CCQM-P206, Nitrous Oxide (N_2O) in air, Ambient level Pilot Study run in parallel with CCQM-K68.2019 Final Report

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Summary

The Pilot Study CCQM-P206 was conducted in parallel with the Key Comparison CCQM-K68.2019, which was aimed at evaluating the level of comparability of laboratories' capabilities for nitrous oxide in air primary reference mixtures at ambient amount fractions, in the range 320 nmol mol^{-1} to 350 nmol mol^{-1}. The Pilot Study was setup to allow the participation of the Scripps Institution of Oceanography of the University of California San Diego (SIO/UCSD) as guest expert laboratory of the CCQM.

The SIO/UCSD was invited by the CCQM in view of its long experience in accurate measurements of nitrous oxide in the atmosphere and is the calibration laboratory for this compound in the AGAGE (Advanced Global Atmospheric Gases Experiment) global measurement network. The laboratory has developed a unique method which provides an independent assessment of the N_2O amount fraction compared to participants in CCQM-K68.2019. Its participation was also seen as the occasion to contribute to a more general reflexion on the compared advantages of two different systems to ensure traceability: a unique scale maintained by one central laboratory, or the dissemination of materials all traceable to the SI by multiple national metrology institutes.

The comparison CCQM-K68.2019 was coordinated by the BIPM and the KRISS. It consisted in the simultaneous comparison of a suite of 2*n* 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 N_2O in air, namely Gas Chromatography with an Electron Capture Detector (GC−ECD) and Quantum Cascade Laser Absorption Spectroscopy (QCLAS).

For the Pilot Study, SIO/UCSD provided results of measurements of the N_2O amount fraction in the two standards submitted by the Global Monitoring Laboratory of the National Oceanic and Atmospheric Administration (NOAA), a participant in the Key Comparison. Therefore, this study consists in looking at the agreement between SIO/UCSD measurement results and the Key Comparison reference value.

All details on the Key Comparison CCQM-K68.2019, included its protocol and its results, can be found in its report. This report focuses on SIO/UCSD results and agreement with participants in the Key Comparison.

1 Content

2 Purpose

The CCQM-K68.2019 comparison was designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) capabilities for nitrous oxide (N_2O) in air reference mixtures at ambient amount fractions. The parallel Pilot Study CCQM-P206 was organised to invite the expert laboratory SIO/UCSD to also measure the N_2O amount fraction in reference mixtures that took part in the Key comparison using their measurement capabilities.

The range of N_2O amount fractions covered by the comparison was from 320 nmol mol^{-1} to 350 nmol mol^{-1}. N_2O was to be prepared in a matrix of dry air, with constraints imposed on the composition of this matrix.

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}, µmol mol^{-1} or nmol mol^{-1}).

4 Participants

The Pilot Study included one sole participant, the Scripps Institution of Oceanography of the University of California San Diego (SIO/UCSD).

5 Measurement schedule

The Pilot Study schedule followed these of the Key Comparison, organised by the BIPM as displayed in Table 1.

Table 1: schedule of events in CCQM−K168.2019 and CCQM−P206 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 – 1st model proposed based on Error−In−Variable (EIV) regression and selection of a consistent calibration set.
11 May 2021	1st Draft A discussion meeting followed by requests of additional information on the purity of the matrix gas.
11 June 2021	2nd Draft A discussion meeting followed by proposal of a 2nd model to include a dark uncertainty component in the KCRV
11 Nov. 2021	3rd 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	4th Draft A discussion meeting – decision to use the EIV regression with shades of dark uncertainty to calculate the KCRVs

6 Measurements of SIO/UCSD

SIO/UCSD reported N_2O amount fractions in the standards prepared by NOAA, value assigned against a set of in-house primary standards. To analyse their results, it is therefore important to look at the composition of both kind of standards, and to describe the analytical methods used to measured N_2O.

6.1 SIO/UCSD Standards

6.1.1 Standards preparation technique

As further described in their report (See annex), SIO/UCSD prepared a set of 19 reference standards by adding aliquots of mixtures of pure N_2O and pure CO_2, with known near-ambient molar ratios, to large volumes of N_2O-free and CO_2-free dry artificial “zero air”. The molar N_2O/CO_2 ratios were determined by volumetric measurement of the pure CO_2 and N_2O components, with virial equation-of-state corrections applied for each pure gas. The CO_2 amount fraction of these 19 standard mixtures was measured by dual-catalyst flame ionization gas chromatography (GC-FID), a method chosen for its independence from isotopic and matrix composition effects, against CO_2 in air standards on the Scripps CO2 laboratory X12 (2012) calibration scale [1, 2].

6.1.2 Traces of N_2O and CO_2 in the matrix gas

A purity table of the matrix gas was required to be reported by participants. Particular attention should be paid to traces of N_2O present in the nitrogen or synthetic air used to dilute pure N_2O, as the amount fraction can easily be of the same order as the final combined uncertainty of the total N_2O amount fraction.

In the case of SIO/UCSD, this issue was of importance in preparation of the primary standards, which started with N_2O-free air. As reported in annex, the amount fraction of N_2O in this dilution air was assumed to be zero as no signal for N_2O could be detected, with a detection limit of 0.14 nmol mol^{-1}. An asymmetric (positive only) uncertainty component was derived from this.

Additionally, because SIO/UCSD measurements involve the determination of the CO_2 amount fraction in the set of primary standards, the correct estimation of CO_2 traces in the same dilution air was also important. This was assumed to be zero as no signal for CO_2 could be detected, with a detection limit of 0.003 µmol mol^{-1}. Again, an asymmetric uncertainty component was derived from this.

6.2 NOAA Standards

6.2.1 Standards preparation technique

The two standards provided by NOAA for this comparison are described in their result form attached to CCQM-K68.2019 report. Briefly, they were samples consisting of whole air in 5.9-L aluminum cylinders (Airgas, USA). The whole air was collected at NOAA site in the Colorado mountains using a Rix SA-6 oil-free compressor. Each cylinder was first evacuated (~30 mtorr) and flushed with zero-grade air, then filled with a mixture of N_2O-free air, aliquots of N_2O, and whole air collected at various times to reach target N_2O amount fraction values as required in the Key Comparison protocol.

6.2.2 Matrix composition

To avoid possible biases of measurements by QCLAS, 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 amount fractions. Limits of the amount fraction of the major constituents were provided in the protocol [see CCQM-K68.2018 report]. As explained above, the matrix in the standards prepared by NOAA was scrubbed real air.

6.3 Analytical technique(s) for calibration

All participants in the parallel Key Comparison used an analytical technique to verify the N_2O amount fraction in the prepared standards by comparison to other sets of their standards. For two of them, FMI and NOAA, this step constituted a calibration, with results traceable to the primary set (VSL standards for FMI and WMO-N2O-X2006A scale [3] for NOAA). This principle also applies for the Pilot Study, as SIO/UCSD assigned the N_2O amount fraction in the NOAA standards by measuring them against a set of 19 in-house primary standards (described below) using GC-ECD. More details on GC-ECD measurements at SIO/UCSD can be found in Prinn et al. [4].

Additionally, the value of the N_2O/CO_2 fraction injected in the primary standards was derived from the volumetric measurements, and the amount fraction of CO_2 in air resulting from this operation was estimated by GC-FID against another set of standards of CO_2 in air. Therefore, the three techniques (GC-ECD, GC-FID and volumetric measurements) impacted the final measurement results and uncertainties.

6.4 N_2O amount fraction and uncertainties reported by SIO/UCSD

Using the steps described above and in annex, SIO/UCSD reported the following N_2O amount fractions in the standards prepared by NOAA:

Table 2: cylinder reference (REF), amount fraction of N_2O assigned by participants (x) and associated standard uncertainty (u)

REF	x (nmol mol^{-1})	u (nmol mol^{-1})
FF57617	327.18	0.50
FF57625	343.31	0.55

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 1 – SIO/UCSD report):

- 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.

7 Measurements at the BIPM

The BIPM facility is described in more details in the associated Key Comparison report. Briefly, it consisted in two analysers based on independent analytical techniques and maintained under repeatability conditions: one GC-ECD, and one QC-LAS. Each analyser was connected to an autosampler to allow the successive analysis of standards grouped in two batches. The comparison was performed following the protocol sent to participants on 14 March 2019, described again below.

7.1 Preparation of cylinders

Cylinders were tracked at the BIPM with their reference as provided by the participants. All pressures were measured upon their arrival and before their return in participant’s laboratories.

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 reducer 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.

7.2 Series of analysis

Standards were analysed in two batches of similar N_2O amount fractions, divided by the median. 3 BIPM cylinders were added to the batches as quality control. Each batch was analysed sequentially in series together with the control cylinder. 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).

7.3 Calculation of analysers responses and standard uncertainty

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 $\delta R_{\mathrm{mean}} = 1.68\times10^{-3}$. 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 $u(y_{\mathrm{GC}})$ reported in Annex.

With the QCLAS instrument, sequences of measurements included sampling each standard for 20 minutes to average the response over the 5 last minutes. 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}.

7.4 Measurement results and reference values for SIO/UCSD

Detailed results of measurements performed at the BIPM with the GC-ECD and QCLAS analysers can be found in the associated Key Comparison report. Results of all participants need to be considered to understand the reference values assigned to the NOAA cylinders. By principle, each participant in the Key Comparison was assumed to provide an independent best determination of the N_2O amount fraction in their two standards. Therefore, all standards were considered to form a calibration set defining the calibration functions of the analysers.

In a first approach, the calibration function was calculated by Generalized Least Square regression to include uncertainties from the participants and from the analytical measurements. Results displayed in the Key Comparison report show that a good agreement was observed between the measurement results obtained with the two main techniques, 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-µECD) 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 the comparison.

After consultation with all participants, the mathematical approach chosen to calculate the reference values was a Bayesian Errors−In−Variables regression with shades of dark uncertainty, with calculations performed by B. Toman and A. Possolo. The detail of this treatment is not repeated here and can be found in CCQM−K68.2019 report. SIO/UCSD results are compared with the Key Comparison reference values obtained on the two NOAA standards after calibration of the QCLAS instrument with all standards.

The difference from the reference value for cylinder i is defined as:

$$D_i = x_i - \xi_i, \tag{3}$$

where x_i is the observed amount fraction reported by SIO for each of the two NOAA cylinders. 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,

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

where the u_i are the uncertainties reported by SIO. These results are given in Table 3 and plotted in Figure 1, together with the Degrees of Equivalence of the Key Comparison CCQM−K68.2019.

Table 3 : Cylinder identification (ID), N_2O amount fractions reported by SIO/UCSD (x_i) and their uncertainty u_i, the reference values defined in CCQM−K68.2019 (ξ_i) and associated uncertainty $u(\xi_i)$, the differences from the reference values D_i and their expanded uncertainties.

ID	x_i nmol mol^{-1}	u_i (nmol mol^{-1})	ξ_i nmol mol^{-1}	(ξ_i) / (nmol mol^{-1})	D_i nmol mol^{-1}	$U(D_i)$ nmol mol^{-1}
FF57617	327.18	0.50	326.70	0.21	0.48	1.08
FF57625	343.31	0.55	343.00	0.15	0.31	1.14

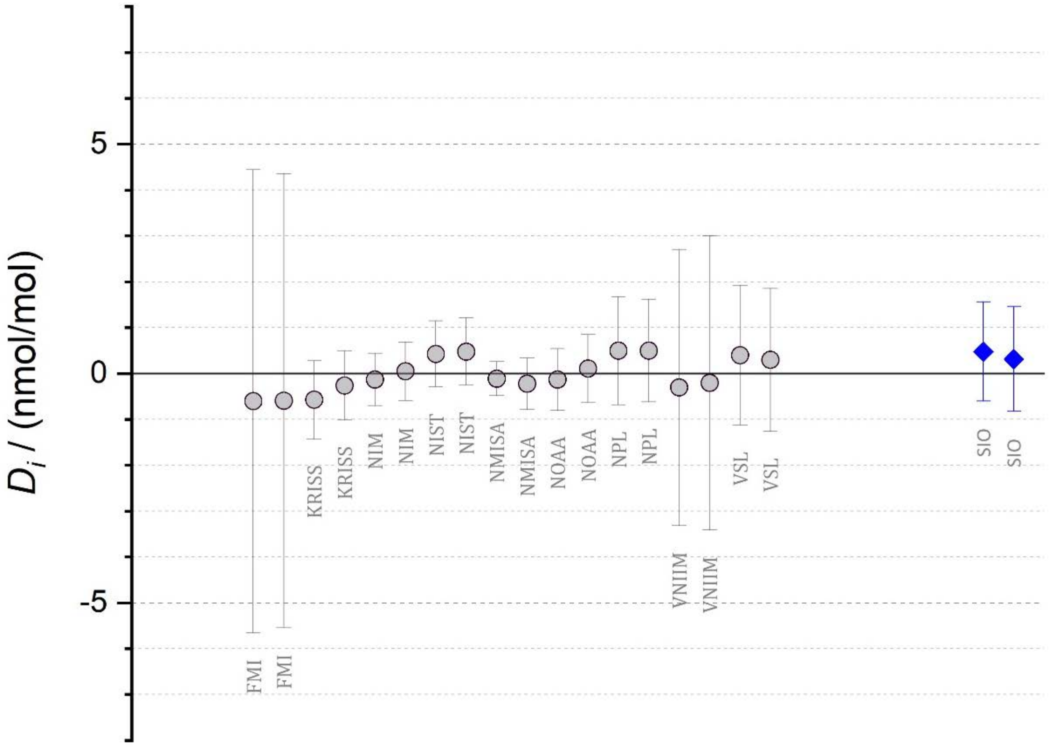

Figure 1: Degrees of equivalence of the Key Comparison CCQM−K68.2019 (grey dots) together with the difference from the reference values for SIO/UCSD (blue diamonds) in the Pilot Study CCQM−P206.

8 Conclusions

The Pilot Study CCQM-P206 was conducted as a parallel comparison to the Key Comparison CCQM−K68.2019, to allow the participation of the expert laboratory SIO/UCSD. The laboratory has developed a unique method which provided an independent assessment of the N_2O amount fraction compared to participants in CCQM−K68.2019. When all other participants normally prepare N_2O in air standards by gravimetry, SIO/UCSD uses a combination of a volumetric technique and measurements against their CO_2 scale to determine the N_2O amount fraction in their standards.

The results of the Pilot Study CCQM-P206 show a very good agreement between SIO/UCSD and participants in the associated Key Comparison. N_2O amount fractions measured by SIO/UCSD in the two cylinders shared with them by NOAA agree very well with the reference values estimated from the comparison, using an innovative mathematical model based on Bayesian Errors−In−Variables regression with shades of dark uncertainty.

As explained in CCQM-K68.2019 report, results obtained with the QCLAS analyser by the coordinator showed a noticeable internal consistency between the two standards submitted by each participant. A mean value of 0.12 nmol mol^{-1} was calculated for the 9 participants, which can be compared with a spread (standard deviation) of 0.38 nmol mol^{-1} when considering all degrees of equivalence. This is also the case for SIO/UCSD, for which a difference of 0.17 nmol mol^{-1} was found in between their two measurements, compared to a mean difference from the reference values of 0.4 nmol mol^{-1}.

9 Annex 1 – SIO/UCSD report

The full report submitted by SIO/UCSD is displayed in the following pages (PDF version only).

10 References

[1] Keeling R., Guenther P., Walker S. and Moss D. 2016 Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards : revision of 2012. Scripps Institution of Oceanography),

[2] Weiss R.F., 1981, Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography, *Journal of Chromatographic Science*, **19**, 611-616,

[3] Hall B., Dutton G. and Elkins J., 2007, The NOAA nitrous oxide standard scale for atmospheric observations, *Journal of Geophysical Research: Atmospheres*, **112**,

[4] Prinn R., Weiss R., Fraser P., Simmonds P., Cunnold D., Alyea F., O'doherty S., Salameh P., Miller B. and Huang J., 2000, A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *Journal of Geophysical Research: Atmospheres*, **105**, 17751-17792,

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.

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Information on Standards sent to the BIPM		
	Standard 1	**Standard 2**
Nominal N_2O mole fraction	327 nmol mol^{-1}	343 nmol mol^{-1}
Date of preparation	June 10, 2019	June 10, 2019
Serial number	FF57617	FF57625
Pressure (before shipment)	1400 psi (9.7 Mpa)	1300 psi (9.0 Mpa)
Volume	5.9 L	5.9 L
Connection type	CGA-590	CGA-590

Results of Measurements

Please indicate below the final value and associated expanded uncertainty of the N_2O mole fraction in each of the two standards.

Nominal mole fraction / nmol mol^{-1}	**N_2O mole fraction $x(N_2O)$ / nmol mol^{-1}**	**Expanded uncertainty $U(x(N_2O))$ / nmol mol^{-1}**	**Coverage factor**
327 nmol mol^{-1}	327.18 nmol mol^{-1}	1.01 nmol mol^{-1}	2
343 nmol mol^{-1}	343.31 nmol mol^{-1}	1.06 nmol mol^{-1}	2

Measurement Procedure

Ambient-level N_2O standard mixtures were prepared by adding aliquots of mixtures of pure N_2O and pure CO_2, with known near-ambient molar ratios, to large volumes of N_2O-free and CO_2-free dry artificial “zero air”. The molar N_2O/CO_2 ratios were determined by volumetric measurement of the pure CO_2 and N_2O components, with virial equation-of-state corrections applied for each pure gas. This produced standards with CO_2 and N_2O mole fractions at near-ambient levels, and with known molar N_2O/CO_2 ratios. The CO_2 mole fractions of these standard mixtures were then measured by dual-catalyst flame ionization gas chromatography, a method chosen for its independence from isotopic and matrix composition effects, against CO_2 in air standards on the Scripps CO_2 laboratory X12 (2012) calibration scale. The N_2O dry air mole fractions of these mixtures were then obtained by multiplying their measured CO_2 mole fractions by the prepared N_2O/CO_2 molar ratios of the added aliquots. The resulting ambient-level N_2O standard mixtures were then measured against each other by electron capture gas chromatography to establish the SIO-16 N_2O calibration scale. During this verification step 2 of 19 prepared mixtures were eliminated due to poor internal agreement. The N_2O mole fractions in the dry whole air standard gases used in this comparison were measured against this scale, also by electron capture gas chromatography. Importantly for the error analysis, the CO_2/air and N_2O/CO_2 ratio determinations that underpin both the Scripps X12 CO_2 calibration scale and the SIO-16 N_2O calibration scale, respectively, were made on the same Scripps precision manometer system. Descriptions of the various methods are given by: Prinn et al. (2000) for the standard preparation approach and electron capture N_2O measurements; Weiss (1981) for the dual catalyst flame ionization CO_2 measurements; and Keeling et al. (2016) for the Scripps manometer and CO_2 X12 calibration scale.

Uncertainty Budget

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

First, we describe the uncertainty budget for the preparation of the suite of 17 primary reference gas mixtures. Second, we provide specific uncertainty contributions for our measurements of the travelling whole air standard.

N_2O Primary Standard Main Equation

The main equation to derive the uncertainty budget for the primary standard is:

$$x_{N_2O\ in\ std} = M * \left(x_{CO_2,meas} - x_{CO_2,impurities}\right) + x_{N_2O,impurities}$$

where:

$x_{N_2O\ in\ std}$ is the mole fraction of N_2O in the prepared primary standard in the synthetic air dilution gas;

M is the prepared molar ratio of the N_2O/CO_2 mixture spiked into the dilution gas.

$x_{CO_2,meas}$ is the measured mole fraction of CO_2 in the N_2O primary standard measured on the Scripps CO_2 X12 calibration scale.

$x_{CO_2,impurities}$ is the mole fraction of CO_2 impurity present in the dilution gas. This is assumed to be zero as no signal for CO_2 could be detected in the dilution gas, with a detection limit of 0.003 μmol mol^{-1}. This uncertainty is one-sided as a mole fraction cannot be negative.

$x_{N_2O,impurities}$ is the mole fraction of N_2O impurities present in the dilution gas. This is assumed to be zero as no signal for N_2O could be detected in the dilution gas, with a detection limit of 0.14 nmol mol^{-1}. This uncertainty is one-sided as a mole fraction cannot be negative.

We provide below further details regarding the uncertainties of some of these components:

Prepared N_2O/CO_2 Molar Ratio *M*

The numbers of moles (*n*) of N_2O and CO_2 that are combined to make the N_2O/CO_2 mixture that is spiked into the dilution gas is given by the standard gas equation for real gases:

$$n_{N_2O} = \frac{P_{N_2O}\, V_{small}}{R\, Z_{N_2O}\, T_{N_2O}}$$

$$n_{CO_2} = \frac{P_{CO_2}\, V_{large}}{R\, Z_{CO_2}\, T_{CO_2}}$$

Where *P* is the pressure, *T* is the temperature, *R* is the ideal gas constant, *Z* is the compressibility factor for the pure real gas as determined from the virial equation of state, and *V* is the volume in which the gas is measured. The Scripps precision manometer has a small volume of about 3.8 cm^3 and a large volume of about 5000 cm^3. Accordingly, the N_2O/CO_2 ratio in the prepared mixture is given by:

$$M = \frac{n_{N_2O}}{n_{CO_2}} = \frac{P_{N_2O}}{P_{CO_2}} * \frac{T_{CO_2}}{T_{N_2O}} * \frac{V_{small}}{V_{large}} * \frac{Z_{CO_2}}{Z_{N_2O}}$$

In which the gas constant *R* cancels, any multiplicative errors in *P* and *T* cancel, and the uncertainties in *Z* are negligible. As is discussed in considerable detail by Keeling et al. (2016), the dominant systematic uncertainty in this method lies in the determination of V_{small} as it affects the V_{small}/V_{large} ratio, which they estimate as 1 part in 1500, or 0.067%. The other systematic uncertainties, including that of V_{large}, are very much smaller and are effectively negligible.

Measured CO_2 Mole Fraction $x_{CO_2,meas}$

The uncertainty of the CO_2 mole fraction in the prepared N_2O standard mixtures is the combined uncertainties of the CO_2 measurement and the Scripps X12 CO_2 calibration scale. The type A uncertainty in the dual catalyst flame ionization measurements of CO_2 in the prepared mixture for N_2O against the X12 CO_2 standards is 0.037%. As is the case above for the N_2O/CO_2 ratio, the systematic uncertainty in the X12 CO_2 calibration scale is also dominated by the determination of the small volume used in the manometric system. This is the same 0.067%, but applied now, with the same sign, to the x_{CO_2} determination rather than to the N_2O/CO_2 molar ratio *M*. In comparison, all other sources of uncertainty are an order of magnitude lower and can be neglected.

Rewritten N_2O Primary Standard Main Equation

The general equation can therefore be rewritten, and it appears in particular that the uncertainty of the small volume of the manometric system has to be counted twice:

$$x_{N_2O\ in\ std} = f_{N_2O/CO_2} * V_{small} * \left(f_{CO_2/air} * I_{response} * V_{small} - x_{CO_2,impurities}\right) + x_{N_2O,impurities}$$

where:

$I_{response}$ is the instrumental response obtained for the measurement of CO_2.

f_{N_2O/CO_2} is a function representing all input values except V_{small} in *M*, the uncertainties of which can be neglected, except for V_{small}.

$f_{CO_2/air}$ is a similar function to f_{N_2O/CO_2}, representing all input values except V_{small}, but for the manometric measurement of CO_2 in air, the uncertainties of which can be neglected, except for V_{small}.

Combined Uncertainty

The combined uncertainty is computed using the general formula for error propagation, according to JCGM (2008), equation 10. When expressing all uncertainty contributions in percentage, the sum of uncertainties is, for the upper uncertainty value:

$$u_c^2(\%) = (2 * u_{V_{small}})^2 + u_{I_{response}}^2 + u_{x_{N2O,impurities}}^2$$

And for the lower uncertainty value:

$$u_c^2(\%) = (2 * u_{V_{small}})^2 + u_{I_{response}}^2 + u_{x_{CO2,impurities}}^2$$

Note that $u_{x_{CO2,impurities}}^2$ can only contribute to the lower uncertainty value, and $u_{x_{N2O,impurities}}^2$ can only contribute to the upper uncertainty value. As a result, the upper uncertainty value is slightly more than the lower uncertainty value. However, to simplify the comparison, we use the maximum value for both upper and lower uncertainties.

As an example, we provide below a table detailing the uncertainty values for the preparation of one of the 17 primary standards that define the SIO-16 N_2O calibration scale, mixture SIO-16-N2O-05. As is discussed above, the large majority (85%) of the final uncertainty is caused by the small volume determination of the manometric system. The final N_2O mole fraction for this mixture, after verification, is 329.09 nmol/mol.

Variable	**Description**	**Uncertainty, % (k=1)**	**Contribution to total uncertainty, nmol/mol (k=1)**	**Contribution to total uncertainty, %**
$u_{V_{small}}$	Uncertainty for the small volume of the manometric system	0.067	0.4065	85.0
$u_{I_{response}}$	Measurement uncertainty for CO_2	0.037	0.03099	6.48
$u_{x_{CO_2,impurities}}$	Maximum CO_2 impurities in zero air	0.0008	0.000014	0.003
$u_{x_{N_2O,impurities}}$	Maximum N_2O impurities in zero air	0.043	0.04097	8.56
Total Uncertainty Contribution		0.1455	0.4784	100

References

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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.

Whole Air Standards Measured in this Comparison

The two standard gas cylinders we measured, rather than having been prepared from pure components, are dry whole air compressed by NOAA in Colorado and sent to us for measurement. Please consult the CCQM-K68.2019 Report Form submitted by NOAA for details of their preparation and the adjustment of their N_2O mole fractions. As is discussed above, these two cylinders were measured against whole air working standards maintained at SIO that have in turn been calibrated against the suite of 17 primary gas mixtures that constitute the SIO-16 N_2O calibration scale. The stabilities of the two standard gas cylinders we measured were confirmed by both having been measured by NOAA before and after measurement at SIO and BIPM, and no detectable drifts were found.

For these two whole air standards, we combine the measurement uncertainties of the primary standard *vs* the secondary standard with that of the secondary standard *vs* the whole air. We assume that these measurement uncertainties are due mostly to random noise and can be considered as independent.