. This resulted in typical experimental standard deviations in the measured ratio, which was always close to 1, of between 3×10^{-4} and 2×10^{-3} . Over the eight repeats of the series, the first one was systematically discarded to keep only repeatable ratios. The experimental standard deviation of the averages over 6 ratios was calculated to be also between 3×10^{-4} and 2×10^{-3} , very consistent with the repeatability.

The typical standard deviations reported above are higher than best values reported in the literature [2]. This is believed to come from different performances of the micro-ECD compared to the older ECD version. During the validation, small variations in the baseline of the chromatograms were noted, which could result in a degraded repeatability due to the short integration window defined for the software. Therefore, a manual integration method of the peaks was tested after the comparison on measurements performed with 10 standards. This exercise demonstrated no significant improvement, with similar or sometimes worse standard deviations. The results presented in this report are those obtained with automatic integration only.

GC-ECD is known to suffer from non-linearities versus the N₂O amount fraction. Particular attention was brought to test the linearity of the BIPM instrument with the two series of standards produced by the KRISS for the validation. All results obtained during

the validation appeared to be consistent with a calibration line (straight line with an intercept not constrained to zero), within the uncertainties.

7.2 Quantum Cascade Laser Absorption Spectroscopy (QCLAS).

7.2.1 Analyser and samples injection method

A second series of analysis was performed with a QCLAS analyser, model Aerodyne MiniTrace, equipped with a mid-IR laser centred at 4.5 μm and a multipass absorption gas cell (path length 76 m) (see for example [10]). The wavelength of the QC laser was tuned at high frequency within a narrow bandwidth, typically 2242.3 cm^{-1} and 2243 cm^{-1} . This allowed absorption peaks of N_2O , CO_2 and H_2O to be scanned and further modelled by the instrument control software (TLDWintel). The software reported amount fraction values directly, using non-linear curve fits of the absorption peaks and comparison with models constructed from molecular parameters issued from the database HITRAN version 2012. For the purpose of the comparison, values provided by the software were considered uncalibrated and may be displayed in this report in ppb instead of nmol mol^{-1} .

The input of the analyser was connected to the output of the autosampler described in section 8.1. The input flow to the analyser was controlled automatically by the instrument to maintain a constant pressure of 40 mbar (absolute) inside the gas cell. This resulted in a flow rate around 400 mL min^{-1} .

7.2.2 Measurement method and performances

Prior to the comparison measurements, the noise of the analyser was checked by recording times series of its response to N_2O in a control cylinder. From these data, the Allan deviation was calculated and found to be below 0.003 nmol mol^{-1} for an averaging time of 100 second. This demonstrated the good condition of the analyser.

Although the instrument demonstrated good stability over several hours of analysis, a ratio to a control cylinder method was implemented to correct for potential drifts. Each sample was flown through the gas cell for 20 minutes, and the average over the last 100 seconds was taken as measurement result. This was repeated for the control cylinder, and the ratio of the two calculated. After all samples were analysed, the entire series was repeated a total of 3 times. Typically, the repeatability of the ratio was close to 5×10^{-5} (experimental standard deviation).

8 Measurements at the BIPM

The comparison was performed following the protocol sent to participants on 14 March 2019, summarised below.

8.1 Handling of cylinders

Cylinders were tracked at the BIPM with their serial number as provided by the participants. All pressures were measured upon their arrival and before their return in participant's laboratories (see Table 4).

On receipt by the BIPM, all cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders were then rolled for at least 1 hour to ensure homogeneity of the mixture.

Each cylinder was connected to one inlet of a 16-inlet automatic gas sampler connected to the gas analysers (first the GC-ECD, then the QCLAS).

The pressure regulator (Rotarex SI240) of each cylinder was flushed nine times with the mixture. The cylinder valve was then closed leaving the high-pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa. The cylinders were left to stand for at least 24 hours, to allow conditioning of the pressure reducers.

Immediately prior to an analysis, each cylinder valve was opened again and the pressure reducer flushed a further three times.

8.2 Series of analysis

Standards were analysed in two batches of similar N₂O amount fractions, divided by the median (see Figure 1). Three BIPM cylinders were added to the batches as quality controls. Each batch was analysed sequentially in series together with the control cylinder, following the schemes described in 7.1.2 for the GC-ECD and 7.2.2 for the QCLAS. On completion of measurements, the cylinder valves were closed and the pressure reducer and connection to the gas sampler left under pressure (typically during the night).

8.3 Calculation of analysers responses and standard uncertainty

As reported in 7.1.2, sequences of measurements with the GC-ECD included 5 successive injections of the samples and the control cylinder, a correction for drifts via interpolation of the control cylinder responses in between two measurements, and a final average over the 7 repeated sequences for each batch of cylinders. The experimental standard deviation of the averages over 7 drift corrected ratios to the control cylinder was chosen as estimator of the type A uncertainty with the GC-ECD, with typical values between 3×10^{-4} and 2×10^{-3} . The entire analysis for the two batches of cylinders was repeated another time after one month. Differences in the ratio to the control cylinder, δR , were found to lie between 6×10^{-4} and 2×10^{-3} , with an average of $\delta R_{\text{mean}} = 1.68 \times 10^{-3}$. To take these observations into account, the final ratio was estimated from the average of the two values for each cylinder. An additional variance was estimated from the average difference δR_{mean} , assuming a rectangular distribution of width equal to δR_{mean} , resulting in an uncertainty component equal to 4.84×10^{-4} . This component was combined with the uncertainty resulting from the average, to obtain the final standard uncertainty $u(y_{\text{GC}})$ reported in Annex 1 – BIPM measurements results.

With the QCLAS instrument, as reported in 7.2.2, sequences of measurements included sampling each standard for 20 minutes to average the response over the last 100 s. A correction for drift via bracketing with a control cylinder was also introduced, and sequences were repeated a total of 3 times. The experimental standard deviation of the averages over 3 drift corrected ratios to the control cylinder was chosen as estimator of the type A uncertainty, with typical values between 1.5×10^{-5} and 5×10^{-5} .

8.4 Measurement results

Detailed results of measurements performed at the BIPM with the GC-ECD and QCLAS analysers are reported in *Annex 1 – BIPM measurements results* and plotted in this section.

Figure 2 below shows the drift corrected ratio to the control cylinder obtained from the measurements performed with the GC-ECD and QCLAS analysers, plotted on the same graph. Error bars are the expanded uncertainties obtained on the ratio (they cannot be seen for the QCLAS as they are smaller than the dots). The two sets of ratio measurements are well correlated and generally agree with each other within their uncertainties, with a clear dominance of uncertainties associated with the GC-ECD.

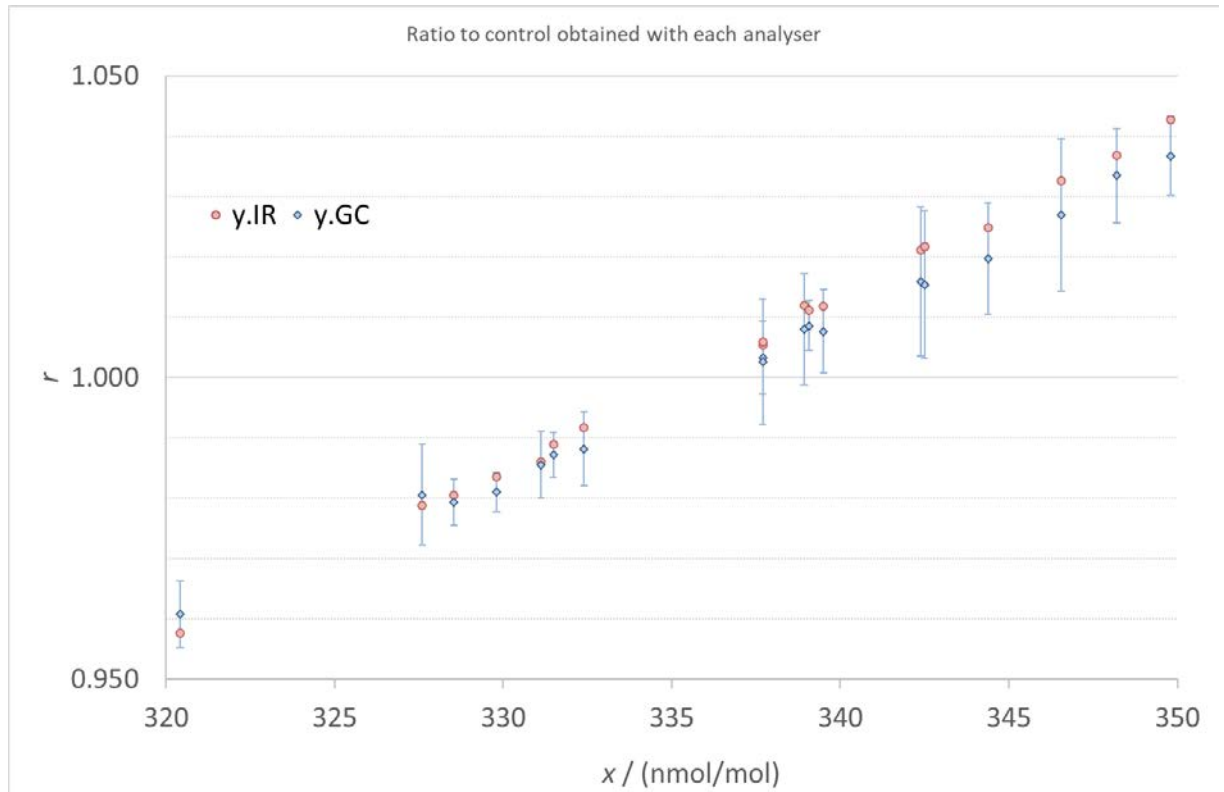


Figure 2: drift corrected ratio to the control cylinder obtained with GC-ECD (blue diamonds) and QCLAS (red dots) analysers against the nominal N₂O amount fraction in the comparison standards.

9 Choice of the comparator for the comparison

For results obtained from each of the two analysers, a generalised least-square (GLS) regression was performed on the ensemble of values submitted by participants together with the averaged corrected responses of the analysers and associated standard uncertainties. A linear model was assumed. The software used for that purpose was XLGenline v1.1.

It was noted that one participant (FMI), who chose mixtures prepared from scrubbed natural air, sent two standards with N₂O amount fractions lower than the nominal value, which could constitute a reason of non-inclusion in a GLS regression. The GLS regression was performed with and without this participant, and the agreement between all participants was found to be unchanged. This was expected as the standard uncertainty submitted by FMI is the largest of the group, resulting in little weight in the regression.

The table below displays the results of the GLS regression performed on the two sets of measurement results with XLGenline. Measurements performed with the GC-ECD agree with a calibration line when all standards are included. A second order calibration curve was also tested as this technique can easily be non-linear, and the results were very

similar. Measurements performed with the QCLAS appear linear, although the maximum absolute weighted residual error is equal to 3.75, due to the small uncertainty values. This could trigger rejection of outliers if the goal was to determine which values constitute a consistent calibration set for the instrument. Here, the goal was to observe if the comparison results would show agreement or not, depending on the instrument.

Table 5 : Generalised Least-Square parameters calculated with XLGenline on measurement results obtained with the GC-ECD and QCLAS analysers.

Analyser	GC-ECD	QCLAS
Number of points	18	18
Gradient <i>m</i> :	0.00268	0.00292
Uncertainty associated with <i>m</i> :	0.00010	0.00002
Intercept with y-axis <i>c</i> :	0.09928	0.01885
Uncertainty associated with <i>c</i> :	0.03325	0.00610
Covariance associated with <i>m</i> and <i>c</i> :	-3.03×10^{-6}	-1.11×10^{-7}
Root mean square residual error:	0.34	1.75
Maximum absolute weighted residual:	0.60	3.75

To look for possible biases between the two analytical techniques, the difference between the predicted values obtained from the two regressions of the N₂O amount fractions submitted by participants and drift corrected ratios obtained with the QCLAS and GC-ECD analysers are plotted in Figure 3. All values agree within the combined expanded uncertainty. Considering the smaller measurement uncertainties obtained with the QCLAS, this instrument was chosen as comparator to calculate the Key Comparison Reference Values displayed in the next section.

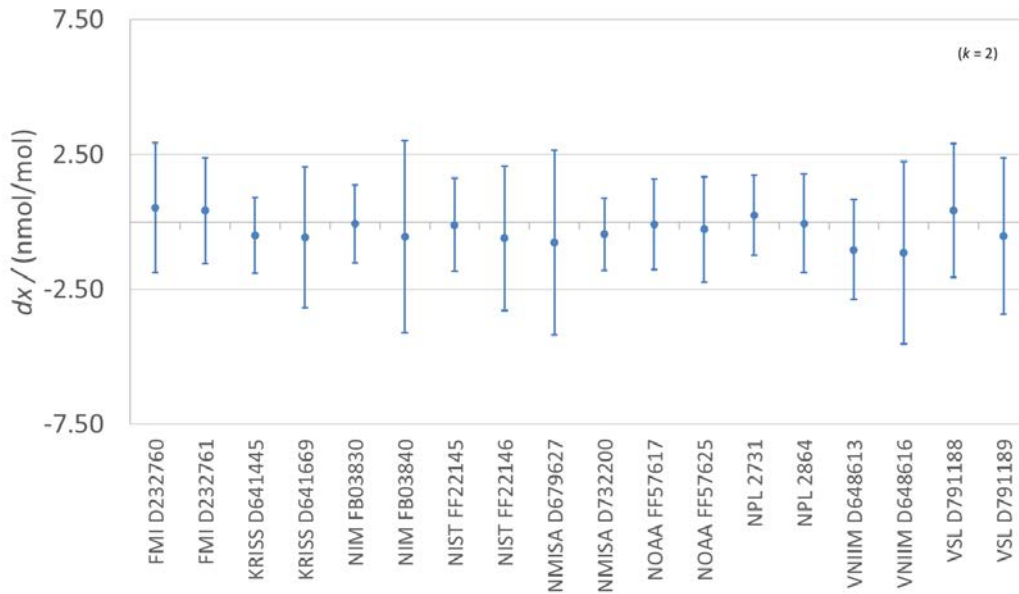


Figure 3: difference between the predicted values from a linear regression of N₂O amount fractions submitted by participants and drift corrected ratios obtained with the QCLAS and GC-ECD analysers (uncertainties at $k = 2$).

10 Method to obtain the Key Comparison results

Since the circulation of the Draft A1 report in April 2021, four meetings took place with participants to discuss the mathematical treatment of the comparisons results, and several models were proposed. The model chosen by participants is the Bayesian Errors–In–Variables regression with shades of dark uncertainty, described in detail below.

10.1 Errors-in-variables model for the analysis function

Table 6 below is an extract of the table displayed in *Annex 1 – BIPM measurements results* in which symbols for the quantities are redefined for the purpose of the demonstration. It lists the N₂O amount fractions, x_i , as reported by the participants, and the corresponding response ratios (between sample i and the control cylinder), r_i , as measured by the BIPM using QCLAS. The associated standard uncertainties, $u(x_i)$ and $u(r_i)$, are assumed to be based on large numbers of degrees of freedom.

Table 6 : Amount fractions of N₂O assigned by participants (x_i), and results of QCLAS measurements performed at the BIPM (r_i), with associated standard uncertainties.

Lab	$x_i /$ (nmol mol ⁻¹)	$u(x_i) /$ (nmol mol ⁻¹)	r_i	$u(r_i)$
FMI2	327.6	2.52	0.97880	0.000026
FMI1	320.41	2.46	0.95756	0.000042
KRISS1	328.54	0.33	0.98046	0.000038
KRISS2	338.93	0.34	1.01192	0.000023
NIM1	339.07	0.26	1.01114	0.000055
NIM2	346.55	0.26	1.03257	0.000030
NIST1	331.13	0.07	0.98605	0.000031
NIST2	344.38	0.07	1.02488	0.000029
NMISA1	342.38	0.24	1.02113	0.000044
NMISA2	331.49	0.11	0.98886	0.000021
NOAA1	326.81	0.31	0.97446	0.000026
NOAA2	342.87	0.30	1.02218	0.000015
NPL1	326.5	0.55	0.97234	0.000055
NPL2	337.7	0.55	1.00532	0.000035
VNIIM1	332.4	1.6	0.99166	0.000032
VNIIM2	342.5	1.5	1.02167	0.000025
VSL2	348.2	0.75	1.03682	0.000021
VSL1	337.8	0.75	1.00592	0.000021

The analysis function, or key comparison reference function (KCRF), relating the pairs of observations (r_i, x_i), is assumed to be of the form $\xi = \beta_1 + \beta_2 \rho$, where ξ denotes the true value of the amount fraction corresponding to the true value ρ of the ratio determined using QCLAS. When depicting the ratios and amount fractions graphically, as in Figure 4, the ratios are plotted against the horizontal axis, and the amount fractions are plotted against the vertical axis.

The measured values and corresponding true values for cylinder $i = 1, \dots, n$, where $n = 18$ is the total number of participant cylinders, are assumed to be related as follows:

$$\xi_i = \beta_1 + \beta_2 \rho_i, \quad r_i = \rho_i + \delta_i, \quad x_i = \xi_i + \lambda_i + \varepsilon_i \quad (1)$$

The measurement errors, δ_i for the ratios and ε_i for the amount fractions, are assumed to be non-observable outcomes of independent Gaussian random variables, all with mean 0 and standard deviations equal to their corresponding standard uncertainties, $u(r_i)$ and $u(x_i)$, respectively.

The presence of measurement errors in the values of both the ratios and the amount fractions is the reason why the model for the relationship between the r_i and the x_i is called an errors-in-variables (EIV) regression model [11].

The model in Equation 1 is not the conventional EIV model because it also recognizes the possible presence of one additional source of uncertainty. The λ_i in the part of the

model for the amount fractions, $x_i = \xi_i + \lambda_i + \varepsilon_i$, are cylinder effects assumed to be a sample from a Gaussian distribution with mean 0 and standard deviation τ .

The standard deviation, τ , characterizes the “dark uncertainty” for the amount fractions, a concept that Thomson and Ellison [12] introduced in the context of interlaboratory studies. This uncertainty component is described as “dark” because it does not appear in the uncertainty budgets prepared by the individual participants and reveals itself only after a line has been fitted to all the measurement results together.

This model for the gravimetric determinations accommodates the fact that the vertical residuals, $x_i - \xi_i$, are more dispersed than the reported uncertainties $u(x_i)$ suggest that they should be. No such excess dispersion is apparent for the horizontal residuals, $r_i - \rho_i$.

In this case, the estimate of τ is both statistically and substantively significant, estimated at $0.32 \text{ nmol mol}^{-1}$. In comparison to the participants’ reported uncertainties, this amounts to about 96 % of the median of the $u(x_i)$.

10.2 Bayesian approach

The EIV model described above and summarized in Equation 1 was fitted to the data using a Bayesian procedure which Cecelski *et al.* [13] describe in detail, and which is summarized below.

The Bayesian procedure is driven not only by the measurement results, but also by prior expectations about where the solution is likely to be. These expectations derive from the structure of the problem, from the design of the experiment, and from prior knowledge about fitting EIV models to data of this kind.

For example, we expect that the ratios of instrumental indications (between responses to the samples and the control cylinder) will be around 1, given the constraints imposed on the range of N_2O amount fractions covered by this comparison (as defined in the protocol), and since the composition of the reference mixture used by the BIPM as control stands roughly middlemost relative to the compositions of the mixtures prepared by the participants (the QCLAS instrumental readings obtained for this reference mixture were used to define the ratios r_i). That said, we also expect that the ratios will exhibit considerable dispersion around 1, seeing that the mixtures prepared by the participants were deliberately chosen to span the entirety of this range, best to anchor the regression line.

Since the ratios should be around 1, and considering that the slope of the line must be positive, we also expect that β_2 will have a numerical value close to the average of the amount fractions determined by the participants. Not only this, we also expect that both β_1 and β_2 will be close to their ordinary least squares estimates, because the relative uncertainties for the ratios are all very small.

The Bayesian approach uses probability distributions to encapsulate such prior knowledge about the values of the parameters. For example, Gaussian distributions are assigned to the intercept and to the slope.

The prior distribution for the slope is centred at the median amount fraction measured by the participants, and its standard deviation is set to three times the standard deviation of the measured amount fractions, to give the procedure plenty of freedom to look for the optimal slope.

The prior distribution for the intercept is centred at zero, which is its expected value in the absence of any N₂O. However, we allow for large deviations from zero by specifying a large prior standard deviation for β_1 .

Finally, we specify that τ is as likely to be smaller as to be larger than the typical vertical residual, whose preliminary estimate is the standard deviation of the residuals from an ordinary least squares regression line fitted to the measured values.

We impose the constraint that τ must have a non-negative numerical value by assigning to it a prior distribution that is concentrated on the positive numbers, and otherwise choose it so that it rules out no positive values whatever, no matter how large, but with decreasing probability for values of τ that are increasingly far from that preliminary estimate. We accomplish all this by assigning to τ a Cauchy distribution truncated at zero, with median equal to the preliminary estimate.

The Bayesian procedure does not deliver a particular solution. That is, it does not produce a specific set of “optimal” values for β_1 , β_2 , τ , and ρ_i . Instead, it samples the multidimensional space comprising the different parameters, guided by the defined prior expectations and by the statistical model for the data in Equation 1.

The samples of parameter values are drawn using a Bayesian procedure called Markov Chain Monte Carlo (MCMC) sampling [14]. The estimates of the parameters are the means of the corresponding samples drawn by the MCMC procedure, except for τ , whose estimate is the median of the corresponding sample. In particular, the means for β_1 and β_2 are the intercept and the slope of the EIV line drawn in Figure 4.

In addition to its meticulous, exploratory character, the Bayesian approach offers this great practical advantage relative to the classical approach: in a single stroke, it provides all the elements needed to evaluate the uncertainty surrounding the KCRF (represented by the light blue band in Figure 4), as well as the expanded uncertainties that are part and parcel of the degrees of equivalence, which are depicted in Figure 6 and listed in Table 7.

The regression parameters for the analysis function are estimated as $\beta_1 = -4.8 \text{ nmol mol}^{-1}$ with standard uncertainty of $5.5 \text{ nmol mol}^{-1}$, and $\beta_2 = 340$ with standard uncertainty of 5.5. The parameter τ estimated by the median of its posterior distribution is $0.32 \text{ nmol mol}^{-1}$.

10.3 Bayesian EIV model with shades of dark uncertainty

Having examined the results of the model just described, the GAWG concluded that the need for dark uncertainty was not uniform across all cylinders prepared by the participants. In fact, the results for some cylinders did not appear over dispersed by comparison with their reported uncertainties, while others did. For this reason, the GAWG decided to employ a variant of the EIV regression model described above, which assigns different amounts (or “shades”) of the dark uncertainty τ to different cylinders.

The idea was originally described by Merkatas et al. [15] for use in the context of interlaboratory studies involving scalar measurands. The version described next is referred to as “EIV-SHADES” in [13].

The smallest fraction of dark uncertainty is assigned to those cylinders that are already in fair mutual agreement among themselves, and the largest fraction is assigned to those that are in more marked disagreement with the bulk of the others, either because their measured values lie farther out of alignment with the others, or because their reported uncertainties may be relatively much too small.

After such adaptive “adjustment” to the reported uncertainties $u(x_i)$, the measurement results become mutually consistent in the sense that a single EIV regression line is adequate for all of them together.

Each “adjusted” (squared) uncertainty has the structure:

$$v_i^2 = u^2(x_i) + a_i\tau^2, \quad (2)$$

where a_i is 1 with probability p_i and 0 with probability $1 - p_i$. This is a round-about way of adding just the right fraction of τ^2 to each reported squared uncertainty to achieve mutual consistency of all the results and thus warrant fitting a single straight line to all of them. The $\{p_i\}$ are tuned appropriately, in a way that is responsive to the data, during the MCMC sampling procedure.

The end-result is that the “adjusted” standard uncertainty, v_i , that the model effectively associates with each measured amount fraction, x_i , can take any value between the reported uncertainty, $u(x_i)$, and $\sqrt{u^2(x_i) + \tau^2}$, for some $\tau > 0$.

Both this τ , and how much of this τ should go into each “adjusted” standard uncertainty, are determined by the Bayesian procedure as it effectively auscultates the data about the variable extent of their needs for some contribution from dark uncertainty.

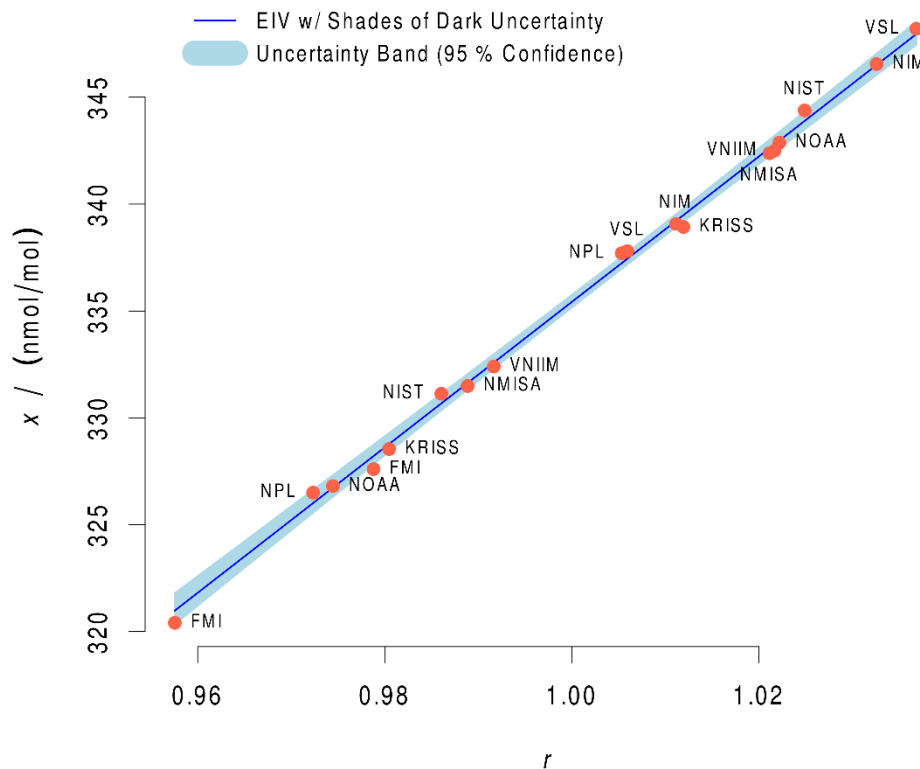


Figure 4 : Key comparison reference function (KCRF) based on the amount fractions reported by the participants and the corresponding response ratios measured by the BIPM. The dark blue line with light blue shading represents the Bayesian EIV regression and associated uncertainty, which accommodates the application of different “shades” of dark uncertainty to different participants’ results. The light blue band includes the “true” line with 95 % probability.

11 Key Comparison results

The degree of equivalence for cylinder i is:

$$D_i = x_i - \xi_i, \quad (3)$$

where x_i is the observed amount fraction reported by each participant. The estimates of the ξ_i , which are the key comparison reference values (KCRVs), are the predicted amount fractions based on the KCRF. The expanded uncertainty is estimated as two times the square root of the estimated variance of the predictive distribution,

$$U(D_i) = 2\sqrt{u^2(\xi_i) + (v_i)^2}, \quad (4)$$

where the v_i are the “adjusted” uncertainties that incorporate suitable fractions of the dark uncertainty. These results are given in Table 7 and plotted in Figure 6.

Table 7: results of CCQM-K68.2019: participant (Lab), amount fraction of N₂O reported by the participant (x_i) and its standard uncertainty (u_i), “adjusted” uncertainties (v_i), Key Comparison Reference Values (ξ_i) and associated uncertainty $u(\xi_i)$; and degree of equivalence (D_i) and associated expanded uncertainty for 95 % confidence $U(D_i)$; All values are expressed in nmol mol⁻¹.

Lab	x_i	u_i	v_i	ξ_i	$u(\xi_i)$	D_i	$u(D_i)$
FMI	327.60	2.52	2.52	328.2	0.19	-0.60	5.05
FMI	320.41	2.46	2.46	321.0	0.29	-0.59	4.95
KRISS	328.54	0.33	0.33	328.8	0.18	-0.26	0.75
KRISS	338.93	0.34	0.41	339.5	0.12	-0.57	0.85
NIM	339.07	0.26	0.26	339.2	0.12	-0.13	0.57
NIM	346.55	0.26	0.26	346.5	0.19	0.05	0.64
NIST	331.13	0.07	0.32	330.7	0.16	0.43	0.72
NIST	344.38	0.07	0.33	343.9	0.16	0.48	0.73
NMISA	342.38	0.24	0.24	342.6	0.14	-0.22	0.56
NMISA	331.49	0.11	0.11	331.6	0.15	-0.11	0.37
NOAA	326.81	0.31	0.31	326.7	0.21	0.11	0.74
NOAA	342.87	0.30	0.30	343.0	0.15	-0.13	0.67
NPL	326.50	0.55	0.55	326.0	0.22	0.50	1.18
NPL	337.70	0.55	0.55	337.2	0.11	0.50	1.12
VNIIM	332.40	1.60	1.6	332.6	0.14	-0.20	3.21
VNIIM	342.50	1.50	1.5	342.8	0.14	-0.30	3.01
VSL	348.20	0.75	0.75	347.9	0.21	0.30	1.56
VSL	337.80	0.75	0.75	337.4	0.11	0.40	1.52

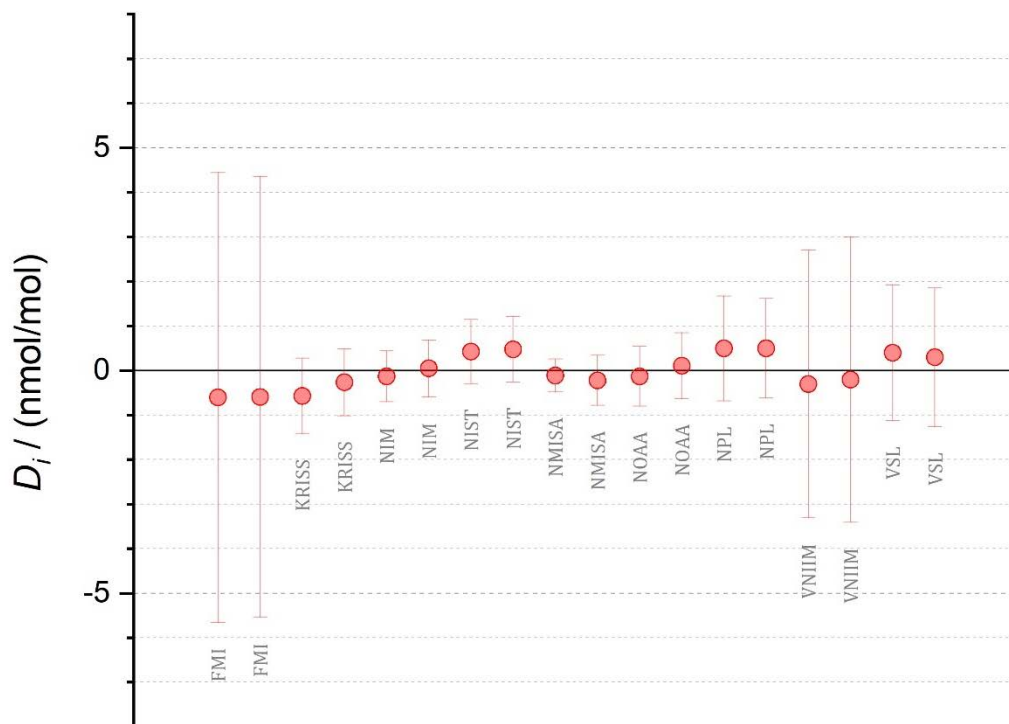


Figure 5: graph of equivalence of CCQM-K68.2019 (uncertainties at $k = 2$).

12 Analysis of results and comparison with CCQM-K68.2008

Results of this comparison with the previous exercise of 2008 are compared in Figure 6. It highlights that those laboratories who took part in both comparisons generally improved the preparation of their standards and claimed much smaller uncertainties in the 2019 exercise, while maintaining the good agreement among all participants. The mean of all degrees of equivalences was of $-0.55 \text{ nmol mol}^{-1}$ in 2008, with a spread of $0.66 \text{ nmol mol}^{-1}$. It was further reduced to a mean value of $-0.02 \text{ nmol mol}^{-1}$ in 2019, with a spread of $0.38 \text{ nmol mol}^{-1}$.

The same figure also indicates the Data Quality Objectives set by experts in atmospheric monitoring of Greenhouse Gases, as indicated in the report of their 2019 meeting [9]. The challenging objective of a general agreement between measurements better than $0.1 \text{ nmol mol}^{-1}$ was defined, to allow meaningful interpretation of trends in N_2O amount fractions and comparison between sampling sites. The spread of results in the comparison is almost four times larger than this target. It means that two laboratories proposing independent standards could not ensure that the DQO is met when measurements are performed in monitoring stations. In that regard, it is interesting to look at the agreement between the pairs of results of participants, displayed in Figure 7.

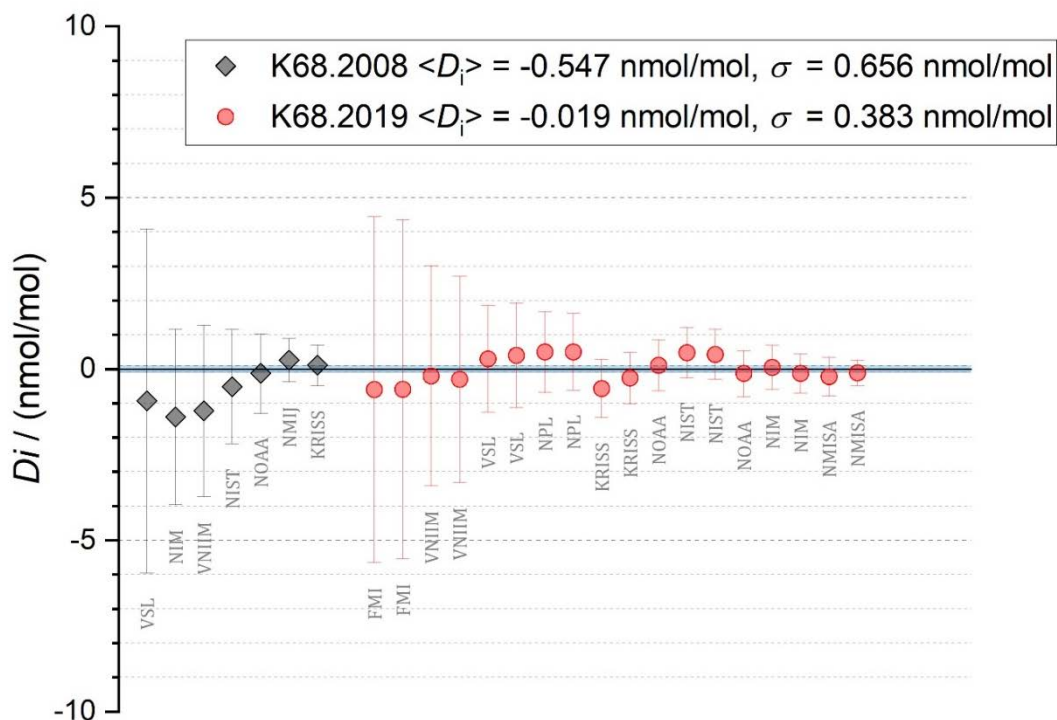


Figure 6: Degrees of equivalence in the two comparisons organised within CCQM-GAWG on N₂O in air standards, first in 2008 (black diamonds) and then in 2019 (red dots). The mean of the degrees of equivalence is indicated $\langle D_i \rangle$, with the standard deviation σ . The blue shaded zone indicates the Data Quality Objectives (0.1 nmol mol⁻¹) set by experts in atmospheric monitoring.

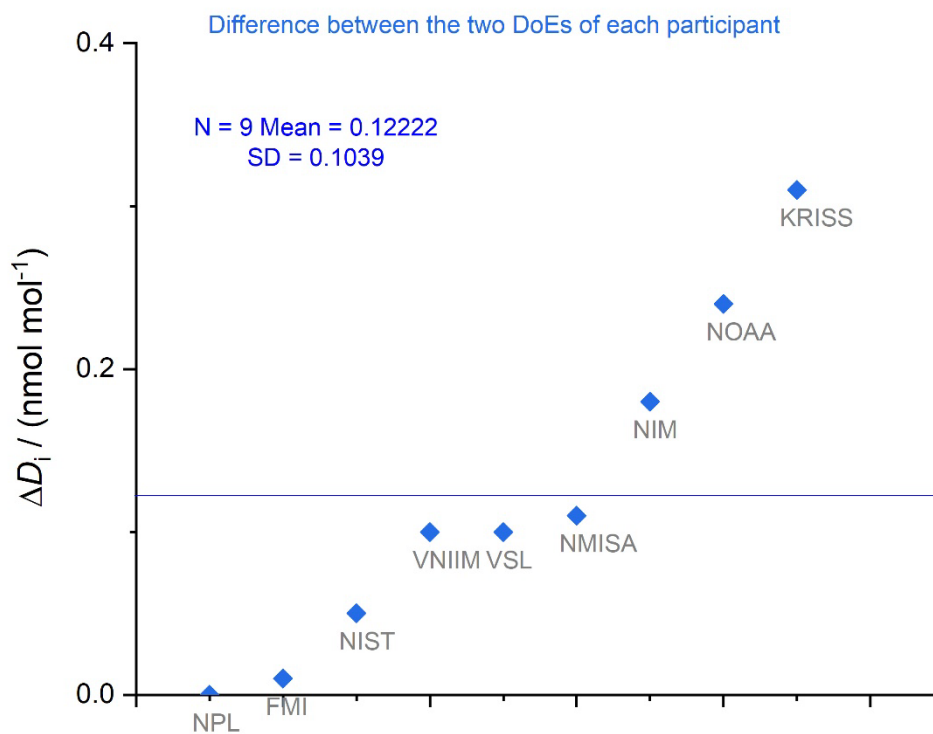


Figure 7: absolute difference between the two degrees of equivalence of each participant in CCQM-K68.2019. The blue line indicates the mean value.

Figure 7 shows a noticeable internal consistency between the two standards submitted by each participant, expressed as the absolute difference between the two degrees of equivalence obtained in the comparison. The difference ranges between zero for NPL and 0.3 nmol mol⁻¹ for KRISS, with a mean value of 0.12 nmol mol⁻¹ for the 9 participants. This is three times smaller than the spread (standard deviation) of 0.38 nmol mol⁻¹ when considering all degrees of equivalence, and much smaller than the maximum difference between two participants (1.1 nmol mol⁻¹). It supports the scale approach for N₂O, in which one laboratory maintain an ensemble of primary standards to disseminate the values, as an interesting strategy to calibrate measurement networks with tight requirements on the level of agreement within the network, as discussed for example in Brewer et al. [16].

13 Conclusions

The Key Comparison CCQM-K68.2019 has demonstrated a generally good agreement between N₂O in air reference standards prepared by its nine participants.

A good agreement was observed between the measurement results obtained with the two main techniques employed by the coordinating laboratory, GC-ECD and QCLAS, demonstrating the absence of biases specific to each technique. However, the performances of the two instruments were notably different, with smaller uncertainties obtained by QCLAS. The GC-ECD analyser operated by the coordinating laboratory was a recent model equipped with a micro ECD (GC- μ ECD) which is believed to be less stable than former instruments. This led to the choice of the QCLAS to provide the final measurement results of this comparison.

Participants in this comparison generally demonstrated improvements in the preparation of N₂O in air reference materials, compared to the previous exercise organised in 2008. One technical challenge was however highlighted: the difficulty to accurately estimate traces of N₂O in the matrix. Only three participants over nine were able to demonstrate that they considered this effect, either by doing proper measurements or by showing that it was negligible compared to other effects.

An innovative statistical model was applied to obtain the Key Comparison Reference Values, based on the Bayesian Errors-In-Variables regression with shades of dark uncertainty. Some of the participants' uncertainties had to be adjusted to obtain agreement between all of them. There was not enough information to understand the source of this additional uncertainty with confidence, but the only technical challenge revealed during discussions among participants was the correct estimation of N₂O traces in the matrix gas.

Participants having sent two standards each, it was also the occasion to highlight the better agreement within participants compared to between them. This probably results from differences in the standards preparation procedures which would introduce uncorrected biases. It emphasizes the interest of the atmospheric monitoring community for a traceability scheme relying on one central laboratory maintaining N₂O in air standards, with the network reporting values on the same scale, to avoid uncertainties arising from the preparation method.

14 Supported claims

Preparation of N₂O in dry air at ambient amount fractions and in the matrix imposed by this protocol is considered to represent an analytical challenge, therefore the key comparison CCQM-K68.2019 is a Track C comparison.

Preparation of N₂O in pure nitrogen at the same amount fraction is less challenging, as it does not require accurate mixing of the air components. The challenge associated with the purity of the matrix is only valid for nitrogen, and mixtures are generally more stable in nitrogen than in air. Therefore, this comparison can also be used to support standards of N₂O in nitrogen.

To summarise, the following Calibration and Measurement Capabilities claims can be underpinned by this comparison:

- a) nitrous oxide in air for standards and calibrations services, matrix matched to real air, over the amount fraction range of 200 nmol mol⁻¹ to 400 nmol mol⁻¹.
- b) nitrous oxide in nitrogen for standards and calibrations services, over the amount fraction range of 200 nmol mol⁻¹ to 400 nmol mol⁻¹.

Further guidance will be provided in a specific guidance document to be published with other similar documents on the webpage of the CCQM/GAWG:

<https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg>

15 Annex 1 – BIPM measurements results

Results of all measurements performed at the BIPM are presented in Table 8 below.

Table 8: results of measurements performed at the BIPM: cylinder reference (ID), mole fraction of N₂O assigned by participants (x), standard uncertainty (u), average of corrected responses with the GC-ECD analyser (\bar{y}_{GC}) and associated uncertainty $u(\bar{y}_{GC})$, average of corrected responses with the QCLAS analyser (\bar{y}_{LAS}) and associated uncertainty $u(\bar{y}_{LAS})$.

ID	$x /$ (nmol mol ⁻¹)	$u /$ (nmol mol ⁻¹)	\bar{y}_{GC}	$u(\bar{y}_{GC})$	\bar{y}_{LAS}	$u(\bar{y}_{LAS})$
FMI D232760	327.60	2.52	0.98056	0.00418	0.97880	2.60×10 ⁻⁵
FMI D232761	320.41	2.46	0.96080	0.00276	0.95756	4.20×10 ⁻⁵
KRISS D641445	328.54	0.33	0.97932	0.00191	0.98046	3.80×10 ⁻⁵
KRISS D641669	338.93	0.34	1.00797	0.00462	1.01192	2.30×10 ⁻⁵
NIM FB03830	339.07	0.26	1.00859	0.00204	1.01114	5.50×10 ⁻⁵
NIM FB03840	346.55	0.26	1.02694	0.00631	1.03257	3.00×10 ⁻⁵
NIST FF22145	331.13	0.07	0.98550	0.00278	0.98605	3.10×10 ⁻⁵
NIST FF22146	344.38	0.07	1.01973	0.00460	1.02488	2.90×10 ⁻⁵
NMISA D679627	342.38	0.24	1.01589	0.00616	1.02113	4.40×10 ⁻⁵
NMISA D732200	331.49	0.11	0.98716	0.00188	0.98886	2.10×10 ⁻⁵
NOAA FF57617	326.81	0.31	0.97492	0.00252	0.97446	2.60×10 ⁻⁵
NOAA FF57625	342.87	0.30	1.01816	0.00306	1.02218	1.50×10 ⁻⁵
NPL 2731	326.50	0.55	0.97386	0.00196	0.97234	5.50×10 ⁻⁵
NPL 2864	337.70	0.55	1.00329	0.00301	1.00532	3.50×10 ⁻⁵
VNIIM D648613	332.40	1.60	0.98816	0.00305	0.99166	3.20×10 ⁻⁵
VNIIM D648616	342.50	1.50	1.01536	0.00611	1.02167	2.50×10 ⁻⁵
VSL D791188	348.20	0.75	1.03346	0.00389	1.03682	2.10×10 ⁻⁵
VSL D791189	337.80	0.75	1.00260	0.00520	1.00592	2.10×10 ⁻⁵

15.1 QCLAS measurements details

Further details of the QCLAS measurements are provided in this section for information. It is for example interesting to compare the uncalibrated N₂O amount fractions calculated by the analyser's software (TDLWintel) after a nonlinear fit of the N₂O absorption peak (assumed to show a Voigt profile) and further synthetic calibration using molecular parameters of the HITRAN database. This results in measured values which are about 3% lower than the values submitted by participants, as observed in Figure 8. An ordinary linear regression performed on the entire set of data of the comparison also confirms the good linearity of the analyser, with residuals always lower than 0.5 nmol mol⁻¹.

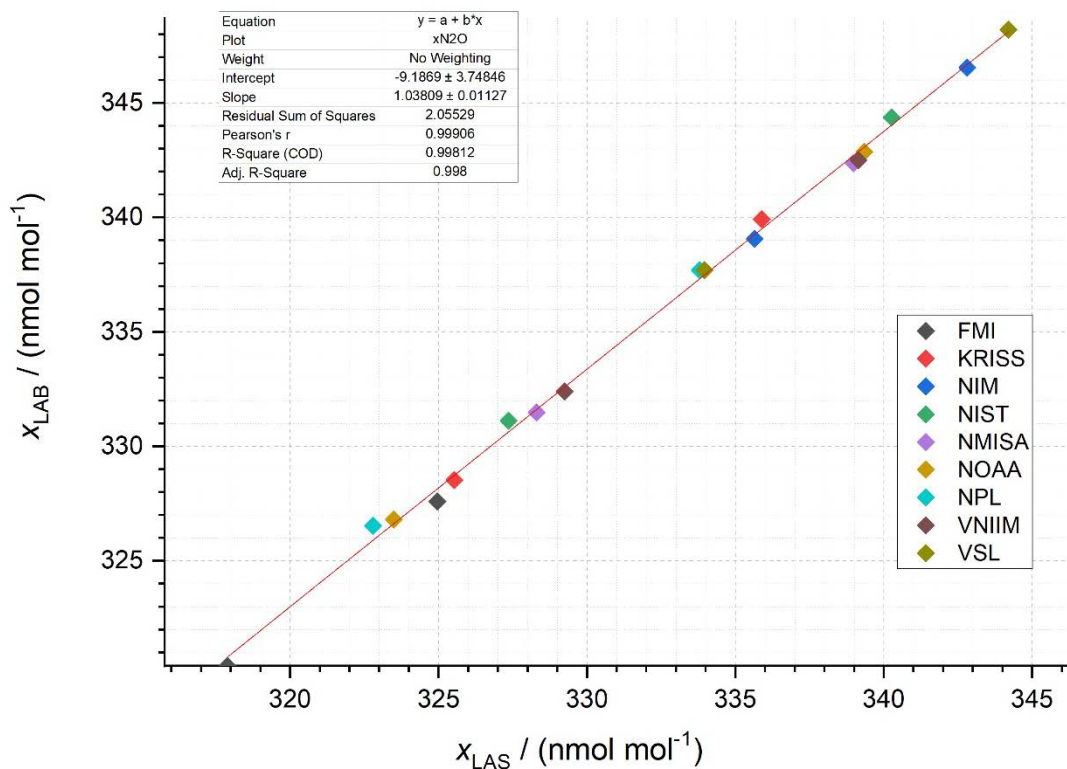


Figure 8: Ordinary linear regression of N₂O amount fractions submitted by participants (x_{lab}) against the values measured by QCLAS without calibration (x_{LAS}).

The QCLAS analyser also measures CO₂ amount fractions with the same principle as for N₂O, using an absorption peak present at 2242.9 cm⁻¹. It is also interesting to look at the agreement between its measured values and those submitted by participants, who were asked to describe the balance gas of their cylinders. The results are plotted in Figure 9 together with the output of a linear regression. Measured values are about 4% larger than submitted values, but again with a very linear response over the larger range of 4 μmol mol⁻¹ to 425 μmol mol⁻¹.

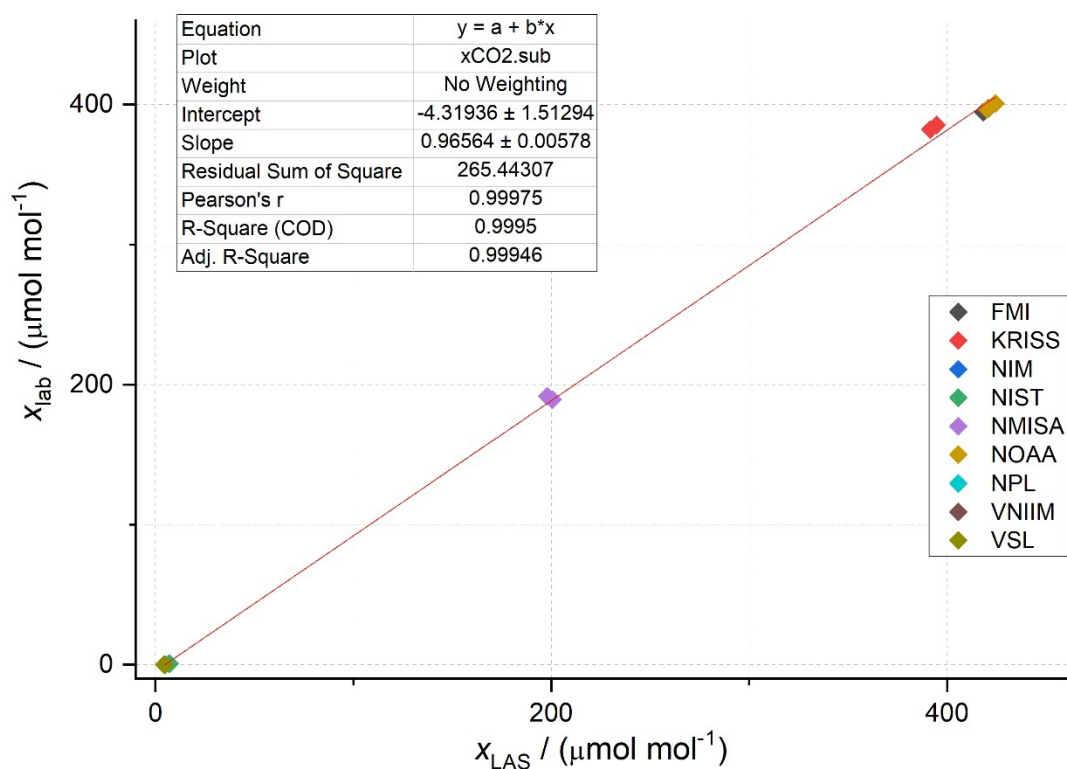


Figure 9: Ordinary linear regression of CO₂ amount fractions submitted by participants (x_{lab}) against the values measured by QCLAS without calibration (x_{LAS}).

16 Annex 2 – Participants reports

All reports are displayed entirely in the following pages, followed by all additional information sent after the first meeting (PDF version only).

17 References

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- [13] Cecelski C.E., Toman B., Liu F.-H., Meija J. and Possolo A., 2022, Errors-in-variables calibration with dark uncertainty, *Metrologia*, **59**, 045002, 10.1088/1681-7575/ac711c
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Laboratory name: Finnish Meteorological Institute (DI, Standard Laboratory)

Results of measurements

Nominal mole fraction / $\mu\text{mol mol}^{-1}$	N_2O mole fraction $x(\text{N}_2\text{O}) / \mu\text{mol mol}^{-1}$	Expanded uncertainty $U(x(\text{N}_2\text{O})) / \mu\text{mol mol}^{-1}$	Coverage factor
	0.3276	0.0050	2
	0.3204	0.0049	2

Uncertainty budget

Sources of uncertainty of the performance characteristics of the analyzer, gas dilutor, zero gas and the gas standard are listed in the table below for FMI cylinder with the higher N_2O mole fraction. Uncertainty was estimated similarly for the cylinder with the lower N_2O mole fraction.

Quantity xi	Estimate xi(%; nmol mol^{-1})	Evaluation Type (A or B)	Distribution	Standard Uncertainty, u(xi)	Sensitivity Coefficient, ci	Contribution ui(y)
Repeatability	0.323	A	Rectangular	0.186	1	0.186
Linearity	0.189	A	Rectangular	0.109	1	0.109
Zero gas, purity	0.5	B	Gaussian	0.5	1	0.5
Gas standard	0.30%	B	Gaussian	0.30%	1	0.30%
Dilution flow	0.50%	B	Gaussian	0.50%	1	0.50%
Span flow	0.50%	B	Gaussian	0.50%	1	0.50%
Combined std uncertainty uc(xi)						2.503
Expanded uncertainty U (nmol mol^{-1})						5.006
Coverage factor, k						2

Measurement procedure

Analysis instrument:

The analyzer used for the measurements was N_2O -CO- H_2O analyzer by Los Gatos Research, Inc. It is based on Off-Axis Integrated-Cavity Output Spectroscopy (OA-ICOS).

Calibration standards:

The calibration standard was purchased from VSL, the Netherlands. The concentration of the gas standard was $40.15 \mu\text{mol mol}^{-1}$ in synthetic air, with the uncertainty of $0.12 \mu\text{mol mol}^{-1}$.

Instrument calibration:

The calibration of the analyzer was made by dilution of the gas standard at the concentration range of CCQM-K68.2019. Synthetic air was used for dilution of the gas standard. The purity of the synthetic air was examined by comparison of the respond of the instrument for synthetic air and to nitrogen gas (purity grade 6.0). The linear regression line was fitted into the measured mean values of the analyzer against the value of the calibration concentration. The gas diluter, Environics 4000, was calibrated against the flow measurement system of Molbloc laminar flow element by DHI, which was calibrated against the primary flow measurement system by VTT MIKES. Linearity of the analyzer as well as standard error of the estimate of the regression line was used to examine the performance of the analyzer during calibration. The lack of linearity was included into the uncertainty budget for the measurement results. During the

measurements the temperature and the air pressure of the laboratory room were recorded. The changes of both quantities were within the acceptable range and no correction on the results based on these were made.

Sampling handling:

The pressure regulators (two stages) were connected into the cylinders over a month before the measurements and flushed several times with the cylinder gas. The sample was directed to the analyzer through a stainless-steel tubing at ambient pressure. The excess of about 0.3 l min^{-1} was used to maintain the gas at ambient pressure.

Additional information

The cylinders were filled with ambient air at a remote site in the Finnish Arctic in 2015/2016. The air was scrubbed from typical impurities and humidity before filling into the cylinders. The cylinders were acclimatized in laboratory for several months before the analysis. The cylinders were sent to the BIPM in 13 September 2019.

Participant Report Form

CCQM-K683.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

- This form should be completed by participants in the key comparison CCQM-K168.2019 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.
- Comparison coordinator: Dr Joële Viallon
Chemistry Department
Bureau International des Poids et Mesures
Pavillon de Breteuil
F-92312 SEVRES CEDEX
Tel: +33 1 45 07 62 70
Email: jviallon@bipm.org

Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information (for the comparison report)

Author(s)	Jeong Sik Lim
Institute	KRISS
Address	Gajeong-ro 267, Yuseong-gu, Daejeon, Republic of Korea

Information on standards sent to the BIPM

	Standard 1	Standard 2
Nominal N₂O mole fraction	328.54	338.93
Date of preparation	2018. 8. 16	2018. 8. 16
Serial number	D641445	D641669
Pressure (before shipment)	> 120 bar	> 120 bar
Volume	10 L	10 L
Connection type		

Results of measurements

Please indicate below the final value and associated expanded uncertainty of the N₂O mole fraction in each of the two standards.

Nominal mole fraction /nmol mol ⁻¹	N ₂ O mole fraction $x(\text{N}_2\text{O})$ /nmol mol ⁻¹	Expanded uncertainty $U(x(\text{N}_2\text{O}))$ / nmol mol ⁻¹	Coverage factor
330	328.54	0.66	2
340	338.93	0.68	2

Uncertainty budget

Gravimetric uncertainty was evaluated according to ISO 6142-2019. Uncertainties of purity assessments and gravimetric preparation were sources for the gravimetric values of N₂O mole fraction. And uncertainty of reference values included those of gravimetric values and verification tests. Below table is uncertainty budget for submitted reference value of gravimetric standards.

Cylinder ID	Uncertainty of gravimetry	Uncertainty of verification	Standard uncertainty of reference value ($k=2$)
D641445	0.05	0.33	0.66
D641669	0.05	0.34	0.68

Measurement procedure

A GC- μ ECD (Agilent 6890) was used for measurements of CCQM-K68.2019. A separation column was Resil-C (80/100, 12 ft, 1/8 inch). Oven temperature was set at 80°C. A strong oxygen peak which exhibited long tail was sufficiently separated from N₂O peak. Samples and standards were injected via mass flow controller at a few tens of mL/min and then loaded to a sample loop of a few mL size. Carrier gas was 5% CH₄ in Ar (P5). Detector temperature was around 370°C. Flow restrictor (frit filter, valco) was installed at the vents of sample loop and detector in order for pressurized injection and instrument isolation from environment pressure fluctuation, leading overall instrumental drift was lower than 0.5%. During this key comparison, overall measurement precision was observed lower than about 0.06%. Instrumental drift was corrected by monitoring response variation of a working standard. Therefore, measurement of sample or standard was bracketed by the working standard in sequence of R-S-R.... Every measurement was repeated by 1+4 submeasurements. The first submeasurement was discarded for removing memory of previous measurement.

Additional information

- a purity table with uncertainties for the nominally pure parent gases;

- Purity table of N₂ raw gases. Nominal values are represented

				(mol/mol)
	value	method	distribution	uncertainty (<i>k</i> =2)
N ₂ O	9.50E-11	precon-GC-μECD	normal	1.20E-11
CO ₂	2.07E-08	GC-FID	normal	3.80E-09
Ar	1.62E-05	LN ₂ -GC-TCD	normal	5.50E-07
O ₂	5.40E-07	LN ₂ -GC-TCD	normal	3.40E-07
CO	1.80E-08	GC-FID	normal	4.40E-09
CH ₄	2.30E-09	GC-FID	rectangular	2.00E-09
H ₂ O	3.20E-07	H ₂ O analyzer	normal	1.00E-07
N ₂	0.9999829			0.0000007

- Purity table of O₂ raw gases. Nominal values are represented

				(mol/mol)
	value	method	distribution	uncertainty (<i>k</i> =2)
N ₂ O	5.00E-08	precon-GC-μECD	normal	1.45E-12
CO ₂	1.23E-07	GC-FID	normal	2.00E-10
CO	5.00E-07	GC-FID	rectangular	2.89E-07
CH ₄	5.00E-07	GC-FID	rectangular	2.89E-07
H ₂ O	3.95E-07	H ₂ O analyzer	normal	7.90E-08
O ₂	0.99999947			0.00000008

- Purity table of Ar raw gases. Nominal values are represented

				(mol/mol)
	value	method	distribution	uncertainty (<i>k</i> =2)
N ₂ O	3.00E-11	precon-GC-μECD	normal	2.00E-12
CO ₂	1.00E-09	GC-FID	rectangular	1.20E-09
O ₂	3.80E-06	O ₂ analyzer	normal	1.50E-06
N ₂	1.22E-05	LN ₂ -GC-TCD	normal	9.90E-06
CO	8.20E-08	GC-FID	normal	8.80E-09
CH ₄	1.00E-09	GC-FID	rectangular	8.20E-10
H ₂ O	2.80E-07	H ₂ O analyzer	normal	1.10E-07
Ar	0.9999836			0.0000049

- Purity table of N₂O raw gas.

(mol/mol)

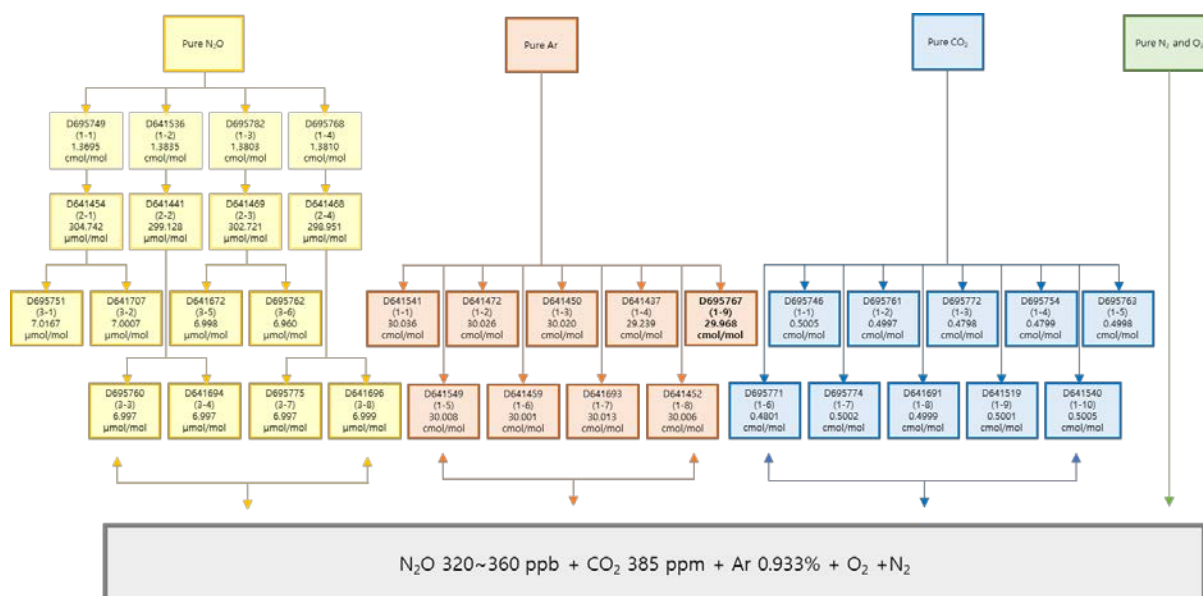
	value	method	distribution	uncertainty (k=2)
CO ₂	1.50E-07	GC-TCD	rectangular	8.66E-08
Ar	1.50E-06	GC-TCD	rectangular	8.66E-07
O ₂	1.50E-07	GC-TCD	rectangular	8.66E-08
N ₂	1.22E-05	GC-TCD	normal	2.44E-06
CO	7.00E-08	GC-FID	normal	1.10E-08
CH ₄	2.10E-08	GC-FID	normal	4.20E-09
N ₂ O	0.9999859			0.0000003

- Purity table of CO₂ raw gas.

	value	method	distribution	uncertainty (k=2)
N ₂ O	3.00E-11	precon-GC-μECD	normal	6.50E-12
Ar	1.50E-06	GC-TCD	rectangular	8.66E-07
O ₂	5.03E-06	GC-TCD	normal	4.40E-07
N ₂	1.53E-06	GC-TCD	normal	6.12E-08
CO	2.60E-08	GC-FID	normal	9.10E-09
CH ₄	2.80E-08	GC-FID	normal	4.60E-09
H ₂ O	6.21E-06	H ₂ O analyzer	normal	1.24E-06
CO ₂	0.9999857			0.0000016

• a brief outline of the dilution series undertaken to produce the final mixtures;

- Dilution agent is high purity N₂ of which impurity was nominally assigned as tabulated above. Automatic weighing machine was used for the measurement of added gas weight.



- a purity table for each of the final mixtures, including the uncertainties;

D641445	unit	value	uncertainty ($k=2$)
N ₂ O	nmol/mol	328.54	0.08
CO ₂	μmol/mol	382.34	0.14
Ar	mmol/mol	9.39675	0.00092
O ₂	mmol/mol	209.7405	0.0058
N ₂	mmol/mol	780.4797	0.0060
CO	nmol/mol	15.9	3.1
CH ₄	nmol/mol	2.9	1.8
H ₂ O	nmol/mol	336	73

D641669	unit	value	uncertainty ($k=2$)
N ₂ O	nmol/mol	338.93	0.09
CO ₂	μmol/mol	385.46	0.15
Ar	mmol/mol	9.29155	0.00091
O ₂	mmol/mol	209.2240	0.0057
N ₂	mmol/mol	781.0983	0.0059
CO	nmol/mol	15.1	3.0
CH ₄	nmol/mol	2.9	1.8
H ₂ O	nmol/mol	336	73

- a brief outline of the verification procedure applied to the final mixtures;

Verification test was conducted with 10 gravimetric standards of which N₂O mole fractions ranged from 320 to 360 nmol/mol. Verification tests were repeated by 3 times. Every verification tests were passed a criteria of $|\chi_{grav} - \chi_{ver}| \leq 2 \cdot \sqrt{u_{grav}^2 + u_{ver}^2}$. For assigning verification value of each standard, regression analysis was performed with a model of second order polynomial. Therefore, verification values were taken by optimized parameters of second order polynomial function at measured μECD response of corresponding standard. In this regard, verification uncertainty was composed of measurement reproducibility of each standard and deviation between verified and gravimetric values. Averaged reproducibility and deviations were taken to give total verification uncertainty 0.10% in relative at 65% confidence level.

Participant Report Form

CCQM-K683.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

- This form should be completed by participants in the key comparison CCQM-K168.2019 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.
- Comparison coordinator: Dr Joële Viallon
Chemistry Department
Bureau International des Poids et Mesures
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Email: jviallon@bipm.org

Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information (for the comparison report)

Author(s)	Zhe Bi
Institute	National Institute of Metrology, China
Address	Room 217, NO. 17# National Institute of Metrology, China 18, Bei San Huan Dong Lu; Chaoyang District; Beijing

Information on standards sent to the BIPM

	Standard 1	Standard 2
Nominal N₂O mole fraction	346.55 nmol/mol	339.07 nmol/mol
Date of preparation	25 th Sep.	25 th Sep.
Serial number	FB03840	FF03830
Pressure (before shipment)	90bar	90bar
Volume	6L	6L
Connection type	CGA580	CGA580

Results of measurements

Please indicate below the final value and associated expanded uncertainty of the N₂O mole fraction in each of the two standards.

Nominal mole fraction / nmol mol ⁻¹	N ₂ O mole fraction $x(\text{N}_2\text{O})$ / nmol mol ⁻¹	Expanded uncertainty $U(x(\text{N}_2\text{O}))$ / nmol mol ⁻¹	Coverage factor
346.55	346.55	0.52	2
339.07	339.07	0.51	2

Uncertainty budget

Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the nitrogen monoxide mole fraction.

Cylinder	Gravimetric value/nmol/mol	Component	distribution	Standard uncertainty/nmol/mol
FB03840	346.55	Combined uncertainty of Purity, Molecular and Weighing	Normal	0.21
		Repeatability of the measurement	Normal	0.15
Combined standard uncertainty				
FF03830	339.07	Combined uncertainty of Purity, Molecular and Weighing	Normal	0.22
		Repeatability of the measurement	Normal	0.14

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation, indicating which analyser(s) were used.

Five primary standard cylinders of N₂O in air mixture were measured by CRDs. The gravimetric values were used to calibrate CRDs. For each point, an average of data recorded in 5 minutes was collected. The verification was done by the comparison of gravimetric values and the calculated values.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure parent gases;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including the uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Purity table for the nominally pure N₂O:

Component	Amount fraction (10 ⁻⁶ mol/mol)	Standard uncertainty (10 ⁻⁶ mol/mol)	Assumed distribution
H ₂ O	15	3	Normal
CO	1	0.58	Rectangular
CO ₂	5	1	Normal
CH ₄	1	0.58	Rectangular
O ₂	9	3	Normal
N ₂	25	5	Normal
Ar	1	0.58	Rectangular
N₂O	999943	6.71	Normal

Purity table for the nominally pure N₂:

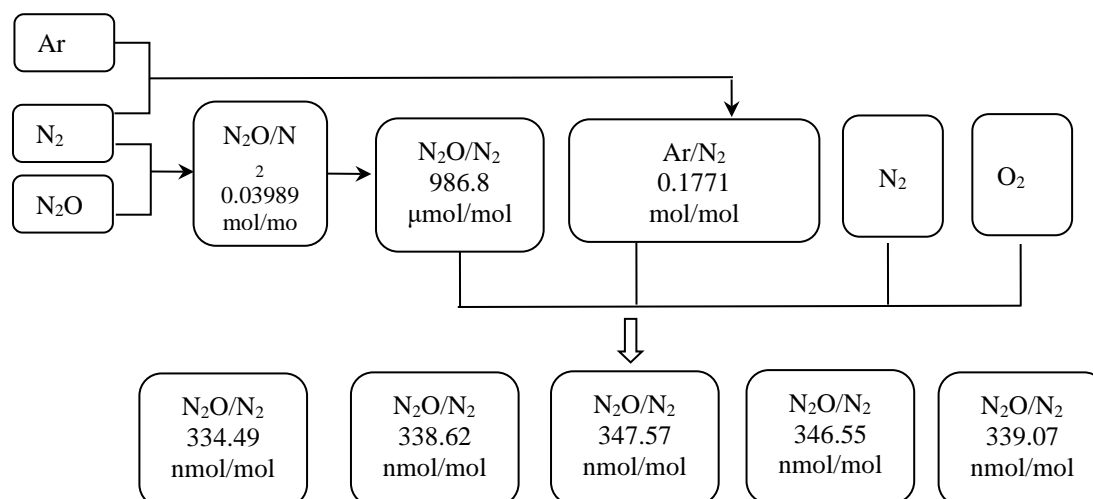
Component	Amount fraction (10 ⁻⁶ mol/mol)	Standard uncertainty (10 ⁻⁶ mol/mol)	Assumed distribution
CH ₄	0.001	0.0005	Rectangular
Ar	48.3	4.8	Normal
O ₂	0.02	0.006	Normal
CO ₂	0.010	0.003	Normal
H ₂ O	0.10	0.04	Normal
N ₂ O	0.0001	0.000029	Rectangular
N₂	999951.6	4.8	Normal

Purity table for the nominally pure O₂:

Component	Amount fraction (10 ⁻⁶ mol/mol)	Standard uncertainty (10 ⁻⁶ mol/mol)	Assumed distribution
CH ₄	0.001	0.0003	Normal
Ar	2.0	1.0	Normal
N ₂	1.1	0.5	Normal
CO ₂	0.0012	0.0004	Rectangular
H ₂ O	1.2	0.6	Normal
N ₂ O	0.0013	0.000013	Normal
O₂	999995.7	1.3	Normal

Purity table for the nominally pure Ar:

Component	Amount fraction (10 ⁻⁶ mol/mol)	Standard uncertainty (10 ⁻⁶ mol/mol)	Assumed distribution
CH ₄	0.001	0.0003	Normal
O ₂	0.10	0.5	Normal
N ₂	0.10	0.5	Normal
CO ₂	0.001	0.0004	Rectangular
H ₂ O	0.10	0.4	Normal
N ₂ O	0.0001	0.00001	Rectangular
Ar	999999.8	0.7	Normal

Brief outline for the dilution series**Purity for the final mixtures****FB03840**

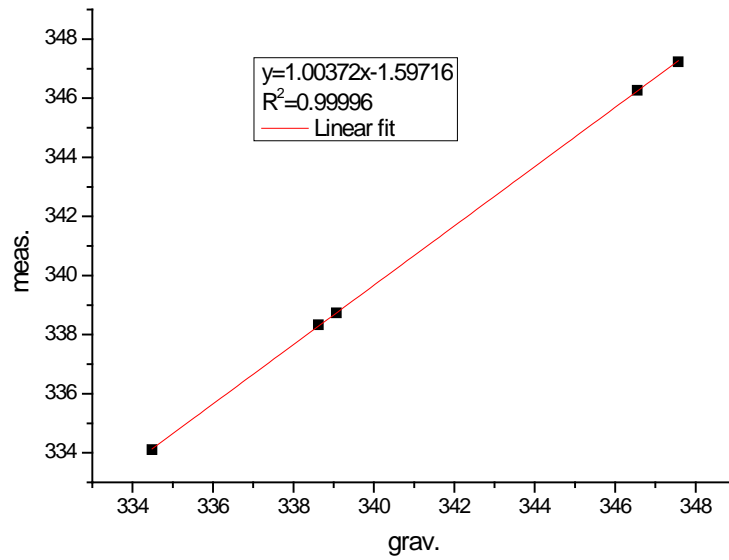
Component	Amount fraction (mol/mol)
CH ₄	1.0088E-09
CO	9.1082E-12
CO ₂	8.0745E-09
H ₂ O	3.3103E-07
H ₂	3.5048E-12
N ₂	7.8117E-01
O ₂	2.0943E-01
Ar	9.4016E-03
N ₂ O	3.4655E-07

FB03830

Component	Amount fraction (mol/mol)
CH ₄	1.0086E-09
CO	8.9116E-12
CO ₂	8.0786E-09
H ₂ O	3.3034E-07
H ₂	3.4291E-12
N ₂	7.8106E-01
O ₂	2.0939E-01
Ar	9.5486E-03
N ₂ O	3.3907E-07

Brief outline of the verification procedure

Five primary standard cylinders of N₂O in air mixture were measured by CRDs. A linearity regression was established based on the gravimetric value. For each point, an average of data recorded in 5 minutes was used. The verification was done by the comparison of gravimetric values and the calculated values.



Stability test

A cylinder prepared in 2009 was measured against the newly prepared cylinder. No significant drift of the values was observed for the old cylinder.

Participant Report Form

CCQM-K68.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

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- Comparison coordinator: Dr Joële Viallon
Chemistry Department
Bureau International des Poids et Mesures
Pavillon de Breteuil
F-92312 SEVRES CEDEX
Tel: +33 1 45 07 62 70
Email: jviallon@bipm.org

Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information (for the comparison report)

Author(s)	Christina Cecelski; Jennifer Carney
Institute	National Institute of Standards and Technology (NIST)
Address	100 Bureau Drive, Stop 8393 Gaithersburg, MD 20899-8393 USA

Information on standards sent to the BIPM

	Standard 1	Standard 2
Nominal N₂O mole fraction	331 nmol/mol	344 nmol/mol
Date of preparation	September 4, 2014	September 4, 2014
Serial number	FF22145	FF22146
Pressure (before shipment)	1200 psi	1300 psi
Volume	6 L	6 L
Connection type	CGA 590	CGA 590

Results of measurements

Please indicate below the final value and associated expanded uncertainty of the N₂O mole fraction in each of the two standards.

Nominal mole fraction / nmol mol ⁻¹	N ₂ O mole fraction $x(\text{N}_2\text{O})$ / nmol mol ⁻¹	Expanded uncertainty $U(x(\text{N}_2\text{O}))$ / nmol mol ⁻¹	Coverage factor
331	331.13	0.13	2
344	344.38	0.14	2

Overview

Two gas cylinders (FF22145, FF22146) containing nitrous oxide (N₂O) in air were provided by NIST for this key comparison. The mixtures were prepared as part of a suite of six N₂O primary standard mixtures (PSMs) ranging from (315 to 344) nmol/mol. The PSMs were prepared gravimetrically in 6 L aluminium cylinders in accordance with ISO 6142 [1]. Gravimetric parent mixtures ranging from (3.0 to 4.0) µmol/mol N₂O in air were used as the source gases for this level of dilutions.

Gravimetric preparation

The cylinders were connected to a fill manifold along with a cylinder of the appropriate parent mix (Table 1) and Linweld Ultra Zero Plus® (UZ+Ar) air with argon added (Table 2). The contents of the six candidate cylinders were vented, purged with 0.14 MPa (20 psia) of BIP® nitrogen, and evacuated a minimum of four times. The final evacuation reduced the cylinder pressure to approximately 0.27 Pa (0.002 Torr). The six cylinders were then left overnight to equilibrate to room temperature. Ten replicate mass measurements of each evacuated cylinder were made using an automated weighing system provided by KRISS. The balance in the KRISS system has a capacity of 10.1 kg and a resolution of 0.001 g. The reproducibility is typically ± 0.0012 g. Three cylinders at a time were measured consecutively and then bracketed by a mass measurement of a control mass.

The evacuated cylinders were reattached to the fill manifold, and the manifold was purged, vented and evacuated at least four times with the appropriate parent mix. The candidate cylinder was opened and filled with the parent mix to a predetermined pressure. It was then allowed to equilibrate for 30 min to achieve room temperature. After equilibration, the manifold was re-pressurized with the same parent mix and the cylinder was adjusted to the final fill pressure. The cylinder valve was closed, and the cylinder was left for at least 3 h to equilibrate. Three cylinders in each group were then weighed in the same manner as described above.

The cylinders were once again attached to the manifold and the manifold was purged, vented and evacuated at least four times with (UZ+Ar) air. Each candidate cylinder was consecutively opened and filled with (UZ+Ar) air to a predetermined pressure. The cylinders were then set aside for 2 h to achieve temperature equilibration with the room. The manifold was re-pressurized with (UZ+Ar) air and each cylinder was adjusted to a final fill pressure of 12.5 MPa (1815 psia). After filling, the cylinder valves were closed, and the cylinders were left to equilibrate for (5 to 10) h, after which they were weighed in the same manner as before. When weighing was completed, the contents of the cylinders were mixed by rolling for 3 h on a Fredlov® cylinder roller. The amount fractions were calculated from the masses and purities of the added gases.

Table 1. Parent mixtures utilized in preparing NIST N₂O in air PSMs.

Parent mixture	Parent amount fraction, $\mu\text{mol/mol}$ ($k = 2$)	PSM(s) prepared from parent	PSM nominal amount fraction, nmol/mol
FF10196	3.9738 ± 0.0012	FF22146	344
FB03267	3.6954 ± 0.0012	FF22181	338
CAL9875	3.4274 ± 0.0010	FF22145; CAL016773	331; 326
FF10205	3.0249 ± 0.0008	FF22225; FF22270	320; 315

Table 2. Assay of Linweld Ultra Zero Plus[®] (UZ+Ar) air, cylinder # VW635, used in the preparation of CCQM samples FF22145 and FF22146.

Component	$\mu\text{mol/mol}$ ($k = 1$)
Nitrous oxide (measured)	0.000190 ± 0.00002
Oxygen (measured)	208688 ± 35
Carbon dioxide (measured)	0.933 ± 0.021
Argon (measured)	9758 ± 4
Nitrogen (difference)	781553 ± 35

Uncertainty budget

The stated total uncertainty, u_c , was determined from the following sources of uncertainty in the gravimetric preparation and verification of the PSMs:

1. Gravimetric preparation (weighing process), $u(x_{\text{grav}})$
2. Purity of the starting gases, $u(x_{\text{purity}})$
3. Verification of the gas mixtures, $u(x_{\text{ver}})$

The uncertainty is expressed as an expanded uncertainty $U = ku_c$ with a coverage factor k of 2. The true value is therefore asserted to lie in the interval defined by $\pm U$ with a level of confidence of 95 %.

Verification

Each PSM was verified using a Los Gatos Research Model N₂O/CO-23d off-axis cavity enhanced absorption spectrometer (CEAS). Sample selection was achieved using a computer operated gas analysis system (COGAS # 16) with stainless steel sample lines.

A NIST Standard Reference Material (SRM) lot standard (LS) 1720-AL-27 (CC324321) [2] served as the control cylinder. Ten ratios of each PSM to the control cylinder were obtained over a two-day period giving a total of 60 data points. The data were evaluated using a first-order generalized least-squares regression (GenLine) compliant with ISO 6143 [3,4] (Figure 1). The six PSMs predicted the LS to be (322.87 ± 0.06) nmol/mol N₂O ($k = 2$). This value agrees with the NIST certified value of (322.83 ± 0.20) nmol/mol ($k = 2$), as well as the NOAA assigned value of (323.09 ± 0.50) nmol/mol ($k = 2$), which was determined relative to the WMO/CCL scale X2006A.

GENLINE - Linear ($y=b_0+b_1*x$)				
	Value	Std Error		
b0	-1.4567651	0.94606266		
b1	324.3265980	0.93009035		
cov(b0,b1)		-0.87952453		
rms residual error		1.88435376		

X	Y	X-Solution	Y-Solution	uTest
1.06680	344.38	1.06673	344.51	PASS
1.04743	338.39	1.04751	338.28	PASS
1.02523	331.13	1.02525	331.06	PASS
1.01049	326.32	1.01049	326.27	PASS
0.99048	319.65	0.99045	319.77	PASS
0.97551	314.95	0.97552	314.93	PASS

Sample #	Xin	uXin	Yeval	uYeval
LS 1720-AL-27	1.00000	0.00000	322.87	0.03

	Value	uValue	Difference
NOAA	323.09	0.25	0.22
NIST Certified	322.83	0.10	-0.04

Difference = Value - Yeval

Figure 1. Verification of NIST N₂O PSMs using ISO 6143 compliant GenLine. Amount fractions are expressed as nmol/mol. Uncertainties are listed as standard uncertainties ($k = 1$).

Stability

Stability of the standards was monitored for approximately 5 years prior to this key comparison (Figure 2). The results of the second verification (2019) agreed with the initial verification (2014) within the stated uncertainties, demonstrating long-term stability for both mixtures.

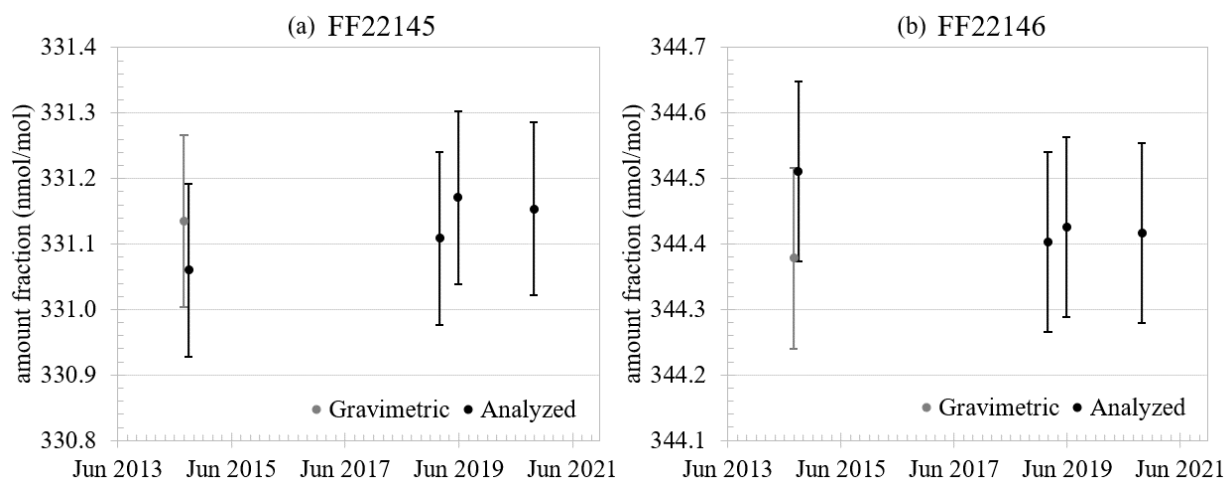


Figure 2. Stability testing of (a) FF22145 and (b) FF22146. The grey and black points represent the gravimetric and analyzed values, respectively. Error bars represent $k = 2$ expanded uncertainties.

The mixtures were again reanalyzed for stability after their return to NIST, in October 2020. The results of this analysis, which are included in Figure 2, show that the amount fractions for both standards remained stable over the course of the key comparison.

Additional information

The CCQM samples were prepared using a multiple step dilution starting from pure materials. The steps involved in this dilution process are outlined in Figure 3. The purity analysis of the pure N₂O used to prepare the mixtures can be found in Table 3. The final compositions of the CCQM samples, as determined by gravimetry, are listed in Table 4.

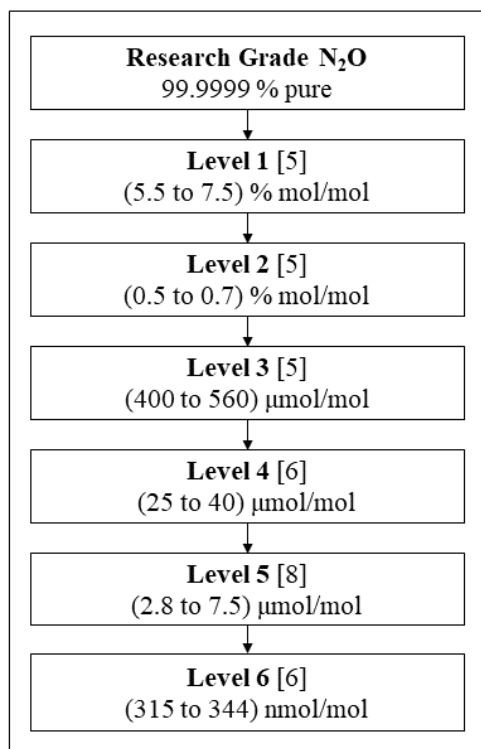


Figure 3. Outline of the dilution process by which the CCQM samples were prepared. The numbers listed in square brackets represent the total number of cylinders produced at each dilution level.

Table 3. Purity analysis of research grade N₂O, cylinder # SG9103953.

Component	$\mu\text{mol/mol}$ ($k = 1$)
Nitrogen	0.1 ± 0.1
Oxygen	0.1 ± 0.1
Carbon dioxide	0.1 ± 0.1
Argon	0.1 ± 0.1

Table 4. Composition of final mixtures used for this key comparison.

Component	FF22145 $\mu\text{mol/mol}$ ($k = 1$)	FF22146 $\mu\text{mol/mol}$ ($k = 1$)
Nitrous oxide	0.33113 ± 0.00006	0.34438 ± 0.00006
Nitrogen	781619 ± 49	781612 ± 49
Oxygen	208712 ± 33	208710 ± 33
Carbon dioxide	0.885 ± 0.019	0.890 ± 0.019
Argon	9662 ± 4	9678 ± 4

References

1. International Organization for Standardization, ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures, 1st edition.
2. G. C. Rhoderick, D. R. Kitzi, M. E. Kelley, W. R. Miller, B. D. Hall, E. J. Dlugokencky, P. P. Tans, A. Possolo, and J. Carney, “Development of a Northern Continental Air Standard Reference Material”, *Anal Chem*, 88(6), 3376–3385, 2016, doi:10.1021/acs.analchem.6b00123.
3. International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition.
4. M. J. T. Milton, P. M. Harris, I. M. Smith, A. S. Brown, and B. A. Goody, “Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures”, *Metrologia*, 4(4), S291–S298, 2006.

Measurement report

Institute	NMISA
Section	Gas Analysis
Project	CCQM-K68.2019
Date	09 December 2020

Participant Report Form

CCQM-K683.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

Participant information (for the comparison report)

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*Table 1: Final reported results of measurements (second submission)

Cylinder number	Nominal mole fraction / $\mu\text{mol mol}^{-1}$	N ₂ O mole fraction $x(\text{N}_2\text{O})/\mu\text{mol mol}^{-1}$	Expanded uncertainty (combined) $U(x(\text{N}_2\text{O}))/\mu\text{mol mol}^{-1}$	Coverage Factor
D732200	0.330 – 0.335	0.33149	0.00022	2
D67 9627	0.340 – 0.345	0.34238	0.00048	2

**Considering the second verification after the mixtures were delivered back from BIPM. No changes were made to the first submitted values.*

***Table 2:** Uncertainty budget for the two final mixtures ($\mu\text{mol/mol}$) with final uncertainty taking into account the second verification

Cylinder/Serial Number	First verification uncertainty ($\mu\text{mol/mol}$), U_{ver}	Second verification uncertainty ($\mu\text{mol/mol}$), U_{ver}	Combined uncertainty ($\mu\text{mol/mol}$), U_{comb}	Coverage Factor
D73 2200	0.0002236	0.0000050	0.00022	$k=2$
D67 9627	0.0004837	0.0000210	0.00048	$k=2$

The measurement uncertainty of the second verification did not have a significant change to the initial submitted results. No changes were made to the initially submitted values.

Uncertainty Budget

The results for each day yielded an average mole fraction and a standard deviation through the use of Cavity Ring-Down Spectroscopy (CRDS). The average mole fraction and ESDM were obtained by the method of multi-point calibration at 0.331, 0.334 and 0.340 $\mu\text{mol/mol}$. The mole fractions obtained for the samples from analysis during a three-day period were averaged, and a standard deviation calculated for the three values. The uncertainties for the three different days and the verification uncertainty (ESDM) were combined as shown in Equation 1 and 2.

$$u_c^2 = \frac{u_{Day1}^2 + u_{Day2}^2 + u_{Day3}^2}{3} \dots + (u_{ESDM})^2 + u_{grv}^2 + u_{stability}^2 \dots \text{Equation 1 (first submission)}$$

$$u_c^2 = \frac{u_{Day1}^2 + u_{Day2}^2 + u_{Day3}^2 + u_{Day4}^2}{4} \dots + (u_{ESDM})^2 + u_{first\ submission}^2 \dots \text{Equation 2 second submission)}$$

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor $k = 2$ as shown in Equation 2.

$$U = k \times u_c, \text{ where } k = 2 \dots \text{Equation 3}$$

The combined uncertainty budget of the nitrous oxide mole fraction in the final mixtures was calculated using the equation 1, 2 and 3.

Table 3: Uncertainty budget for the two final mixtures ($\mu\text{mol/mol}$) (first submission with corrections to gravimetric uncertainty and verification uncertainty)

Cylinder/Serial Number	Gravimetric uncertainty ($\mu\text{mol/mol}$), U_{grav}	Verification uncertainty ($\mu\text{mol/mol}$), U_{ver}	Stability uncertainty ($\mu\text{mol/mol}$), U_{stab}	Combined uncertainty ($\mu\text{mol/mol}$), U_{comb}	Coverage Factor
D73 2200	0.00008350 [#]	0.00018001	0.000103056	0.00022	$k=2$
D67 9627	0.00008556 [#]	0.000464783	0.000103056	0.00048	$k=2$

[#] The uncertainties in Table 3 are the corrected uncertainty from the previously submitted report.

Measurement procedure

The Cavity Ring-down Spectrometer - G5310 was used to measure N_2O in the standard gas mixtures prepared. The G5310 can measure N_2O , carbon monoxide (CO) and moisture (H_2O) simultaneously. It was calibrated at three points; 0.33072, 0.33380 and 0.34024 $\mu\text{mol/mol}$, using standard gas mixtures (synthetic air balance) prepared at NMISA. Configuration of analysis system is gas cylinder >> regulator >> MFC >> CRDS >> results.

Table 4: The analytical conditions of the verification of nitrous oxide in synthetic air using Cavity Ring Down Spectroscopy (CRDS).

Parameter	Setting
Laser Baseplate temperature	27 °C
Cavity temperature	40 °C
Cavity pressure	100 Torr
MFC	150 ml/min

Additional information

Purity analysis

The purity table of source materials or parent gases nitrogen (N_2), oxygen (O_2), methane (CH_4), carbon dioxide (CO_2), argon (Ar) and nitrous oxide (N_2O) are shown in table 2 to 7. The

N₂, O₂, CH₄, CO₂ and Ar were purchased from Air Products South Africa and N₂O was purchased from Air Liquide South Africa.

Table 5: Purity table with uncertainties for the high pure nitrogen BIP™ (N₂) source gas.

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
Ar	165.720	Normal	165.720	0.540	1.08
C ₂ H ₆	0,12*	Type B rectangular	0.060	0.035	0.07
CH ₄	0.288*	Type B rectangular	0.144	0.083	0.166
CO	0.49*	Type B rectangular	0.245	0.141	0.282
CO ₂	0.0348*	Type B rectangular	0.017	0.010	0.02
H ₂	<1#	Type B rectangular	0.500	0.289	0.578
H ₂ O	<0.02#	Type B rectangular	0.010	0.006	0.012
O ₂	52.660	Normal	52.660	0.200	0.40
N ₂ O	<0.000424*	Type B rectangular	0.000212	0.000122	0.00024
N ₂		μmol/mol	999780.644	0.666	1.332
		% mol/mol	99.9779644	0.000069	0.000138

* limit of detection

manufacturer specification

Table 6: Purity table with uncertainties for the high pure oxygen source gas

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
Ar	<5#	Type B rectangular	2.500	1.440	2.88
C ₂ H ₆	0.120*	Type B rectangular	0.060	0.035	0.07
CH ₄	0.288*	Type B rectangular	0.144	0.083	0.166
CO	0.49*	Type B rectangular	0.245	0.141	0.282
CO ₂	1.331	Normal	1.331	0.032	0.064
H ₂ O	<2#	Type B rectangular	1.000	0.577	1.154
N ₂	411.200	Normal	411.200	3.000	6.0
H ₂	30.700	Normal	30.700	0.320	0.64
N ₂ O	<0.424*	Type B rectangular	0.000212	0.000122	0.00024
		Total impurities	447.18		
O ₂		μmol/mol	999552.820	3.397	6.793
		% mol/mol	99.955282	0.0003397	0.0006793

* limit of detection

manufacturer specification

Table 7: Purity table with uncertainties for the high pure methane source gas

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
Ar	0.26	Normal	0.26	0.15	0.3
C ₂ H ₆	0.13*	Type B rectangular	0.065	0.037	0.074
CO ₂	0.108*	Type B rectangular	0.054	0.031	0.062
H ₂	0.725*	Normal	0.725	0.079	0.158
H ₂ O	<5.0#	Type B rectangular	2.5	1.4	2.8
N ₂	3.114	Normal	3.114	0.025	0.05
O ₂	0.109	Normal	0.109	0.063	0.126
N ₂ O	<0.424*	Type B rectangular	0.000212	0.000122	0.00024
CH ₄		μmol/mol	999993.173	1.41268	2.82536
		% mol/mol	99.9993173	0.000141	0.000283

* limit of detection

manufacturer specification

Table 8: Purity table with uncertainties for the high pure carbon dioxide source gas

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
Ar	0.2200	Normal	0.2200	0.0110	0.022
C ₂ H ₆	0.012*	Type B rectangular	0.0060	0.0035	0.007
CH ₄	4.2700	Normal	4.2700	0.6400	1.28
CO	0.0448*	Type B rectangular	0.0224	0.0130	0.026
H ₂	0.08*	Type B rectangular	0.0400	0.0020	0.004
H ₂ O	<0.052#	Type B rectangular	0.0260	0.0150	0.03
N ₂	823.0000	Normal	823.0000	41.2000	82.4
N ₂ O	<0.424*	Type B rectangular	0.000212	0.000122	0.00024
CO ₂		μmol/mol	999172.415	41.205	82.41
		% mol/mol	99.917415	0.00041205	0.008241

* limit of detection

manufacturer specification

Table 9: Purity table with uncertainties for the high pure argon source gas

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
CH ₄	0.288*	Type B rectangular	0.1440	0.0832	0.1664
CO	0.49*	Type B rectangular	0.2450	0.1410	0.282
CO ₂	0.0348*	Type B rectangular	0.0174	0.0100	0.02
O ₂	0.01 [#]	Type B rectangular	0.0050	0.0029	0.0058
H ₂ O	0.02 [#]	Type B rectangular	0.0100	0.0058	0.0116
N ₂	1 [#]	Type B rectangular	0.5000	0.2890	0.578
H ₂	40.7100	Normal	40.7100	0.4400	0.88
C ₂ H ₆	0.12*	Type B rectangular	0.0600	0.0346	0.0692
N ₂ O	<0.424*	Type B rectangular	0.000212	0.000122	0.00024
Ar		μmol/mol	999958.3086	0.553	1.105
		% mol/mol	99.99583086	0.0000553	0.0001105

* limit of detection

[#] manufacturer specification

Table 10: Purity table with uncertainties for the high pure nitrous oxide source gas

Component	Analysis mole fraction (μmol/mol)	Distribution	Mole fraction (μmol/mol)	Standard Uncertainty (μmol/mol) (k = 1)	Standard Uncertainty (μmol/mol) (k = 2)
Ar	<0.5 [#]	Type B rectangular	0.250	0.144	0.288
NH ₃	<5 [#]	Type B rectangular	2.500	1.440	2.88
CH ₄	<0.1 [#]	Type B rectangular	0.050	0.029	0.058
CO	<1 [#]	Type B rectangular	0.500	0.289	0.578
CO ₂	<1 [#]	Type B rectangular	0.500	0.289	0.578
NO ₂	<1 [#]	Type B rectangular	0.500	0.289	0.578
NO	26.240	Normal	26.240	0.105	0.21
H ₂ O	<1 [#]	Type B rectangular	0.500	0.289	0.578
N ₂	<5 [#]	Type B rectangular	2.500	1.440	2.88
O ₂	<5 [#]	Type B rectangular	0.250	0.144	0.288
		Total impurities	33.79		
N ₂ O		μmol/mol	999966.210	2.130	4.26
		% mol/mol	99.9966210	0.000213	0.000426

[#] manufacturer specification

Production diagram

A five-step dilution process was undertaken to prepare the mixtures, with intermediate nitrous oxide mole fractions of 13000 $\mu\text{mol/mol}$, 1000 $\mu\text{mol/mol}$, 300 $\mu\text{mol/mol}$, and 9 $\mu\text{mol/mol}$ and then 0.330 – 0.345 $\mu\text{mol/mol}$. Oxygen, argon, carbon dioxide and methane were added in the last dilution step. **Figure 1** shows a schematic diagram of the dilution process.

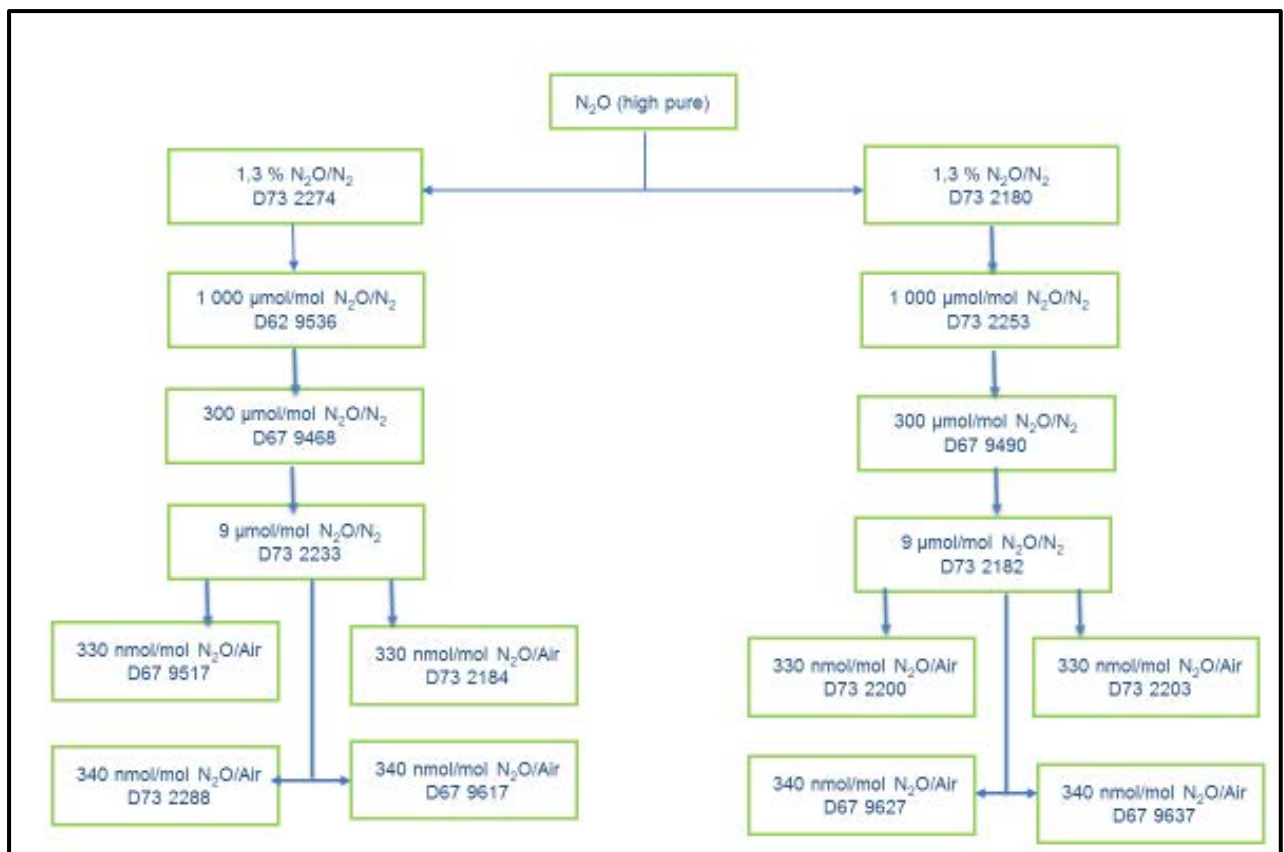


Figure 1: A five-step dilution for preparation of N_2O in artificial air

The purity tables for the mole fractions and uncertainties of nitrous oxide in air are shown in table 8 to 9 which were generated using GravCal software developed by NPL.

Table 11: Purity table with uncertainties for the N₂O (cylinder number: D73 2200)

OUTPUTS =====			
Component	μmol/mol	uncertainty	% u/c
N2	780971.8942	4.96122373	0.001
O2	209301.9587	4.70665215	0.002
Ar	9616.858771	1.28939056	0.013
CO2	191.8147572	0.01598093	0.008
H2	7.20112247	0.20058123	2.785
CH4	1.04277877	0.05718261	5.484
N2O	0.33148814	0.00004175	0.013
CO	0.24372668	0.09711448	39.846
H2O	0.21717509	0.12087665	55.659
C2H6	0.06001107	0.02381573	39.686
NO	0.00000870	0.00000003	0.400
NH3	0.00000083	0.00000048	57.583
NO2	0.00000017	0.00000010	57.813
INPUTS =====			
File	Mass (g)	u/c (g)	
GRAVCAL2018\NMIS	54.08500	0.00200	
GRAVCAL2018\NMIS	57.46800	0.00200	
BIPAr328877.txt	16.17600	0.00200	
O2UHP334129.txt	285.9070	0.00200	
BIPN214652888.tx	778.5530	0.00200	
GRAVCAL2018\NMIS	44.20800	0.00200	

Table 12: Purity table with uncertainties for the N₂O (cylinder number D67 9627)

OUTPUTS =====			
Component	μmol/mol	uncertainty	% u/c
N2	780777.5602	4.94344980	0.001
O2	209366.925	4.69317483	0.002
Ar	9748.63001	1.25265444	0.013
CO2	189.4346653	0.01579316	0.008
H2	7.20838569	0.20054182	2.782
CH4	1.02994356	0.05717057	5.551
N2O	0.34238039	0.00004278	0.012
CO	0.24374016	0.09709406	39.835
H2O	0.21723935	0.12091411	55.659
C2H6	0.06001089	0.02381071	39.677
NO	0.00000898	0.00000004	0.400
NH3	0.00000086	0.00000049	57.583
NO2	0.00000017	0.00000010	57.813
INPUTS =====			
File	Mass (g)	u/c (g)	
GRAVCAL2018\NMIS	47.36800	0.00200	
GRAVCAL2018\NMIS	55.30600	0.00200	
GRAVCAL2018\NMIS	58.87600	0.00200	
BIPAr328877.txt	17.01400	0.00200	
O2UHP334129.txt	296.6900	0.00200	
BIPN214652888.tx	807.4550	0.00200	

Analysis

The samples were verified against NMISA Primary Standard Gas Mixtures (PSGMs) of the same matrix that were prepared gravimetrically according to ISO 6142 (*Gas Analysis – Preparation of calibration gas mixtures*)

- The second verification was performed between October and December 2020 after the mixtures were received back from BIPM.

- The measurement uncertainty of the second verification did not have a significant change to the initial submitted results. No changes were made to the initially submitted values.

Provisional Report for CCQM K68.2019

NOAA Global Monitoring Division

Brad Hall

March 25, 2020

updated November 23, 2020

Results of measurements

Results are reported on the WMO-N₂O-X2006A scale.

	mole fraction (nmol mol ⁻¹)	uncertainty, k=2, (nmol mol ⁻¹)
FF57617	326.81	0.61
FF57625	342.87	0.59

Uncertainty budget

The WMO-N₂O-X2006A is defined using 13 gravimetrically-prepared standards in 5.9-L aluminum cylinders. These were prepared from four parent mixtures, ~1500-2400 μmol mol⁻¹. Typical uncertainty components for the parent mixtures (Level 1) and daughter standards (Level 2) are shown below.

Level 1 (~1500 μmol mol⁻¹)

component	Value	Standard uncertainty	Distribution
reagent purity	1.0	0.00023	rectangular
MW major component	44.013 g/mol	0.0006 g/mol	rectangular
MW dilution gas	28.9603 g/mol	0.0048 g/mol	rectangular
Mass of major component	2.0694 g	0.0038 g	normal
Mass of dilution gas	835.6342 g	0.0037 g	normal
purity of dilution gas	negligible		

Relative uncertainty at Level 1 = 0.1%

Level 2 (~330 nmol mol⁻¹)

component	Value	Standard uncertainty	Distribution
Mole fraction parent	1500 μmol mol ⁻¹	0.1%	normal
Mass of major component	0.1801 g	0.00006 g	normal
Mass of CO ₂	0.436	0.001	Normal
Mass of dilution gas	789.178 g	0.007 g	normal
purity of dilution gas	0.0 ppb N ₂ O	0.20	triangular

Relative uncertainty at Level 2 = 0.12%

The contribution from N₂O in the dilution gas is estimated from measurements of dilution gas performed in 2006. While some samples of dilution gas contained ~ 0.5 ppb N₂O, not all cylinders of dilution gas contained a measurable amount of N₂O. Therefore, we did not correct for N₂O in the dilution gas in 2006. We estimate this contribution to uncertainty using 0.5 ppb and a triangular distribution. For the first K68 comparison, we did not consider the distribution and used 0.5 ppb, so our uncertainties estimated for K68.2019 are lower than those for K68.

The X2006A scale is defined by 13 primary standards over the range 260 to 370 nmol mol⁻¹ (ppb). These standards were used to define a 2nd order polynomial response function on an GC-ECD instrument and value assign secondary standards over the range 270-360 ppb. Fresh 2nd order polynomial response functions are determined from secondary standards approximately once a month. The two K68.2019 samples were analyzed on this same instrument and value-assigned using the most recent response function.

We estimate standard uncertainties associated with value-assignment in the 320-350 ppb range below. Analysis of K68.2019 was performed in July 2019 and again in November 2020. Measurements in July 2019 and November 2020 were consistent (no drift). For reasons unknown, instrument repeatability was higher than normal during the measurement of FF57617, and was observed during both 2019 and 2020 measurement periods. An additional uncertainty component was included to account for the additional variability.

	FF57617	FF57625
Scale uncertainty (13 primary standards)	0.26 ppb	0.27 ppb
Scale transfer	0.11 ppb	0.12 ppb
Excess repeatability	0.12 ppb	0
Total (k=1)	0.307 ppb	0.295 ppb

Measurement procedure

N₂O analysis is performed by gas chromatography with electron capture detection. We use an Agilent 6890 GC with an anode-purged ECD (model G1533A). A 9-ml sample of air is injected onto a 3/16" x 1-m Porapak Q pre-column held at 90 deg C. The O₂/N₂ peak is vented and not allowed to reach the ECD. Then the valve is switched and the N₂O/SF₆ peaks are transferred to a 3/16" x 2-m Porapak Q main column (90 °C) and then to a 1/8" x 1-m molecular sieve 5A column (185 °C). Upon the valve switch, unwanted compounds are "backflushed" off the pre-column.

CO₂-doped nitrogen is used as the carrier gas. The CO₂ is added following the molecular sieve 5A column upstream of the ECD. Pure CO₂ is added at a flowrate of approx. 0.1 cc/min. The carrier gas flowrate is 35 cc/min and the ECD temperature is 370 °C. N₂O elutes at ~400 seconds. The run time is 12 minutes.

Five secondary standards consisting of modified whole air in aluminum cylinders, are used to define the response curve (2nd order polynomial). Stability of the response curve and analytical system is monitored by analyzing check standards (we call them target tanks) every few weeks. Reproducibility, as determined from the target tank analysis, is 0.20-0.24 ppb (k=2).

Additional information

Purity Table for the N₂O reagent (manufacturer's specification 99.9+%)

Component	Amount Fraction	Estimated Uncertainty	method
N ₂ O	99.96%	0.02%	residual
CO ₂	0.03%	0.01%	NDIR
H ₂ O	0.002%	0.001%	NDIR
NO	Not detected		GCMS
Non-condensable gases (CO, CH ₄ , N ₂ , etc)	0.01%	0.005%	cryogenic separation, ΔP

Purity Table for dilution gas, synthetic air O₂/N₂

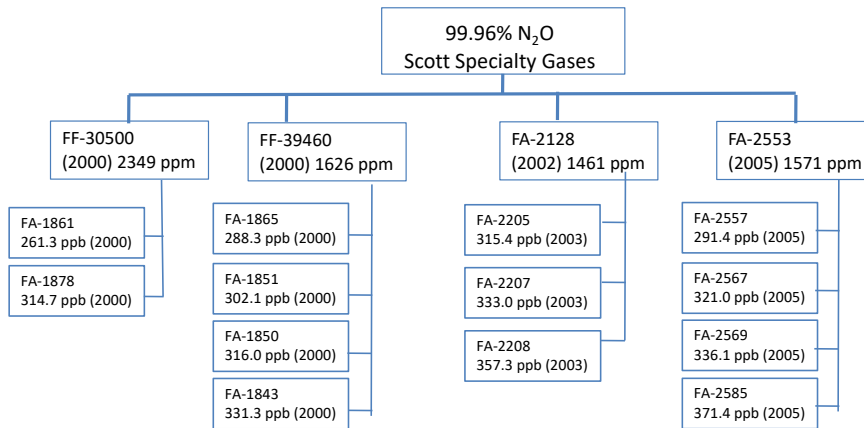
Component	Amount Fraction	Estimated Uncertainty	method
N ₂	78.93%	0.01%	residual
O ₂	21.07 % (typical)	0.01%	paramagnetic
Ar	0		assumption
H ₂ O	< 2 ppm	1 ppm	electrolytic method
CO ₂	not measured		
N ₂ O	< LD to 0.5 ppb *	0.2 ppb	GC-ECD
SF ₆	< 0.04 ppt	0.02 ppt	GC-ECD

* N₂O level of detection (LD) in 2006 was ~ 0.1 ppb

Samples provided for K68.2019

We provided samples consisting of whole air in 5.9-L aluminum cylinders (Airgas, USA). Cylinders were first evacuated (~30 mtorr) and flushed with zero-grade air. Each cylinder was then filled with a mixture of N₂O-free air, aliquots of N₂O, and whole air collected at various times to reach target N₂O values (320-325 ppb; 340-345 ppb) as designated. The whole air was collected at our site in the Colorado mountains using a Rix SA-6 oil-free compressor.

Standards used to define the X2006A scale



CCQM-K68 Measurement report

Authors	Eric B. Mussell Webber, Ruth E. Hill-Pearce, Sivan Van Aswegen, David R. Worton, Paul J. Brewer
Institute	National Physical Laboratory
Address	Hampton Road, Teddington, United Kindom, TW11 0LW

	Standard 1	Standard 2
Nominal amount fraction	326.7 nmol/mol	337.9 nmol/mol
Date of preparation	15/08/2019	04/09/2019
Serial number	2731	2864
Pressure	120 bar	120 bar
Volume	10 Litre	10 Litre
Connection type	BS341 No. 14	BS341 No. 14

Results

Cylinder	Nominal amount fraction / nmol mol⁻¹	N₂O amount fraction $x(\text{N}_2\text{O})$ / nmol mol⁻¹	Expanded uncertainty $U(x(\text{N}_2\text{O}))$ / nmol mol⁻¹	Coverage factor
2731	326.7	326.5	1.1	2
2864	337.9	337.7	1.1	2

Standards preparation

Two NPL Primary reference materials (PRMs) (2731 and 2864) were prepared by dilution from 500 $\mu\text{mol mol}^{-1}$ parent mixtures S305R2 and 2730, respectively, in accordance with ISO 6142-1.¹ A transfer vessel was used for all pure nitrous oxide (Air Liquide) additions and additions from the 500 $\mu\text{mol mol}^{-1}$ parent mixtures, whereas the matrix gas components were added directly through purged 1/16 inch tubing. Argon (Air Products, BIP) was added from a nominally 30 % in nitrogen parent while oxygen (BOC, N6.0), and nitrogen (Air Products, BIP+) were added directly to the PRMs, targeting the ratio of clean atmospheric air. All atmospheric amount fraction and parent mixtures were prepared in 10 L cylinders (Luxfer, Aluminium) with SPECTRA-SEAL passivation (BOC), that had been evacuated to $< 5 \times 10^{-7}$ mBar prior to use. The preparation hierarchy is shown in figure 1, with the purity tables for the two key comparison mixtures shown in tables 1 and 2.

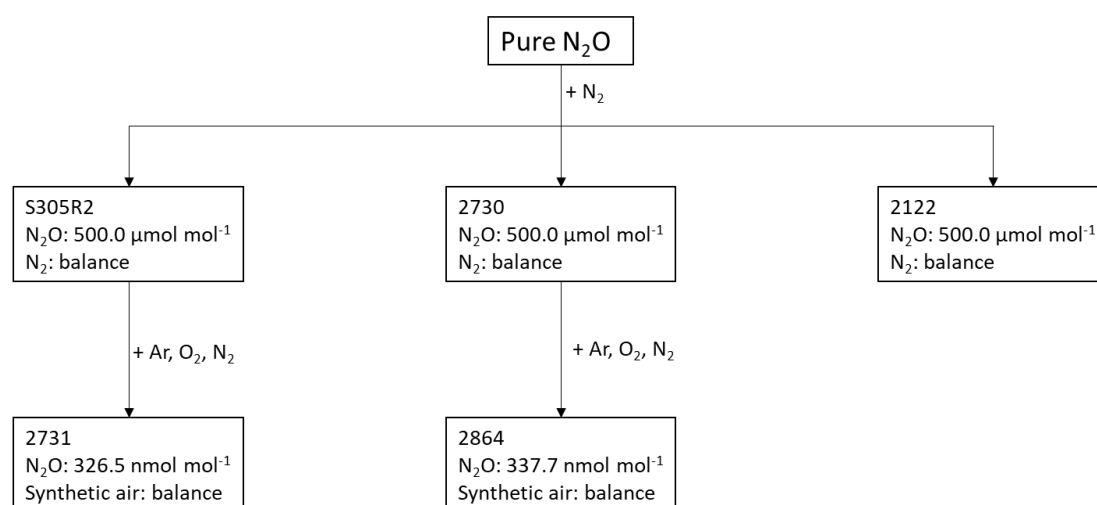


Figure 1 Preparation hierarchy for the key comparison PRMs, 2731 and 2864.

Table 1 Purity of NPL PRM 2731, showing amount fractions and expanded uncertainties (gravimetric).

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
N ₂	781152	10
O ₂	209448	10
Ar	9400.0	3.5
N ₂ O	0.32653	0.0005
CH ₄	0.007	0.005
C _x H _y	0.004	0.004
H ₂ O	0.004	0.002
H ₂	0.0008	0.0008
CO	0.0007	0.0001
CO ₂	0.0005	0.0009
NO	0.0004	0.0002
SO ₂	0.0004	0.0002

Table 2 Purity of NPL PRM 2864, showing amount fractions and expanded uncertainties (gravimetric).

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
N ₂	781212	10
O ₂	209383	10
Ar	9405.1	3.5
N ₂ O	0.3377	0.0005
CH ₄	0.007	0.005
C _x H _y	0.004	0.004
H ₂ O	0.004	0.002
H ₂	0.0008	0.0008
CO	0.0007	0.0001
CO ₂	0.0005	0.0009
NO	0.0004	0.0002
SO ₂	0.0004	0.0002

Validation standards

Four NPL inhouse PRMs were used to validate the amount fraction of 2731 and 2864. Three validation standards were prepared in 2019 for the purposes of CCQM-K68, and one historical standard was used.

Table 3 Information on standards used for the validation of the amount fraction of key comparison standards.

NPL in house PRM	Amount fraction / nmol mol ⁻¹	Date prepared	Parent cylinder	Key comparison standards validated
2171	324.5	18/01/2017	2122	2731, 2864
2721	326.3	23/07/2019	2122	2731
2725	326.5	13/08/2019	2730	2731, 2864
2782	337.3	23/07/2019	2122	2864

Validation method

A Picarro G5131-i cavity ring-down spectrometer was used to validate the amount fraction of N₂O in key comparison standards by comparison of the analytical response with the validation standards. Samples were introduced into the analyser at atmospheric pressure (excess flow of 0.5 L min⁻¹ was passed to vent) using two stage gas regulators. A synthetic air reference material was prepared separately following the same preparation procedures as for the PRMs, from the same pure matrix gas components. The analytical response to the synthetic air (v_z) was recorded at the start and end of the measurement sequence to account for analyser drift. Each standard was sampled for ten minutes, with the averaged analyser response to the last 100 data points (~6 mins) recorded. The sequence was repeated four times.

For each measurement sequence, a ratio of the analyser response to a key comparison standard (v_u) and validation standard (v_s) (both were corrected for the averaged analyser response to the synthetic air) was calculated. Analytically determined amount fractions of the key comparison standards (x_u) were calculated by multiplying the average ratio (\bar{r}) of the four repeat sequences, with the gravimetric amount fraction of the validation standard (x_s). These analytically determined amount fractions were used to validate the submitted gravimetric amount fractions of 2731 and 2864.

$$r = \left(\frac{v_u - v_z}{v_s - v_z} \right)$$

$$x_u = x_s \bar{r}$$

Uncertainty evaluation

Analytical uncertainty

Following the measurement equation above, the combined uncertainty $u(x_u)$ for a single validation measurement was calculated from:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{x_s^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$

The standard uncertainty $u(x_s)$ comes from the gravimetric preparation of the validation standard and the standard uncertainty $u(\bar{r})$ is the standard deviation of the four ratio measurements. Sensitivity coefficients are calculated by taking the partial derivative with respect to each measurement input. Table 4 shows an example uncertainty budget for one validation of NPL PRM 2731.

Table 4 Example uncertainty budget for a single validation measurement of the NPL PRM 2731 with in house NPL PRM 2721.

	unit	value	standard u/c	Sensitivity coefficient	u/c contribution	u/c type	distribution
x_s	nmol/mol	326.33	0.47447	1.0006	0.159448	A	normal
\bar{r}	-	1.0006	0.00016	326.33	0.053574	A	normal
x_u	nmol/mol	326.53					
$u(x_u)$	nmol/mol	0.4778					
$U(x_u)$	nmol/mol	0.9555					

All the measurements are combined by taking a weighted average, according to the uncertainty in each measurement, to give x_a . Sensitivity coefficients are given to provide equal input from each measurement, giving the analytical uncertainty for the final measurement $u(x_a)$.

Table 5 Example uncertainty budget combining the results of three validation measurements of NPL PRM 2731.

	unit	value	standard u/c	Sensitivity coefficient	u/c contribution	u/c type	distribution
x_1	nmol/mol	326.53	0.48	0.333	0.159	A	normal
x_2	nmol/mol	326.25	0.22	0.333	0.073	A	normal
x_3	nmol/mol	326.40	0.47	0.333	0.156	A	normal
x_a	nmol/mol	326.35					
$u(x_a)$	nmol/mol	0.23					
$U(x_a)$	nmol/mol	0.47					

Gravimetric uncertainty

Standard addition analysis was performed to measure the amount fraction of residual N₂O in the matrix gas. A 325 nmol mol⁻¹ NPL PRM was diluted dynamically using an ‘adjustable gas standard’² that produces dilutions between 1:350 and 1:2000. The in-house reference standard was diluted in the matrix gas used in the preparation of the NPL PRMs 2731 and 2864. A calibration line is produced by plotting the corrected analytical response of the CRDS against the amount fractions calculated from the seven distinct dilution ratios. The amount fraction of residual N₂O is the point at which the analyser reading equals zero. This was calculated as 0.37 (± 0.09) nmol mol⁻¹.

Combined uncertainty

The combined uncertainty (analytical plus gravimetric), $u(x)$, is calculated by summing in quadrature the analytical, $u(x_a)$, and gravimetric, $u(x_g)$, uncertainties:

$$u(x) = \sqrt{u(x_g)^2 + u(x_a)^2}$$

Table 6 Example uncertainty budget showing the final combined uncertainty for the NPL PRM 2731.

	unit	value
$u(x_a)$	nmol/mol	0.234
$u(x_g)$	nmol/mol	0.474
x	nmol/mol	326.532
$u(x)$	nmol/mol	0.529
$U(x) (k = 2)$	nmol/mol	1.057

Purity tables for nominally pure gases

Table 7 Purity of nitrous oxide (N₂O), showing amount fractions and expanded uncertainties.

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
N ₂ O	999999.940	0.016
N ₂	0.025	0.014
NO ₂	0.0050	0.0029
CO ₂	0.0050	0.0029
CH ₄	0.00050	0.00029
H ₂ O	0.0050	0.0029
NH ₃	0.0050	0.0029
CO	0.0050	0.0029
NO	0.0050	0.0029
O ₂	0.0025	0.0014
Ar	0.0020	0.0014

Table 8 Purity of argon, showing amount fractions and expanded uncertainties.

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
Ar	999999.77	5
CO ₂	0.05	0.1
C _x H _y	0.05	0.1
H ₂ O	0.02	0.1
N ₂	0.1	0.1
O ₂	0.01	0.1

Table 9 Purity of oxygen, showing amount fractions and expanded uncertainties.

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
O ₂	999999.888	0.09
N ₂	0.08	0.05
CO	0.002	0.00005
CH ₄	0.03	0.02

Table 10 Purity of nitrogen, showing amount fractions and expanded uncertainties.

Component	Amount Fraction ($\mu\text{mol mol}^{-1}$)	Expanded Uncertainty ($\mu\text{mol mol}^{-1}$)
N ₂	999999.4812	0.9
Ar	0.5	0.05

CO	0.0003	0.0002
O ₂	0.005	0.003
C _x H _y	0.005	0.005
H ₂ O	0.005	0.002
NO	0.0005	0.0003
SO ₂	0.0005	0.0003
CH ₄	0.001	0.001
H ₂	0.001	0.001
N ₂ O	0.0005	0.0004

References

1. BSI Standards Publication Gas analysis — Preparation of calibration gas mixtures Part 1 : Gravimetric method for Class I mixtures. (2015).
2. Hill-Pearce, R. E., Resner, K. V, Worton, D. R. & Brewer, P. J. Synthetic Zero Air Reference Material for High Accuracy Greenhouse Gas Measurements. *Anal. Chem.* **91**, 1974–1979 (2019).

Participant Report Form CCQM–K68.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

- This form should be completed by participants in the key comparison CCQM-K168.2019 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.
- Comparison coordinator: Dr Joële Viallon
 Chemistry Department
 Bureau International des Poids et Mesures
 Pavillon de Breteuil
 F-92312 SEVRES CEDEX
 Tel: +33 1 45 07 62 70
 Email: jviallon@bipm.org

Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information (for the comparison report)

Author(s)	L. Konopelko, Y. Kustikov, A. Kolobova, A. Klimov, O. Efremova	
Institute	D.I. Mendeleev Institute for Metrology (VNIIM)	
Address	19 Moskovsky pr., St. Petersburg, 190005, Russia	
Information on standards sent to the BIPM		
	Standard 1	Standard 2
Nominal N₂O mole fraction	0,332 μmol/mol	0,342 μmol/mol
Date of preparation	16.09.2019	18.09.2019
Serial number	D648613	D648616
Pressure (before shipment)	10.6 MPa	10.4 MPa
Volume	5 L	5 L
Connection type	DIN 6	DIN 6

1 Results of measurements

Please indicate below the final value and associated expanded uncertainty of the N₂O mole fraction in each of the two standards.

Table1

Nominal mole fraction, / $\mu\text{mol mol}^{-1}$	N ₂ O mole fraction $x(\text{N}_2\text{O}) / \mu\text{mol mol}^{-1}$	Expanded uncertainty $U(x(\text{N}_2\text{O})) / \mu\text{mol mol}^{-1}$	Coverage factor
330-335	0.3324	0.0032	2
340-345	0.3425	0.0030	2

2 Uncertainty budgets

Table 2: Uncertainty budget for N₂O mole fraction for the cylinder D648613

Uncertainty source X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ $\mu\text{mol/mol}$	
Purity of N ₂	999998.67 $\mu\text{mol/mol}$	B	Rectangular	0.029 $\mu\text{mol/mol}$	0.00000007	$2.0 \cdot 10^{-9}$	
Purity of O ₂	999999.57 $\mu\text{mol/mol}$	B	Rectangular	0.007 $\mu\text{mol/mol}$	$2.9 \cdot 10^{-8}$	$2.0 \cdot 10^{-10}$	
Purity of Ar	999999.66 $\mu\text{mol/mol}$	B	Rectangular	0.063 $\mu\text{mol/mol}$	$2.9 \cdot 10^{-9}$	$1.8 \cdot 10^{-10}$	
Purity of N ₂ O	997958.98 $\mu\text{mol/mol}$	B	Rectangular	20 $\mu\text{mol/mol}$	0,00000021	$4.2 \cdot 10^{-6}$	
Weighing 1 stage premixture (1,22 %)	N ₂ O	11.465366 g	B	Normal	0.002041 g	-0.028444	-0.00005805
	N ₂	594.487315 g	B	Normal	0.010884 g	0.000549	0.00000597
Weighing 2 stage premixture (223,6 $\mu\text{mol/mol}^{-1}$)	1 pre-mixture	11.061284 g	B	Normal	0.002040 g	-0.029494	-0.00006016
	N ₂	585.016301 g	B	Normal	0.01187770 g	0.000558	0.00000662
Weighing 3 stage premixture (8,2 $\mu\text{mol/mol}^{-1}$)	2 pre-mixture	21.74379819 g	B	Normal	0.00214910 g	-0.014724	-0.00003164
	N ₂	568.344603 g	B	Normal	0.01102593 g	0.000563	0.00000621
Weighing final mixture	3 pre-mixture	28.46359971 g	B	Normal	0.00206035 g	-0.011207	-0.0000231
	N ₂	521.55333328 g	B	Normal	0.00999721 g	0.000472	0.00000472
	O ₂	168.59009907 g	B	Normal	0.00386608 g	0.000413	0.00000160
	Ar	9.41502069 g	B	Normal	0.00205621 g	0.000331	0.000000681
Verification	0.3324 $\mu\text{mol/mol}$	A	Normal	0.0016 $\mu\text{mol/mol}$	1	0.0016	
Combined standard uncertainty, $\mu\text{mol/mol}$						0.0016	
Expanded uncertainty $k=2$, $\mu\text{mol/mol}$						0.0032	
Relative expanded uncertainty, %						0.96	

Table 3:Uncertainty budget for N₂O mole fraction for the cylinder D648616

Uncertainty source X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ $\mu\text{mol/mol}$	
Purity of N ₂	999998.67 $\mu\text{mol/mol}$	B	Rectangular	0.029 $\mu\text{mol/mol}$	0.00000007	$2.0 \cdot 10^{-9}$	
Purity of O ₂	999999.57 $\mu\text{mol/mol}$	B	Rectangular	0.008 $\mu\text{mol/mol}$	$2.9 \cdot 10^{-8}$	$2.0 \cdot 10^{-10}$	
Purity of Ar	999999.66 $\mu\text{mol/mol}$	B	Rectangular	0.063 $\mu\text{mol/mol}$	$2.9 \cdot 10^{-9}$	$1.8 \cdot 10^{-10}$	
Purity of N ₂ O	997958.98 $\mu\text{mol/mol}$	B	Rectangular	20 $\mu\text{mol/mol}$	0,00000022	$4.4 \cdot 10^{-6}$	
Weighing 1 stage premixture (1,22 %)	N ₂ O	11.465366 g	B	Normal	0.002041 g	-0.029304	-0.00005981
	N ₂	594.487313 g	B	Normal	0.010884 g	0.000565	0.00000615
Weighing 2 stage premixture (223,6 $\mu\text{mol/mol}^{-1}$)	1 pre- mixture	11.061284 g	B	Normal	0.002040 g	-0.03039	-0.00006198
	N ₂	585.016301 g	B	Normal	0.01187770 g	0.000575	0.00000682
Weighing 3 stage premixture (8,2 $\mu\text{mol/mol}^{-1}$)	2 pre- mixture	21.74379819 g	B	Normal	0.00214910 g	-0.015170	-0.00003260
	N ₂	568.344603 g	B	Normal	0.01102593 g	0.000580	0.00000640
Weighing final mixture	3 pre- mixture	29.25166730 g	B	Normal	0.00209993 g	-0.011220	-0.00002356
	N ₂	519.51111476 g	B	Normal	0.00995034 g	0.000488	0.00000485
	O ₂	168.01491674 g	B	Normal	0.00388794 g	0.000427	0.00000166
	Ar	9.40522888 g	B	Normal	0.00206891 g	0.000342	0.000000707
Verification	0.3425 $\mu\text{mol/mol}$	A	Normal	0.0014 $\mu\text{mol/mol}$	1	0.0015	
Combined standard uncertainty, $\mu\text{mol/mol}$						0.0015	
Expanded uncertainty k=2, $\mu\text{mol/mol}$						0.0030	
Relative expanded uncertainty, %						0.88	

3 Measurement procedure

The principal verification measurements were carried out by Gas chromatography with ECD;
Instrument: Gas Chromatograph ««Chromatec-crystal 5000.2»» with micro ECD (Russia);
Column: ValcoPlot VP-Molesieve, 5Å, 30 m x 0,53 mm; film - 50 μm
Carrier gas: helium 55, flow rate 4 ml/min, Split ratio: 1:1;
Oven conditions: 200 °C;
Sample loop: 1 cm^3 ; t=100°C
Data collection: “Chromatec Analytic ” software;
SD for single measurement -0.6 %.

Supplementary verification measurements were carried out by Chromato-mass-spectrometry;
 Instrument: «Chromatec-crystal 5000.1» with MSD (Russia);
 Column: Restek Rxi-1ms (20 m x 0,15mm x 2 μ m);
 Carrier gas: helium 60, flow rate - 2,1 ml/min;
 Split ratio: 1:12;
 Oven conditions: 0°C;
 Sample loop: 0,25 cm³;
 Selected ion for N₂O: m/z=30;
 Analysis time: 0,8 min;
 SD for single measurement -1.3 %.

4 Additional information

4.1 Characteristics of pure substances used for preparation of the calibration gas mixtures are shown in the tables 6 – 9.

Table 4: Purity table for Nitrous oxide (Cylinder № 3378)

№	Component	Amount of substance fraction		Standard uncertainty (μmol/mol)
			%	
1	N ₂ O	99.795898	%	—
2	N ₂	1959	μmol/mol	20
3	O ₂	71.3	μmol/mol	0.7
4	CO	0.5	μmol/mol	0.3
5	CH ₄	0.12	μmol/mol	0.07
6	CO ₂	1.5	μmol/mol	0.9
7	H ₂ O	8.60	μmol/mol	0.17

Table 5: Purity table for Nitrogen (Cylinder MONO1)

№	Component	Amount of substance fraction		Standard uncertainty (μmol/mol)
			%	
1	N ₂	99.9998672	%	—
2	Ar	0.730	μmol/mol	0.015
3	H ₂ O	0.500	μmol/mol	0.025
4	CH ₄	0.0025	μmol/mol	0.0014
5	CO	0.0010	μmol/mol	0.0006
6	CO ₂	0.0025	μmol/mol	0.0014
7	H ₂	0.0025	μmol/mol	0.0014
8	O ₂	0.0060	μmol/mol	0.0003

Table 6: Purity table for Oxygen (Cylinder №11243)

№	Component	Amount of substance fraction		Standard uncertainty (μmol/mol)
			%	
1	O ₂	99.9999574	%	—
2	Ar	0.0025	μmol/mol	0.0014
3	CH ₄	0.0482	μmol/mol	0.0015
4	CO	0.030	μmol/mol	0.0017

№	Component	Amount of substance fraction		Standard uncertainty (μmol/mol)
5	CO ₂	0.030	μmol/mol	0.0017
6	H ₂	0.0025	μmol/mol	0.0014
7	Kr	0.0025	μmol/mol	0.0014
	N ₂	0.308	μmol/mol	0.006
8	Xe	0.0025	μmol/mol	0.0014

Table 7: Purity table for Argon (Cylinder № 61745)

№	Component	Amount of substance fraction		Standard uncertainty (μmol/mol)
1	Ar	99.9999657	%	—
2	O ₂	0.0050	μmol/mol	0.0003
3	CO	0.010	μmol/mol	0.006
4	CH ₄	0.015	μmol/mol	0.009
5	CO ₂	0.030	μmol/mol	0.017
6	H ₂	0.10	μmol/mol	0.06
7	N ₂	0.183	μmol/mol	0.005

4.2 Brief outline of the dilution series undertaken to produce the final mixtures

Preparation of final mixtures (CO₂ in synthetic air) was carried out from pure substances in 4 stages:

1-st stage – 2 mixtures N₂O /N₂ –level 1.2 %;

2-nd stage – 2 mixtures N₂O /N₂ –level 220 μmol/mol;

3-rd stage – 2 mixtures N₂O /N₂ –level 8 μmol/mol;

4-th stage – 2 target mixtures N₂O/synthetic air 330-335 μmol/mol + 2 target mixtures N₂O/synthetic air 340-345 μmol/mol.

All the mixtures were prepared in Luxfer cylinders (V=5 dm³). For the 3-rd and 4-th stage the cylinders with (Aculife III +Aculife IV) coating were used.

4.3 Purity table for each of the final mixtures, including the uncertainties

Table 8: (Standard 1) Cylinder Identification Number D648613

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
N ₂ O	0.3324	μmol/mol	0.0032	μmol/mol	2
N ₂	78.1037	10 ⁻² mol/mol	0.0010	10 ⁻² mol/mol	2
O ₂	20.9586	10 ⁻² mol/mol	0.0010	10 ⁻² mol/mol	2
Ar	0.9376	10 ⁻² mol/mol	0.0004	10 ⁻² mol/mol	2

Table 9: (Standard 2) Cylinder Identification Number D648616

Component	Mole fraction Value	Unit	Expanded Uncertainty*	Unit	Coverage Factor
N ₂ O	0.3425	μmol/mol	0.0028	μmol/mol	2
N ₂	78.1214	10 ⁻² mol/mol	0.0010	10 ⁻² mol/mol	2
O ₂	20.9396	10 ⁻² mol/mol	0.0010	10 ⁻² mol/mol	2
Ar	0.9390	10 ⁻² mol/mol	0.0004	10 ⁻² mol/mol	2

4.4 Brief outline of the verification procedure applied to the final mixtures

Verification measurements were performed by checking consistency within the group of the 4 prepared mixtures. Each of the Standards was measured against each of other other 3.

$u_{\text{ver}} = (0.4 - 0.5) \%$

2 verifications in repeatability conditions were performed (with 1 week interval), including 6 measurements for GC-ECD and 10 for GC-MSD.

4.5 Brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

The final mixtures were prepared 16.09 -17.09.2019.

First verification measurement was carried out 18.09.2019.

Second verification measurement was carried out 27.09.2019.

Stability testing (short-term) did not show instability within the accuracy of the measurement method.

04.10.2019

Participant Report Form

CCQM–K68.2019, Nitrous oxide in dry air, ambient levels (325–350 nmol mol⁻¹)

Participant information (for the comparison report)

Author(s)	J.I.T. van Wijk, S. Persijn, A.M.H. van der Veen
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Information on standards sent to the BIPM

	Standard 1	Standard 2
Nominal N₂O mole fraction	337.8 nmol/mol	348.2 nmol/mol
Date of preparation	5 August 2019	6 August 2019
Serial number	D791189	D791188
Pressure (before shipment)	12.7 MPa	12.5 MPa
Volume	5 L	5L
Connection type	Din 1	Din 1

Results

Mixture	Amount fraction	Expanded uncertainty, $k = 2$
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Standard 1 (VSL191189)	337.8 nmol/mol	1.5 nmol/mol
Standard 2 (VSL191188)	348.2 nmol/mol	1.5 nmol/mol

Gravimetric preparation

Results of the gravimetric preparation is:

Standard 1(VSL191189): 337.8 nmol/mol

Standard 2 (VSL191188): 348.2 nmol/mol

Based on the purity analysis for N₂O of the pure matrix gas a small correction was applied (+0.1 nmol/mol) to the gravimetric N₂O amount fraction.

Analysis results: pre-measurement

The measurement results for standard 1 are shown in Table 1.

Table 1 Measurement results standard 1 (VSL191189)

Date	Results analysis (nmol/mol)	Standard uncertainty (nmol/mol)	Number of replicates
28 Aug 2019	337.5	1.6	4
29 Aug 2019	337.2	1.3	4
30 Aug 2019	336.5	1.2	4
average	337.1	0.5	

For standard 1 the end result is 337.1 ± 1.0 nmol/mol (k=2).

The measurement results for standard 1 are shown in Table 2.

Table 2 Measurement results standard 2 (VSL191188)

Date	Results analysis (nmol/mol)	Standard uncertainty (nmol/mol)	Number of replicates
28 Aug 2019	347.8	1.4	4
29 Aug 2019	349.2	0.9	4
30 Aug 2019	349.4	0.7	4
average	348.8	0.9	

For standard 2 the end result is 348.8 ± 1.8 nmol/mol ($k=2$).

Analysis results: post-measurement

The post-measurement results for standard 1 are shown in Table 3.

Table 3 Measurement results standard 1 (VSL191189)

Date	Results analysis (nmol/mol)	Standard uncertainty (nmol/mol)	Number of replicates
22 Oct 2020	337.5	1.3	4
18 Dec 2020	338.8	2.8	4
18 Dec 2020	338.3	2.5	4
average	338.2	0.7	

For standard 1 the end result is 338.2 ± 1.4 nmol/mol ($k=2$).

The measurement results for standard 2 are shown in Table 5.

Table 5 Measurement results standard 2 (VSL191188)

Date	Results analysis (nmol/mol)	Standard uncertainty (nmol/mol)	Number of replicates
22 Oct 2020	347.5	3.0	4
18 Dec 2020	347.4	3.4	4

18 Dec 2020	348.4	3.1	4
average	347.8	0.5	

For standard 2 the end result is 347.8 ± 1.1 nmol/mol ($k=2$).

Figure 1 shows graphically an overview of the pre- and post-measurements of the 2 standards and the comparison with gravimetry.

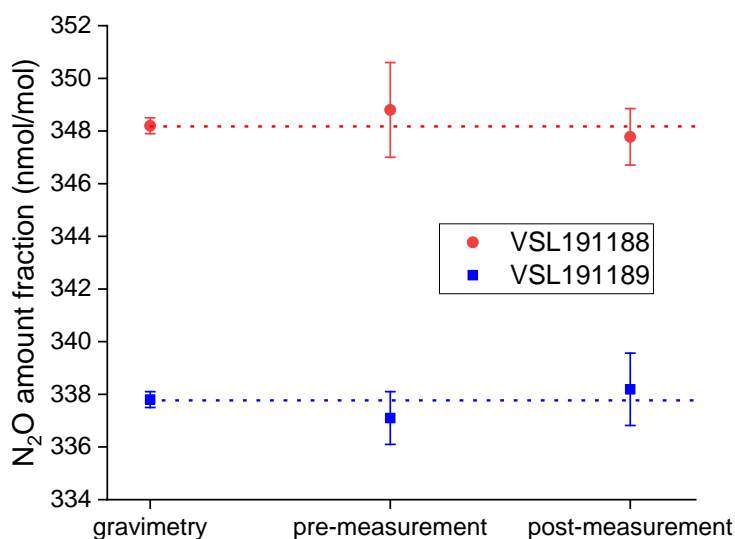


Figure 1 Overview of the pre- and post-measurements at VSL of the 2 standards and the comparisons with gravimetric value.

Instrumentation

The analytical instrument used was a custom-built infrared laser spectrometer based on direct absorption spectroscopy using a quantum cascade laser and a multi-pass absorption cell with an effective pathlength of 76 m. The laser was scanned around the N₂O absorption feature centered at 2191.42 cm^{-1} which consists of one strong line and many adjacent weaker lines.

The pressure in the measurement cell was maintained at 200 mbar using a pressure controller. This pressure was selected to have on the one hand sufficiently low interference from the neighboring R(12) CO absorption line at 2190.02 cm^{-1} while at the same time the N₂O absorption feature is at this pressure sufficiently broad to make the system insensitive to small drifts in laser wavelength.

Measurement procedure

The gas mixtures were continuously flushed through the cell at a flow rate of 10 L/h. Three different N₂O in synthetic air gas mixtures (nominal amount fractions of 333.55 nmol/mol, 342.95 nmol/mol and 351.39 nmol/mol) were used as gas standards. Further, the pure matrix gas was analyzed and served as a background. Each cylinder was measured 5 or 6 times sequentially. The entire measurement sequence was repeated 4 times. Measurements were then repeated on different days (pre-measurement dates: 28, 29 and 30 August 2019 and post-measurement dates were 22 October 2020 and 18 December 2020 (2×)).

Data analysis

From the recorded data of each measurement day the absorption spectra were calculated. The amount fractions were determined by generalised distance regression using CurveFit, implementing the multipoint calibration method of ISO 6143. The data of the different measurements series were then averaged and are reported here.

Uncertainty calculation

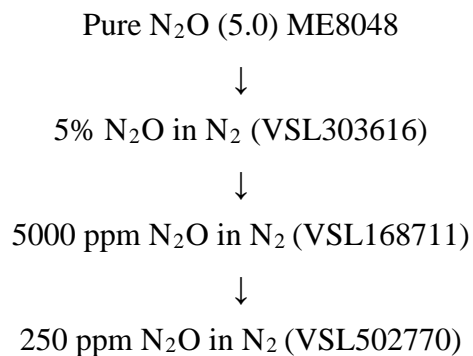
Uncertainty contributions include purity of the gases used to prepare the standards, i.e., both of the pure N₂O and the matrix gas (the latter contained about 0.07 nmol/mol N₂O, which is below the LoD of the CRDS instrument used for the purity analysis), the weighing of the cylinder, reproducibility of the measurements and the analysis. An expanded uncertainty of 1.5 nmol/mol ($k=2$) is assigned to both standards (VSL191188 and VSL191189).

Additional information

Mixture preparation procedure

The two standards in synthetic air and containing 1% argon were prepared out of different N₂O in N₂ standards. This was done via 5 dilutions from the same pure N₂O (5.0 purity).

Standard 1 was prepared as follows:



↓
 10 ppm N₂O in N₂ (VSL191088)
 ↓
 338 ppb N₂O in air (VSL19189)

Standard 2 was prepared as follows:

Pure N₂O (5.0) ME8048
 ↓
 5% N₂O in N₂ (VSL168702)
 ↓
 2000 ppm N₂O in N₂ (VSL405160)
 ↓
 100 ppm N₂O in N₂ (VSL523597)
 ↓
 10 ppm N₂O in N₂ (VSL191182)
 ↓
 348 ppb N₂O in air (VSL19188)

Purity information

The pure matrix gas (synthetic air containing nitrogen, oxygen and argon in similar amount fractions as the gas standards 1 and 2 and the three reference gas standards) was analyzed using CRDS. The measured N₂O amount fraction (0.07 nmol/mol) in the matrix gas was below the limit of detection (0.2 nmol/mol) of the instrument.

Table 3 – Purity table standard 1 (VSL191189), expressed in mole fractions ($\times 10^6$)

Id	Formula	Component Name	x	u(x)	urel(x) (%)
1	Ar	Argon	9382.2	2.7	0.03%
2	CH ₄	Methane	0.012	0.006	54%
3	CO	Carbon monoxide	0.011	0.006	55%
4	CO ₂	Carbon dioxide	0.019	0.008	41%
28	H ₂	hydrogen	0.020	0.011	55%
29	H ₂ O	water	0.060	0.032	53%
31	N ₂	Nitrogen	781420.0	8.5	0.0011%

33	O ₂	Oxygen	209190.0	7.9	0.0038%
35	N ₂ O	Nitrous oxide	0.33771	0.00011	0.03%

Table 4 – Purity table standard 2 (VSL191188) , expressed in mole fractions ($\times 10^6$)

Id	Formula	Component Name	x	u(x)	u _{rel} (x) (%)
1	Ar	Argon	9408.0	2.7	0.03%
2	CH ₄	Methane	0.012	0.006	54%
3	CO	Carbon monoxide	0.012	0.006	55%
4	CO ₂	Carbon dioxide	0.019	0.008	41%
28	H ₂	hydrogen	0.020	0.011	55%
29	H ₂ O	water	0.060	0.032	53%
31	N ₂	Nitrogen	781250.0	8.7	0.0011%
33	O ₂	Oxygen	209340.0	8.0	0.0038%
35	N ₂ O	Nitrous oxide	0.34811	0.00011	0.03%

Table 5 – Purity table matrix gas (VSL191172) , expressed in mole fractions ($\times 10^6$)

Id	Formula	Component Name	x	u(x)	u _{rel} (x) (%)
1	Ar	Argon	9395.0	2.8	0.03%
2	CH ₄	Methane	0.012	0.006	54%
3	CO	Carbon monoxide	0.011	0.006	55%
4	CO ₂	Carbon dioxide	0.019	0.008	42%
28	H ₂	hydrogen	0.020	0.011	58%
29	H ₂ O	water	0.060	0.032	53%
31	N ₂	Nitrogen	781190.0	8.5	0.0011%
33	O ₂	Oxygen	209410.0	7.8	0.0037%

Table 6 – Purity table N₂O (ME8048) , expressed in mole fractions ($\times 10^6$)

Id	Formula	Component Name	x	u(x)	urel(x) (%)
4	CO ₂	Carbon dioxide	1.00	0.30	30%
31	N ₂	Nitrogen	3.00	1.00	33%
33	O ₂	Oxygen	3.00	1.00	33%
35	N ₂ O	Nitrous oxide	999990.00	2.00	0.00020%