Pilot Study CCQM-P172, Spectroscopic methods for HNO₃ value assignment

Final Report

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1 Executive summary

The CCQM-P172 comparison was designed to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Because it is present in NO₂ gas standards as an impurity, HNO₃ was chosen as the analyte for study. As primary reference gas mixtures of HNO_3/N_2 are (generally) unavailable for calibration, traceability for spectroscopic measurements will rely on the use of referenced molecular parameters (such as tabulated in the HITRAN database, acronym for high-resolution transmission molecular absorption database).

Laboratories that took part in this pilot study CCQM-P172 were required to submit one secondary standard of NO₂ in nitrogen at a nominal amount fraction of 10 µmol mol⁻¹ with a requirement that the HNO₃ amount fraction present in the mixture is between 100 nmol mol⁻¹ and 1000 nmol mol⁻¹. As the mixtures are similar to the ones compared in the Key Comparison CCQM-K74.2018, also coordinated by the BIPM during the same period, a similar linear decrease of the main component NO₂ and a correlated linear increase of the major impurity HNO₃ was initially foreseen. The CCQM-P172 protocol was designed to deal with standards that followed a well-behaved decay profile, allowing BIPM measurements to be compared to interpolated values for participants' standards. However, as with CCQM-K74.2018, the behavior of the standards deviated from this expectation, showing nonlinear variations of the components.

The study was further complicated with deviations from the protocol which have been recorded and described in this report. The complications resulted in a reduced number of analyses by the coordinating laboratory for two of the five participants.

The first version of this report distributed in May 2021 described only the measurements performed by the BIPM and the results submitted by participants, without attempting to

provide reference values. Nevertheless, a number of important observations and conclusions were drawn as reported below:

1) The BIPM operated two methods for FTIR quantification of HNO₃, the first based on direct reference to HITRAN parameters the second based on calibration with a permeation system. Whilst both methods demonstrate very good correlation and linearity with respect to each other, the HITRAN method provided measurement results 23% higher than for the permeation system calibrated FTIR method.

2) The fitting of HNO₃ FTIR spectra was often complicated by the presence of other species, in particular the considerable NO₂ absorption band for gas mixtures from cylinders, and the presence of considerable amounts of water in the case of the BIPM permeation calibration gas mixtures in the 1550 cm⁻¹ to 1750 cm⁻¹ spectral window. The effect of the spectral windows used for fitting deserves further consideration.

3) Stabilization of the FTIR signal in the BIPM system (45 m gas cell) with the flows of gas that are permissible from gas cylinders for HNO_3 resulted in residual drift in signal that varied between standards submitted, and in the best cases was characterized by an additional uncertainty component with magnitude of 20 nmol mol⁻¹ (standard uncertainty), and a compromise between increased signal sensitivity and its stability.

4) Due to the complications in the study, the set of results obtained, which had sufficiently complete sets of measurements to compare data were for the cylinders received from NPL and VSL. In the case of the NPL standard, BIPM and NPL FTIR measurements were performed with similar HITRAN based methods, and agreement of results can be concluded if the rise in HNO₃ levels can be considered to have stabilized in the standard at the time of measurement at the BIPM. The VSL method fits individual absorption lines within a different band from BIPM and NPL. For the VSL standards the absolute change in HNO₃ amount fractions between their measurement periods is of the same order of magnitude as the uncertainties reported for the BIPM FTIR measurement methods. As a result both of the BIPM and the VSL results could be considered in agreement, without being able to readily differentiate for which of the BIPM results the agreement is better.

During the GAWG meeting of June 2021, participants agreed to complete the study with the following actions:

- reanalysis of participants' FTIR spectra when feasible: CENAM and NPL spectra were reanalysed using the submitted participants parameters, and the recalculated nitric acid mole fractions. Unfortunately, NMISA and KRISS could not provide enough information to reanalyse their spectra. VSL did not use FTIR for the analysis. The reanalysis confirmed good agreement with NPL and revealed differences with CENAM.
- reanalysis using different regions: the impact of fitting HNO₃ amount fractions in alternative regions, 1240 to 1400 cm⁻¹ and 1240 to 1800 cm⁻¹, was studied. The maximum difference in amount fractions calculated was dependent on the database used.

• the Pacific Northwest National Laboratory (PNNL) database was used as alternative infrared database to retrieve HNO₃ amount fractions of calibration mixtures produced by the permeation facility. A bias of 6.7 %, contrasting with 23 % identified using HITRAN, was found against HNO₃ permeation-based values.

Based on the measurements performed at the BIPM using FTIR calibrated with dynamic standards on one hand, and with molecular parameters found in the two databases HITRAN and PNNL, a strategy to further calibrate HNO₃ values measured by FTIR in standards of NO₂ in nitrogen is proposed. This is based on applying a correction to amount fraction values determined by the FTIR-HITRAN method, with the correction factor determined from the comparison with values from the Permeation system method, considered as the reference method. The corrected FTIR-HITRAN method, with traceability of values to the permeation method, can be applied reproducibly, provided that the FTIR gas cell's pathlength is regularly verified, and the spectral region fitted is defined.

2 Rational for comparison

The CCQM-P172 comparison was designed to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system.

HNO₃ has been chosen as the analyte for study because:

- it is present in gas standards as an impurity;
- it is amenable to measurement by spectroscopic methods;
- primary reference gas mixtures of HNO₃/N₂ are (generally) unavailable for calibration;
- traceability for spectroscopic measurements will rely on use of referenced molecular parameters (such as tabulated in the database HITRAN for example).

3 Quantities and Units

In this protocol the measurand was the amount fraction of nitric acid in nitrogen*, with measurement results being expressed in mol/mol and its multiples µmol/mol or nmol/mol.

(*it was recognized that participants would prepare standards of nitrogen dioxide with the nitrogen balance gas containing a small amount of oxygen that would not normally exceed 1000 μ mol/mol)

4 Schedule

The revised schedule for the project was as follows:

April 2017	Draft protocol distributed to participants;
May 2017 – April 2018	The participating laboratories prepare the mixtures and carry out
	their 1 st set of analysis (verification and stability test);
May to June 2018	Shipment of cylinders to the BIPM (last cylinder arrived in June);
July 2018 – December 2019	Analysis of mixtures at the BIPM;

Mach – April 2019 April 2019 – July 2020 October 2019 – September 2020 May 2021 July 2021	Shipment of cylinders from the BIPM to participants; 2 nd set of analysis of mixtures by the participants (stability); Reports of the participants; and Distribution of Draft A of this report. Distribution of a template form to request participants measured FTIR spectra Distribution of Draft P of this report.
June 2022 October 2022	Distribution of Draft B of this report.
0000001 2022	Distribution of multipole.

5 Standards preparation and measurements of participants

Laboratories taking part in this pilot study were required to submit one secondary standard of NO₂ in nitrogen at a nominal amount fraction of 10 μ mol/mol with a requirement that the HNO₃ amount fraction present in the mixture was between 100 nmol mol⁻¹ and 1000 nmol mol⁻¹.

Each laboratory was requested to submit mixtures contained in cylinders with a volume of 10 L or greater and pressurized to a minimum pressure of 12 MPa.

The choice of cylinder material and passivation technology employed remained the choice of the participant.

Participants were also required to perform measurements on the standards each month during a 3 month period before sending the standards to the BIPM and during the same period after their return.

5.1 Deviations from the protocol

During the course of the comparison, which included measurements at the BIPM starting in July 2018 and ending in December 2019, a number of technical events occurred, with various impacts on the measurements. They are listed below in chronological order:

• June 2018, to avoid potential back contamination due to sonic back flushing, cylinders pressure measurements were avoided at BIPM.

Exceptionally, it was decided to modify the BIPM usual FTIR (Fourier-transform infrared spectroscopy) measuring protocol for nitrogen dioxide measurements (in this occasion applied to nitric acid). In the normal procedure, pressure measurements of each cylinder to be compared are done systematically before the comparison. However, technical discussions with an NMI preparing such standards in June 2018 cautioned against the connection of a pressure gauge to the cylinder, as this could induce water contamination due to sonic back flushing. Water could then react with nitrogen dioxide into the cylinder, forming nitric acid and causing a bias into the measurement. As a result pressure measurements of the cylinders before starting their analysis by FTIR were not performed as usual, but the

assumption made that all submitted standards met the comparison protocol and were submitted with at least 12 M Pa, which later proved to not be the case.

• <u>16 July 2018, NMISA reported low HNO₃ amount fractions in their standards:</u>

The NMISA report was received just prior to the first measurement attempt at the BIPM (17 July 2018), and indicated that the HNO₃ amount fraction in their standard was between 22.0 to 26.3 nmol mol⁻¹, lower than the 100 nmol mol⁻¹ requested in the protocol. This required BIPM had to modify the temperature of the permeation facility to generate lower HNO₃ amount fractions than planned. Therefore, the measurement procedure at the BIPM was modified to perform measurements in two phases (two temperatures) for each of the two time series, which also induced more measurement time to account for the necessary stabilisation of the permeation chamber temperature.

The internal pressure of the cylinder submitted by NMISA was 10.5 MPa and not 12 MPa requested as minimum pressure in the protocol.

• <u>17 July 2018, first KRISS D634058 measurement attempt failed:</u>

The BIPM measurement schedule required measurements to start on 17 July 2018, but this was without knowledge of the nominal amount fraction in the cylinder, with the KRISS result form, indicating the HNO₃ amount fraction range and the cylinder internal pressure, received on 31 August 2018. The HNO₃ amount fraction measured in the cylinder, 260 nmol mol⁻¹, was outside the calibration range of the BIPM permeation facility (80 nmol mol⁻¹ to 250 nmol mol⁻¹), and could not be measured accurately.

The internal pressure of KRISS cylinder stated in the participant report was 8 MPa rather than 12 MPa as requested.

• <u>19 July 2018, first KRISS D634074 measurement attempt failed:</u>

The BIPM measurement schedule required measurements to start on 17 July 2018, but this was without knowledge of the nominal amount fraction in the cylinder, with the KRISS result form, indicating the HNO₃ amount fraction range and the cylinder internal pressure, received on 31 August 2018. The measurements were performed using an amount fraction range of 210 to 300 nmol mol⁻¹ based on the expected value in D634058. The amount fraction in the D634074 standard was however lower than 100 nmol mol⁻¹ and sufficient stability could not be achieved in the FTIR signal, and no result was recorded.

The internal pressure of KRISS cylinder stated in the participant report was 8 MPa rather than 12 MPa as requested.

• <u>31 July 2018, second KRISS D634074 measurement attempt failed:</u>

A second attempt to measure cylinder D634074 was performed on 31 July 2018. A lower amount fraction range on the calibration mixtures was used (45 to 160 nmol

mol⁻¹). However, sufficient stability could not be achieved in the FTIR signal, and no result was recorded.

• <u>6 December 2018, third KRISS D634074 measurement attempt failed:</u>

A third attempt to measure cylinder D634074 was performed on 6 December 2018. In this case a higher amount fraction range on the calibration mixtures was used (114 to 220 nmol mol^{-1}). With a measured amount fraction, close to 135 nmol mol^{-1} , sufficient stability could not be achieved in the FTIR signal, and no result was recorded.

• <u>13 December 2018, third KRISS D634058 measurement attempt:</u>

A third attempt to measure cylinder D634058 was performed on 13 December 2018. On this occasion the FTIR response had again difficulties to reach stability, and with previous attempts to perform the measurements the cylinder was emptied during this analysis. The results obtained on this measurement run were recorded.

• <u>12 February 2019, third KRISS D634058 and second NMISA D626420</u> measurement attempt failed:

Cylinders KRISS D634058 and NMISA D626420 were found empty during the fourth and third series of analyses.

5.2 Summary of participants' reports

Participants were invited to use spectroscopic techniques for the gas analysis (FTIR, TDLAS (Tunable diode laser absorption spectroscopy) and CRDS (Cavity ring-down spectroscopy) using reference data as found in databases of molecular parameters (such as HITRAN 2012). Table 1 summarizes information provided by laboratories, such as the spectroscopic technique, instrument type, detector, instrument purge/vacuum, gas cell path length, temperature and pressure measurements, software, database and region as well as additional information which would be useful in understanding the results of the comparison. All results forms can be found in ANNEX II - Measurement reports of participants.

From the submitted reports, and available information, we can summarize that:

- CENAM sent a standard, reporting HNO₃ amount fractions less than 59 nmol mol⁻¹, as measured by CENAM using FTIR anchored to the HITRAN database of molecular parameters.
- KRISS sent two standards, reporting HNO₃ amount fractions around 10 nmol mol⁻¹, as measured by KRISS using FTIR. They reported use of NO₂ and HNO₃ permeation tubes as gas references.

- NMISA sent one standard, reporting HNO₃ amount fractions less than 26.3 nmol mol⁻¹, as measured by NMISA using FTIR anchored to the HITRAN database of molecular parameters.
- NPL sent one standard reporting HNO₃ amount fractions around 470 nmol mol⁻¹ (first measured value), as measured by them with FTIR (and HITRAN database). The mixture was prepared by gravimetry from a parent mixture made of 500 μmol/mol NO₂ in nitrogen with 5 % O₂, adding 100 μmol/mol of H₂O (in the parent mixture) to induce a reaction with NO₂ and obtain the target HNO₃ amount fraction. The final amount fraction reported by NPL was 980 nmol mol⁻¹.
- VSL sent one standard, reporting HNO₃ amount fractions around 100 nmol mol⁻¹, as measured by them with CRDS using HNO₃ molecular parameters found in the PNNL database. The standard was a nominally 10 μmol mol⁻¹ NO₂ in nitrogen.

5.3 Participants' submitted results

The participants were requested to perform measurements on the standards each month during a 3 months period before sending the standards to the BIPM and during the same period after their return. Table 2 summarises the participants' submitted results where:

NMI	is the acronym of the participating national metrology institute;
Cylinder	identification code of the cylinder received by the participating laboratory;
Date	date at which the participating laboratory performed the value assignment of the specific standard
X _{NMI}	the HNO ₃ amount fraction assigned by the NMI;
$u(x_{\rm NMI})$	the standard uncertainty of the NMI's values.

Participants were also asked to report impurities measured in their standards. NO₂ was identified and quantified by nearly all participants (except CENAM) with amount fractions between 8.810 μ mol mol⁻¹ and 10.026 μ mol mol⁻¹ (see Table 3).

Lab	Spectroscopic technique	Instrument type	Detector	FTIR enclosure	Gas cell type	Gas cell path length	Path length measureme nt technique	Temperature and pressure measurements	Softwar e	Data base	Region
CENAM	FTIR	Thermo Scientific Nicolet 6700 FTIR spectrometer	MCT-high D*	stainless-steel enclosure that was constantly purged with extra dry air produced from a generator flowing at 10 L/min.	?	10 m	Measurement of two mixtures of CH ₄	Mensor barometer and the calibrated 100 Ω RTD temperature probe connected to the gas cell	B_FOS		1660 - 1760 cm ⁻¹
KRISS	FTIR	Bruker	?	?	?	5 m	?	?	?	HITRAN	1322.6 cm ⁻¹ – 1327.2 cm ⁻¹ ,
NMISA	FTIR	NICOLET iS50 FTIR	?	?	Gemini-Mars	10 m	?	?	?	?	?
NPL	FTIR	Thermo Scientific Nicolet 6700 FTIR spectrometer	MCT detector	box purged continuously during measurements with nitrogen at a flow rate of 10 L/min	heated gas cell (Specac, Cyclone C5)	$7.76\pm0.12\ m$	Measurement of N ₂ O, CO and CH ₄ in nitrogen mixtures.	?	BFOSv1. 1 MALT version 5.5.9	HITRAN 2012	1400-1800
VSL	CRDS	VSL homemade	-	-	-	3-4 km	-	-	VSL homemad e	PNNL	The laser was scanned around 3541 cm ⁻
BIPM	FTIR	Vertex70V	MCT-high D*	Vacuum instrument encloser	Gemini	45.3±2.1 m	Measurement of CO ₂ in air mixture	Barometer (Series 6000 Digital Pressure Transducer, Mensor, USA) 100 Ω RTD temperature probe attached to the White cell.	B_FOS	HITRAN 2012	1665-1770 cm ⁻¹

Table 1. Summary of information submitted by participating laboratories.

NMI		Date of	Assigned	Assigned standard	
	Cylinder	measurement	HNO ₃ amount fraction	uncertainty	
			$x_{\rm NMI}$ / (nmol/mol)	$u(x_{\rm NMI}) / (\rm nmol/mol)$	
		08/02/2018	7.6*	0.8	
		23/03/2018	26.0*	1.8	
CENAM	DT0020739	19/04/2018	50.0*	3.4	
		21/05/2020	13.0*	1.4	
		25/06/2020	59.0*	4.1	
		24/07/2020	15.0*	1.4	
		-	11.3*	1.7	
		-	-	-	
KRISS	D63 4058	-	-	-	
		-	-	-	
		-	11.3*	1.7	
		-	-	-	
KRISS	D63 4074	-	-	-	
		-	-	-	
		-	-	-	
		-	-	-	
		15/03/2018	26.3*	2.9	
	D62 6420	15/03/2018	22.0*	1.3	
NMISA		11/04/2018	24.4*	1.8	
		-	-	-	
		-	-	-	
		-	-	-	
		06/03/2018	470.0	35.0	
		29/03/2018	690.0	45.0	
NPL	2451	17/04/2018	810.0	50.0	
		16/04/2019	930.0	55.0	
		22/05/2019	940.0	55.0	
		21/06/2019	980.0	60.0	
		17/01/2018	83.0*	7.5	
		28/02/2018	90.0*	8.0	
VSL	VSL105805	29/03/2018	113.0	10.0	
		31/05/2019	133.0	12.0	
		23/08/2019	124.0	11.0	
		28/08/2019	104.0	9.5	

Table 2. HNO₃ amount fraction reported by participants following measurements performed before sending the cylinders to the BIPM and after their return. Empty cells indicate no value. KRISS and NMISA cylinders were emptied at the BIPM and therefore no further measurements could be performed. *amount fractions out of range of comparison protocol.

NMI		Date of	Assigned	Assigned standard
	Cylinder	measurement	NO ₂ amount fraction	Uncertainty
		by the NMI	$x_{ m NMI}$	$u(x_{\rm NMI})$
			(µmol/mol)	(µmol/mol)
		-	-	-
		-	-	-
CENAM	DT0020739	-	-	-
		-	-	-
		-	-	-
		-	-	-
		-	10.000	-
		-	-	-
KRISS	D63 4058	-	-	-
		-	-	-
		-	-	-
		-	-	-
		-	10.000	-
	D63 4074	-	-	-
KRISS		-	-	-
		-	-	-
		-	-	-
		-	-	-
		15/03/2018	10.026	0.674
		11/04/2018	9.911	0.666
NMISA	D62 6420	08/05/2018	9.888	0.664
		-	-	-
		-	-	-
		-	-	-
		06/03/2018	9.730	0.380
		29/03/2018	9.370	0.370
NPL	2451	17/04/2018	9.240	0.365
		16/04/2019	8.820	0.095
		22/05/2019	8.850	0.095
		21/06/2019	8.810	0.095
		05/01/2018	9.914	0.070
		01/03/2018	9.885	0.070
VSL	VSL105805	28/03/2018	9.804	0.070
		21/05/2019	9.844	0.070
		25/06/2019	9.900	0.070
		25/07/2019	9.914	0.070

Table 3. NO₂ amount fractions reported by participants. CENAM did not report NO₂ amount fractions.

6 BIPM measurement results

The BIPM operated an FTIR spectrometer to detect and quantify HNO₃ in the standards sent by participants. The FTIR responses were calibrated using two very distinct methods: the first based on direct reference to molecular parameters (reported in HITRAN and PNNL databases), the second based on calibration with dynamic mixtures of HNO₃ in nitrogen generated with a permeation system. Although HNO₃ permeation tubes contain a significant amount of H₂O, the permeation facility with its continuous weighing system provided values with typically lower uncertainties than FTIR anchored to either HITRAN or PNNL.

In this section, characteristic spectra observed on the analysed mixtures are displayed to highlight some difficulties in the quantification due to the different compositions of gas standards in cylinders and generated dynamically. BIPM measurement results are then presented with three different methods: first by calibration of the FTIR responses with dynamic mixtures (method 1), then by synthetic calibration anchored to HITRAN molecular parameters (method 2), and finally switching to the PNNL molecular parameters (method 3).

6.1 Characteristic spectra of the analyzed mixtures

In Figures 1-3 the spectra have been chosen as examples of types of spectra observed in the comparison exercise including dry cylinder type and BIPM permeation system ones. This provides a rapid graphical representation of the challenges and differences for fitting the FTIR spectra in different gas mixtures encountered in this study.

Figure 1 plots the absorbance spectrum of the mixture VSL105805 from VSL. The spectrum shows a clear signal for HNO₃ of the v₂ band at 1709 cm⁻¹ that corresponds to 111 nmol mol⁻¹ \pm 30 nmol mol⁻¹. The spectrum also shows a strong HNO₃ signal in the region 1200 cm⁻¹ to 1350 cm⁻¹ (not used for quantification in this work, as explained elsewhere¹) and a small signal in the region 3500 cm⁻¹ to 3700 cm⁻¹ (not used for quantification in this work). The spectrum also shows a strong NO₂ signal in the region 1500 cm⁻¹ to 1660 cm⁻¹ and in the region 2860 cm⁻¹ to 2930 cm⁻¹ that corresponds to an amount fraction of 9.8 to 9.9 µmol mol⁻¹ (see Table 3) according to VSL's submitted results. H₂O amount fraction, with FTIR signals in the regions 1200 cm⁻¹ to 1950 cm⁻¹ to 3500 cm⁻¹ to 4000 cm⁻¹, was below the limit of detection. Trace values of CO₂ and N₂O can also be observed within the regions 2100 cm⁻¹ to 2400 cm⁻¹. Simultaneous measurements of trace water performed by CRDS (HALO analyser) showed that the H₂O amount fraction was 75.6 nmol mol⁻¹ ± 2.3 nmol mol⁻¹. The challenge for the FTIR signal fitting in this case is to choose an appropriate spectral window to minimise and correct for in particular the NO₂ band overlap with the HNO₃ band centred as 1709 cm⁻¹.

Figure 2 plots the absorbance spectrum of a gas mixture generated by the BIPM permeation facility. The HNO₃ amount fraction corresponding to this spectrum is $974 \pm 19 \text{ nmol mol}^{-1}$. The spectrum also shows two weak NO₂ peaks in the region 1500 cm⁻¹ to 1660 cm⁻¹ and 2860 cm⁻¹ to 2930 cm⁻¹. According to BIPM analysis the NO₂ amount fraction corresponds to 0.029 µmol mol⁻¹ \pm 0.20 µmol mol⁻¹. In the case of H₂O according to the HALO analyser the amount fraction present in the spectrum is 1857 nmol mol⁻¹ \pm 111 nmol mol⁻¹. Trace values of CO₂ and N₂O can also be observed within the regions 2100 cm⁻¹ to 2400 cm⁻¹. The challenge for the FTIR signal fitting in this case is to choose

an appropriate spectral window to minimise and correct for in particular the H_2O band overlap with the HNO₃ band centred as 1709 cm⁻¹.

Figure 3 plots the absorbance spectrum of the NPL 2451 mixture. The HNO₃ amount fraction corresponding to this spectrum is 792 nmol $\text{mol}^{-1} \pm 36$ nmol mol^{-1} . In this occasion the NO₂ amount fraction according to the submitted results of NPL corresponds to a range between 8.81 µmol mol^{-1} and 9.73 µmol mol^{-1} . According to the HALO analyser the H₂O amount fraction in the mixture is 1278 nmol $\text{mol}^{-1} \pm 77$ nmol mol^{-1} . Trace values of CO₂ and N₂O can also be observed within the regions 2100 cm⁻¹ to 2400 cm⁻¹. The challenge for the FTIR signal fitting in this case is to choose an appropriate spectral window to minimise and correct for both the NO₂ and the H₂O band overlap with the HNO₃ band centred as 1709 cm⁻¹.



Figure 1. Infrared absorbance spectrum of VSL105805 mixture with a HNO₃ amount fraction of 110.88 nmol mol⁻¹ ± 30.70 nmol mol⁻¹.



Figure 2. Infrared absorbance spectrum of a dynamic mixture generated by the BIPM permeation facility with a HNO₃ amount fraction of 974 nmol mol⁻¹ \pm 19 nmol mol⁻¹.



Figure 3. Infrared absorbance spectrum of NPL 2451 mixture with a HNO₃ amount fraction of 791.71 nmol mol⁻¹ \pm 35.5 nmol mol⁻¹.

6.2 Method 1 - calibration with permeation system

The BIPM-HNO₃ permeation based reference gas facility combines gravimetry with dynamic generation of gas mixtures. The facility includes a magnetic suspension balance, a flow control system for the dynamic generation of gas mixtures and an auto-sampler equipped with a flow control system for the analysis of gas standards in cylinders. To limit adsorption of HNO₃ on surfaces, the auto-sampler was equipped before the comparison with Silcolloy® tubing material. The gas cylinders and the dynamic source of HNO₃ mixtures are ultimately connected to a FTIR Vertex 70V and to a trace water analyser (Tiger Optics HALO⁺), the latter being used only to quantify H₂O amount fractions in the dynamic mixtures. Each cylinder was value assigned using this facility following the procedure described in ANNEX I- BIPM Value assignment procedure.

The results of measurements, calibrated with dynamic standards, performed in all cylinders during the period July to December 2018 are listed in Table 4.

where:

$X_{ ext{BIPM.}i}$	is the i^{th} measurement result by the BIPM ($i = 1$ to 3);		
$u(x_{\text{BIPM},i})$	the standard uncertainty of the BIPM measurement;		

The nitric acid amount fraction reported by each participant (black dots) and the BIPM measured values (red dots) are plotted in Figure 4 to Figure 8, as a function of the measurement's date. The error bars of the participants (black) represent the standard uncertainty associated with the submitted values of the participants. The error bars of the BIPM measured values (red) represent the standard uncertainty associated with the BIPM measurement results.

6.3 Method 2 – referenced to HITRAN

The CCQM-P172 comparison was originally designed to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. For this reason, it is essential to compare the consistency of the BIPM measurements results traceable to dynamic standards against HITRAN values and between participants that performed absolute measurements using HITRAN molecular line parameters. Undeniably systematic uncertainties associated with pathlength and instrument line shape function may be observed but this type of comparison will contribute to a better understanding of such contributions and could lead to reductions in these systematic effects for future comparisons.

Table 5 lists the HNO₃ FTIR responses referenced to HITRAN data base 2012 of each measured spectrum (same as used to value assign the HNO₃ amount fractions listed in Table 4) where:

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X BIPM_HITRAN.i	is the i^{th} measurement result by the BIPM calculated using HITRAN 2012 ($i = 1 \text{ to } 3$);
<i>u(х_{віРМ_}ніт</i> кал,і)	the standard uncertainty of the calculate BIPM measurement;

The uncertainties in the FTIR responses were calculated considering the B-FOS^a contribution (described elsewhere¹) and the response stability defined in section 12.3.1.

When plotting the HNO₃ responses (Table 5) against the HNO₃ amount fractions (Table 4), derived on gases generated from the BIPM permeation facility, a slope of 1.23 is observed (see Figure 9). Reasons for such a deviation could be:

- a potential bias in the HITRAN values for the v_2 band at 1709 cm⁻¹ used for the HNO₃ response analysis (the uncertainty in this quantity was considered by Flores et al. ¹ to be 5%); or
- a bias in the on the optical path length evaluation (45.3 m \pm 2.1 m). The method to measure optical pathlength was based on the measurement of a calibrated CO₂ primary standard that was then retrieved by iterative calculations varying the input optical path length parameter in B-FOS to obtain the correct amount fraction. This method results in a relative standard uncertainty on the path length of 4.6 %, and while greater than the 1.3% reported for the methods of Flores et al.¹, should still be fit for purpose; or
- a bias caused by the presence of elevated water levels in the HNO₃ reference gas from the permeation system and the spectral window used for fitting the FTIR signal or the reference value calculated from the permeation system.

6.4 Method 3 – referenced to PNNL

The PNNL data base was chosen following VSL advice. VSL used PNNL rather than HITRAN data base mainly based on that the specific band (v1) that was used is not available in HITRAN and the proven reliability of the PNNL database².

PNNL is part of existing alternative infrared libraries for gas-analysis monitoring available from commercial and government sources, including also Midac Corporation, Infrared Analysis Corporation, the U.S. Environmental Protection Agency, Nicolet-Aldrich vapor-phase library and the National Institute of Standards and Technology (NIST). However, according to Sharpe et. al. 2004³, with the exception of the NIST and PNNL libraries, there is a lack of sample quantification, chemical impurities, insufficient resolution or system noise, and nonlinearities that limit the usefulness of these spectra for either laboratory analytical work or quantitative remote sensing. In the past PNNL has been compared against NIST data base using 12 different chemicals and 26 corresponding bands with the result that the data agree to within experimental uncertainties (with one

^a B-FOS is a BIPM software that allows the automatic setting of all instrument parameters into Bruker's proprietary OPUS software for control, spectral acquisition and on-line analysis through the use of MALT (Multiple Atmospheric Layer Transmission) spectrum analysis software, version 5.56.

exception). PNNL statistical uncertainty in absorbance values for most compounds is defined as 2% (1 σ) achieved by measuring multiple (typically \geq 9) path length– concentration and fitting a weighted Beer's law plot to each wavenumber channel³. HNO₃ was not included in this study since it is not available in NIST database.

Table 6 list the HNO₃ FTIR responses based on PNNL for each NMI cylinder using the same spectra as used to value assign the HNO₃ amount fractions listed in Table 4, where:

$x_{BIPM_PNNL.i}$	is the i^{th} measurement result by the BIPM calculated using PNNL ($i = 1$ to
	3);

 $u(x_{BIPM PNNL,i})$ the standard uncertainty of the calculate BIPM measurement;

When plotting the HNO₃ responses (Table 6) against the HNO₃ amount fractions (Table 4), derived on gases generated from the BIPM permeation facility, a slope of 1.06 is observed (see Figure 10).

The spectra were evaluated in the spectral region 1665 cm^{-1} to 1770 cm^{-1} . The uncertainties in the FTIR responses were calculated with a similar equation than FTIR responses anchored to HITRAN (see section 6.3), considering also three uncertainties sources due to the stability of HNO₃ in the gas cell defined in section 12.3.1, the uncertainty of the reference, in this case PNNL uncertainty and the contribution of the quantification by the software MALT.

According to PNNL spectra information (HNO3_5T Metadata.pdf, Version 1.0, December, 01) the calculated and estimated errors were "Type A : 2.5%, Type B: Best effort" including the corrections to the HNO₃ partial pressures for the groups of spectra recorded at temperatures of 278.2 K, 298.22 K and 323.15 K.

The combined uncertainty associated with FTIR measurements by PNNL at the nominal amount fraction x in the range 0.03 μ mol mol⁻¹ to 1 μ mol mol⁻¹ with the FTIR spectrometer configured with a 45.3±2.1 m gas cell was described by the following equation, with results expressed in μ mol mol⁻¹:

$$u(x_{BIPM_PNNL}) = \sqrt{\left(u_{stab_HNO3}\right)^2 + \left(u_{PNNL_HNO3}\right)^2 + \left(u_{Calc_HNO3}\right)^2} \quad (1)$$

Consequently, in a numerical equation with results expressed in μ mol mol⁻¹ by:

$$u(x_{BIPM_PNNL}) = \sqrt{(0.02)^2 + (0.025x)^2 + (0.017x)^2}$$
(2)

so that for an amount fraction of 200 nmol mol^{-1} a standard uncertainty of 21 nmol mol^{-1} was calculated.

The bias of around 6% observed between results anchored to PNNL compared to those calibrated by dynamic standards could be related to the production of the PNNL reference spectra. According to Chackerian et. al. 2003^4 the HNO₃ used as reference gas was synthesized by dripping 94% - 98% pure H₂SO₄ into a glass reaction vessel containing

99% pure NaNO₃. Using this procedure significant impurity features due to H₂O, CO₂, NO, NO₂, N₂O, HF and HCl, appeared in several parts of the spectra. These bands were removed by spectral subtraction wherein known absorbances for these molecules were combined with adjusted partial pressures so that impurity features were removed from each spectrum.

NMI	Cylinder	Measurement	1 st BIPM	Standard	Measurement	2 nd BIPM	Standard
		date	HNO ₃ amount fraction measurement	uncertainty	date	HNO3 amount fraction measurement	uncertainty
		1 st measurement	XBIPM1	u(xbipmi)	2 nd measurement	XBIPM2	<i>и(х</i> вірм2)
			nmol/mol	nmol/mol		nmol/mol	nmol/mol
CENAM	DT0020739	31/07/2018	48.8	20.8	05/12/2018	48.1	20.8
KRISS	D634058	19/07/2018	212.8	20.9	13/12/2018	156.4	20.9
KRISS	D634074	31/07/2018	stability not reached	-	06/12/2018	stability not reached	-
NMISA	D626420	17/07/2018	167.7	20.9	13/12/2018	140.1	20.9
NPL	NPL2451	03/08/2018	791.7	21.8	20/12/2018	784.6	22.0
VSL	VSL105805	31/07/2018	110.9	21.0	06/12/2018	117.6	20.8

BIPM HNO₃ amount fraction measurements with permeation system calibrated method

Table 4. Results of BIPM HNO₃ amount fraction measurements.

NMI	Cylinder	Measurement	1 st BIPM	Standard	Measurement	2 nd BIPM	Standard
		date	HNO3 FTIR response	uncertainty	date	HNO ₃ FTIR response	uncertainty
		1 st measurement	XHNO3_HITRANI	<i>u(x</i> hno3_hitran1)	2 nd measurement	XHNO3_HITRAN2	u(xhno3_hitran2)
			nmol/mol	nmol/mol		nmol/mol	nmol/mol
CENAM	DT0020739	31/07/2018	55.8	20.2	05/12/2018	48.2	20.2
KRISS	D634058	19/07/2018	261.9	24.3	13/12/2018	188.5	22.3
KRISS	D634074	31/07/2018	stability not reached	-	06/12/2018	stability not reached	-
NMISA	D626420	17/07/2018	215.8	23.0	13/12/2018	159.3	21.7
NPL	NPL2451	03/08/2018	972.4	55.1	20/12/2018	967.4	54.9
VSL	VSL105805	31/07/2018	143.0	21.4	06/12/2018	145.0	21.4

BIPM HNO3 amount fraction measurements with method referenced to HITRAN

*Table 5. FTIR HNO*₃ responses referenced to HITRAN 2012 data base.

NMI	Cylinder	Measurement	1 st BIPM	Standard	Measurement	2 nd BIPM	Standard
		date	HNO ₃ FTIR response	uncertainty	date	HNO ₃ FTIR response	uncertainty
		1 st measurement	XHNO3_PNNL1	$u(x_{\rm HNO3_PNNL1})$	2 nd measurement	XHNO3_PNNL2	$u(x_{\rm HNO3_PNNL2})$
			nmol/mol	nmol/mol		nmol/mol	nmol/mol
CENAM	DT0020739	31/07/2018	48.9	20.0	05/12/2018	47.7	20.1
KRISS	D634058	19/07/2018	227.7	21.1	13/12/2018	166.2	20.6
KRISS	D634074	31/07/2018	stability not reached		06/12/2018	stability not reached	
NMISA	D626420	17/07/2018	187.6	20.8	13/12/2018	166.2	20.6
NPL	NPL2451	03/08/2018	839.6	32.3	20/12/2018	836.4	32.2
VSL	VSL105805	31/07/2018	124.3	20.4	06/12/2018	129.1	20.4
NMISA NPL VSL	D626420 NPL2451 VSL105805	03/08/2018 31/07/2018	187.6 839.6 124.3	20.8 32.3 20.4	20/12/2018 06/12/2018	166.2 836.4 129.1	20.6 32.2 20.4

BIPM HNO₃ amount fraction measurements with method referenced to PNNL

*Table 6. FTIR HNO*₃ *responses referenced to PNNL reference spectra.*

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Figure 4. a) Nitric acid amount fraction values provided by CENAM (black dots) and measured by the BIPM (red dots) referenced to the HITRAN data base. b) Nitric acid amount fraction values provided by CENAM (black dots) and measured by the BIPM (red dots) calibrated by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value.



Figure 5. a) Nitric acid amount fraction values provided by KRISS (black dots) and measured by the BIPM (red dots) referenced to the HITRAN data base. b) Nitric acid amount fraction values provided by KRISS (black dots) and measured by the BIPM (red dots) calibrated by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value.

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Figure 6. a) Nitric acid amount fraction values provided by NMISA (black dots) and measured by the BIPM (red dots) referenced to the HITRAN data base. b) Nitric acid amount fraction values provided by NMISA (black dots) and measured by the BIPM (red dots) calibrated by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value.



Figure 7. a) Nitric acid amount fraction values provided by NPL (black dots) and measured by the BIPM (red dots) referenced to the HITRAN data base. b) Nitric acid amount fraction values provided by NPL (black dots) and measured by the BIPM (red dots) calibrated by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value.

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Figure 8. a) Nitric acid amount fraction values provided by VSL (black dots) and measured by the BIPM (red dots) referenced to the HITRAN data base. b) Nitric acid amount fraction values provided by VSL (black dots) and measured by the BIPM (red dots) calibrated by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value.



(FTIR calibrated with permeation system method)/ nmol mol⁻¹

Figure 9. Nitric acid amount fractions obtained by FTIR referenced to HITRAN 2012 against values calibrated by the permeation facility, for all cylinders listed in Table 4 and Table 5. The error bar represents the standard uncertainty (k=1) associated with the measured value.



(FTIR calibrated with permeation system method)/ nmol mol⁻¹

Figure 10. Nitric acid amount fractions obtained by FTIR referenced to PNNL against values calibrated by the permeation facility, for all cylinders listed in Table 4 and Table 5. The error bar represents the standard uncertainty (k=1) associated with the measured value.

7 Bias between nitric acid amount fractions anchored to PNNL, HITRAN and dynamic standards

To better characterise the apparent bias between nitric acid amount fractions anchored to PNNL, HITRAN and dynamic standards, the FTIR spectra acquired on the dynamic mixtures were treated also with the PNNL data. Thirty-two HNO₃ calibration spectra measured on mixtures from the permeation facility were reprocessed by B-FOS reconfigured to use PNNL spectra (HNO₃) and HITRAN line parameters (NO₂ and H₂O impurities) simultaneously. The mixtures were generated by the facility with an amount fraction range between 35 nmol mol⁻¹ to 980 nmol mol⁻¹ during July to December 2018.

As result a bias of 6.7% was observed between HNO₃ amount fractions anchored to PNNL and calibrated with permeation-based reference gas (see Figure 12). Such difference resulted four times smaller than when using HITRAN 2012 (23%), see Figure 11. HITRAN biases have been already reported by Pavlyuchko et. al. in 2015⁵, who observed that the average difference for the intensities of the fundamental transitions is only 0.3% for the fundamentals and 40% for the first overtones and combination bands in HITRAN 2012.

Finally Figure 13 shows the consistency between PNNL based CRDS (VSL, Table 2) and FTIR (Table 6) values where, regardless the important difference between the measurements and techniques, the nitric acid amount fractions were consistent.



(FTIR calibrated with permeation system method)/ nmol mol⁻¹

Figure 11. Nitric acid amount fractions obtained by FTIR referenced to HITRAN 2012 against values provided by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value. Measurements were performed on mixtures from the permeation system (water levels in the same order of magnitude as HNO₃ signals and trace NO₂ levels).



(FTIR calibrated with permeation system method)/ nmol mol⁻¹

Figure 12. Nitric acid amount fractions obtained by FTIR referenced to PNNL against values provided by the permeation facility. The error bar represents the standard uncertainty (k=1) associated with the measured value. Measurements were performed on mixtures from the permeation system (water levels in the same order of magnitude as HNO₃ signals and trace NO₂ levels)



Figure 13. a) Nitric acid amount fraction values provided by VSL (black dots) and measured by the BIPM (blue dots) referenced to the PNNL data base. The error bar represents the standard uncertainty (k=1) associated with the measured value.

8 Recalculation of the participants results by the BIPM

During the GAWG meeting in June 2021 it was agreed that the BIPM would distribute a template form to request the measured FTIR spectra of participants for further analysis. It was expected that the results of this analysis would provide further information on the agreement between MALT+CLSⁱⁱ+HITRAN users as well as different software packages used by the participants to generate their synthetic references spectra and to differentiate result disagreements associated with the spectra acquisition and the calculation procedure.

CENAM and NPL provided complete information to allow such analysis. NMISA and KRISS provided only partial information that did not allow this. VSL used CRDS and was not foreseen in this study.

Table 7 and Table 8 list the nitric acid amount fractions obtained using CENAM and NPL spectra and associated information. Since both participants were part of the CBKT trainingⁱⁱⁱ, the synthetic spectra calibration procedure including B-FOS (MALT+CLS) and HITRAN 2012 was the same than the BIPM except that NPL used the region 1400 cm⁻¹ -1800 cm⁻¹, which differs from the region used by the BIPM (1665 cm⁻¹ -1770 cm⁻¹). CENAM used the region 1660 cm⁻¹ -1760 cm⁻¹, that is a very similar region.

The analysis of CENAM spectra resulted in a number of observations listed below:

- Spectra recorded after the return of the cylinders from the BIPM (after May 2020) could not be analyzed correctly. They show strong water absorption features which interfere with the HNO₃ absorption bands. The HNO₃ signal itself is weak and falls below the limit of detection in the spectrum recorded on 25 June 2020.
- Values of HNO₃ recalculated by the BIPM are higher than those calculated by CENAM, with a constant relative bias of 21%. The reason of such difference could be related to the accuracy of the optical path length reported by CENAM.

The analysis of NPL spectra, using the same spectral region as NPL (1400 cm^{-1} - 1800 cm^{-1}), leads to an averaged relative difference of 2%, well covered by the uncertainties.

ⁱⁱ Classical least-squares.

ⁱⁱⁱ The BIPM knowledge transfer programme, also known as the CBKT, is a BIPM training programme aimed to scientists from NMIs/DIs of Member States and Associates to broad their skills on FTIR operation, and interpretation of FTIR spectra for gas analysis. For more details see: <u>https://www.bipm.org/fr/committees/cb/cbkt/cbkt-ca-bipm/secondment-opportunities</u>.

NMI	Cylinder	Date of measurement by the NMI	Value assigned by the laboratory	Value recalculated by the BIPM
			x _{NMI} / (nmol/mol)	x _{BIPMSpectNMI} / (nmol/mol)
		08/02/2018	7.6	9.1
		23/03/2018	26.0	31.93
CENAM	DT0020739	19/04/2018	50.0	60.88
		21/05/2020	13.0	*
		25/06/2020	59.0	**
		24/07/2020	15.0	***

Table 7. Nitric acid value obtained by the BIPM using CENAM submitted spectra, instrumental data and BIPM synthetic spectra calculation procedure in the spectra region 1665 cm⁻¹ to 1770 cm⁻¹ based on HITRAN 2012 data base. * HNO₃ not possible to determine due to the high interference with remaining H_2O . ** HNO₃ not possible to determine due to negative H_2O signal on the spectra region. *** HNO₃ not possible to determine, low HNO₃ signal.

NMI	Cylinder	Date of measurement by the NMI	Value assigned by the laboratory	Value recalculated by the BIPM
			x _{NMI} / (nmol/mol)	x _{BIPMSpectNMI} / (nmol/mol)
		06/03/2018	470.0	470.47
		29/03/2018	690.0	697.89
NPL	2451	17/04/2018	810.0	808.54
		16/04/2019	930.0	935.66
		22/05/2019	940.0	952.72
		21/06/2019	980.0	993.31

Table 8. Nitric acid value obtained by the BIPM using NPL submitted spectra, instrumental data and BIPM synthetic spectra calculation procedure in the spectra region 1400 cm⁻¹ - 1800 cm⁻¹ based on HITRAN 2012 data base.

9 Alternative spectral regions for HNO₃ analysis

The impact of retrieving HNO₃ amount fractions in different spectral regions using different references has been studied. The study was performed analyzing the thirty-two HNO₃ calibration samples generated by the permeation facility retrieved using HITRAN and PNNL in the regions 1240 to 1400 cm⁻¹, Figure 14 and Figure 15, (bands v_3 and v_4) and 1240 to 1800 cm⁻¹, Figure 16 and Figure 17 (bands v_2 , v_3 and v_4 used by NPL) and 1665 to 1770 cm⁻¹ (band v_2 used in this work reported in sections 6.3 and 6.4).

The resulting differences are listed in Table 9. From this study there is a clear difference in the amount fractions retrieved using HITRAN in the different spectral regions. In the

case of PNNL, the three relative differences are all comparable, with any difference between them covered by the uncertainty due to instabilities of the HNO₃ signal in the FTIR gas cell (u_{stab} _HNO₃ = 20 nmol mol⁻¹).

Region	Relative difference between HITRAN	Relative difference between PNNL and permeation method
cm ⁻¹	and permeation method	%
	%	
1200 to 1400	20	6.1
1240 to 1800	31	6.2
1665 to 1770	23	6.7

Table 9. Comparison of HNO₃ amount fractions obtained by FTIR anchored to HITRAN and PNNL database, in three different spectral regions. Results are expressed as the relative difference to values obtained by the permeation method.



Figure 14. Nitric acid amount fractions obtained by FTIR referenced to HITRAN in the region 1200 cm⁻¹ to 1400 cm⁻¹ against values obtained by the permeation facility.



Figure 15. Nitric acid amount fractions obtained by FTIR referenced to PNNL in the region 1200 cm⁻¹ to

1400 cm⁻¹against values obtained by the permeation facility.



Figure 16. Nitric acid amount fractions obtained by FTIR referenced to HITRAN in the region 1240 cm⁻¹ to 1800 cm⁻¹ against values obtained by the permeation facility.



Figure 17. Nitric acid amount fractions obtained by FTIR referenced to PNNL in the region 1240 cm⁻¹ to 1800 cm⁻¹ against values obtained by the permeation facility.

10 Strategy to quantify HNO₃ in gaseous standards of NO₂ accurately

The results of the comparison demonstrate differences in HNO₃ amount fraction determinations in gaseous standards of NO₂, by the 3 different methods studied in detail, notably FTIR-HITRAN, FTIR-PNNL and the Permeation System method, but that the differences are well correlated as a function of amount fraction. In considering the calculated uncertainties of these methods, the Permeation system method can be chosen as a reference method and chosen to correct the other two methods to arrive at consistent HNO₃ amount fraction determinations.

The three methods employed by the BIPM to calibrate HNO₃ responses obtained by FTIR, described in sections 6.2, 6.3 and 6.4, have quite different standard uncertainties, as listed in Table 4, Table 5 and Table 6. Figure 18 displays the standard uncertainty of the HNO₃ amount fraction in the measurements range of this comparison, calculated for all the dynamic mixtures generated by permeation, and for each of the three methods. This plot highlights that:

- Below an amount fraction of 200 nmol mol⁻¹, all three methods are heavily influenced by the uncertainty contribution component that considers the sticky nature of HNO₃ and the instrument (FTIR) noise (see section 12.3.1) (20 nmol mol⁻¹);
- Above 200 nmol mol⁻¹, method 1 (permeation) provides the lowest uncertainties, with a relative value around 2.5 %. In comparison, method 2 (HITRAN) is associated with a relative uncertainty close to 6 % and method 3 (PNNL) close to 4 %.



Figure 18. Uncertainties of the nitric acid amount fractions measured by FTIR calibrated with the permeation facility (black dots, Table 4), HITRAN 2012 (red dots, Table 5) and PNNL (blue dots, Table 6), calculated on all dynamic mixtures generated for this comparison.

It is proposed to use method 1 (permeation) as a reference methods, based on the measurement uncertainties and the confidence in its traceability.

The values produced by FTIR methods (HITRAN and PNNL referenced) can be corrected by the relationships described in this comparison report.

For the case of the PNNL referenced FTIR method, it appears that the correction factor would be almost constants across the various spectral windows considered in this study. However, since the PNNL database is not readily accessible to all users, the BIPM and others will more readily have access to HITRAN referenced FTIR measurements. In this case, the fitted spectral window must be stated, as the correction factor varies as a function of fitted spectral window as demonstrated in Table 9.

An FTIR method for HNO₃ amount fraction determination referenced to HITRAN, in the spectral window 1665 cm⁻¹ to 1770 cm⁻¹, produces values which can be corrected with with the information displayed in Figure 11. As observed in this figure, the measurement results are best fitted with a straight line of equation

$$x_{\rm HITRAN} = b_0 + b_1 x_{\rm BIPM} \tag{3}$$

In which the parameters b_i have the values and uncertainties displayed in Table 10, when the uncertainty associated with x_{HITRAN} is limited to the noise and HNO₃ stability.

Parameter	Value
b_0 / (nmol mol ⁻¹)	-4.26004
b_1	1.23601
$u(b_0) / (nmol mol^{-1})$	11.876
$u(b_1)$	0.0209
$u(b_0,b_1) / (\text{nmol mol}^{-1})^2$	-0.20735

 Table 10. Parameters of a straight-line model calibration function for the FTIR responses (see Figure 11).

Since this is a straight line passing through the origin within it stated uncertainties, this can be approximated also by a simple multiplicative correction factor, where the amount fraction of HNO₃ determined by the FTIR-HITRAN method (from fitting in the spectral window 1665 cm⁻¹ to 1770 cm⁻¹) can be corrected to the Permeation Method Reference values by multiplying by the factor 0.81 and taking into account the uncertainty of the linear fit in Table 10.

The above parameters and strategy will be applied at the BIPM for the quantification of HNO₃ in standards of NO₂ in nitrogen, including dynamic standards and cylinders. Although it is valid for the range of HNO₃ amount fractions between 20 nmol mol⁻¹ and 1000 nmol mol⁻¹, values below 200 nmol mol⁻¹ are expected in these standards. In this range, the uncertainty will be dominated by the instrument noise and HNO₃ stability (20 nmol mol⁻¹).

11 Conclusions of the comparison

The study was complicated by the stability characteristics of the standards measured and potential interferences from other species when fitting FTIR spectra of HNO₃.

Based on the results, notably from BIPM, NPL and VSL measurements, there is evidence to support:

- a) FTIR methods (referenced to the same molecular parameters) can be reproduced in different laboratories for the measurement of HNO₃ amount fractions in the 100 nmol mol⁻¹ to 1000 nmol mol⁻¹ range, within the magnitudes of measurement uncertainty presented in this report;
- b) The Permeation based method for HNO₃ has sufficiently small uncertainties for it to be used as a reference method for nitric acid amount fraction measurements, with correction factors for FTIR methods for HNO₃ absolute quantification that can be calculated and applied using the data presented in this study report;
- c) Two different spectroscopic methods, CRDS and FTIR fitting either individual spectral lines or bands respectively, and using references in spectral databases, for the measurement of HNO₃ amount fractions in the 100 nmol mol⁻¹ to 1000 nmol mol⁻¹ range, were found to be consistent within the magnitudes of measurement uncertainty presented in this report. If the relative uncertainties were reduced, differences in the methods would be expected based on which lines or spectral windows were employed.
- d) Potential biases (with respect to the Permeation reference method) are reduced in calculating HNO₃ absolute amount fractions by using the PNNL data base molecular parameters instead of those found in HITRAN 2012.
- e) HNO₃ amount fractions could be quantified using one or a combination of several of the absorption bands v₂, v₃ and v₄ in the spectral region 1240 cm⁻¹ to 1800 cm⁻¹. In the case of using the PNNL database, the impact of using different spectral regions for calculating HNO₃ amount factions was less than 1 %. This contrasts with the HITRAN 2012 database, where differences as large as 11 % were found.
- f) The production of reference spectra and/or molecular parameters with uncertainties below 1 % is highly recommended to further improve HNO₃ quantification by spectroscopic methods, and consequently for standards of NO₂ in nitrogen in which HNO₃ is still a major impurity.
- g) The HITRAN 2012 HNO₃ line strengths of the absorption bands v₂, v₃ and v₄ were found to be higher compared to PNNL database and the permeation method confirming recent independent observations⁶.

12 ANNEX I- BIPM Value assignment procedure

The BIPM-HNO₃ primary gas facility combines gravimetry with dynamic generation of gas mixtures. The facility includes a magnetic suspension balance, a flow control system for the dynamic generation of gas mixtures and an auto-sampler equipped with a flow control system for the analysis of gas standards in cylinders. To limit adsorption of HNO₃ on surfaces, the auto-sampler was refurnished before the comparison with Silcolloy® tubing material. The gas cylinders and the dynamic source of HNO₃ mixtures are ultimately connected to a FTIR Vertex 70V and to a trace water analyser (Tiger Optics HALO⁺), the latter being used only to quantify H₂O amount fractions in the dynamic mixtures.

The operation and automation of the ensemble of instruments was achieved through a LabView® programme developed by members of the BIPM Chemistry Department.

The amount fractions of the dynamically produced gas mixtures obtained with the BIPM facility, denoted as x_{BIPM} in this document or x_{HNO3} in this section, are calculated following the expression below:

$$x_{\text{HNO}_3} = \left(\frac{P \cdot V_m}{q_v \cdot M_{\text{HNO}_3}}\right) - \left(\frac{M_{\text{NO}_2} \cdot x_{\text{NO}_2}}{M_{\text{HNO}_3}}\right) - \left(\frac{M_{\text{H}_2} \circ \cdot x_{\text{H}_2} \circ}{M_{\text{HNO}_3}}\right)$$
(4)

where:

 $x_{\rm HNO_3}$ is the HNO₃ amount fraction in nmol·mol⁻¹;

P is the HNO₃ permeation rate in ng·min⁻¹;

 $V_{\rm m} = 22.4038 \text{ L} \cdot \text{mol}^{-1}$, is the molar volume of N₂ at standard conditions (273.15 K, 101.3 kPa);

 q_{ν} is the total flow rate of N₂ given by the sum of carrier nitrogen ($q_{\nu \text{ molbloc}2}$) and the diluent nitrogen ($q_{\nu \text{ molbloc}1}$) flows rates in mL·min⁻¹ at standard conditions (273.15 K, 101.325 kPa);

 $M_{\rm HNO_2}$ = 63.0130 g.mol⁻¹, is the molar mass of HNO₃;

 $M_{\rm NO_2}$ = 46.0055 g·mol⁻¹, is the molar mass of NO₂;

 $M_{\rm H_2O}$ = 18.0153 g·mol⁻¹, is the molar mass of H₂O;

 $x_{\rm NO_2}$ is the NO₂ amount fraction in nmol·mol⁻¹ measured by FTIR spectroscopy;

 $x_{\rm H_2O}$ is the H₂O amount fraction in nmol·mol⁻¹ on the mixtures.

The H₂O amount fraction on the mixtures was calculated using the following equation:

$$x_{\rm H_20} = (x_{\rm H20_Cal} - x_{\rm H20_sys}) - x_{\rm H20_std}$$
(5)

Where:

• $x_{\text{H2O}_{\text{Cal}}}$ is the H₂O amount fraction measured by the instrument HALO⁺ analyser calibrated by NPL, typically of the order of 100 nmol mol⁻¹ during the comparison.
The standard relative uncertainty is 3% according to the instrument calibration certificate;

- $x_{\text{H2O}_{\text{sys}}}$ is the amount fraction of H₂O into the system (tubing and permeation chamber without any permeation tube). A typical value of 50 nmol mol⁻¹ was estimated before the comparison, with a standard uncertainty of 11.5 nmol mol⁻¹; and
- $x_{\rm H2O_std}$ is a term to take into account the uncertainty contribution due to the stability of the HALO⁺ response, set to zero with a standard uncertainty equal to 3.66 nmol mol⁻¹ (standard deviation of the mean).

Uncertainties associated with each HNO₃ amount fraction x_{HNO3} in gas mixtures produced by permeation of nitric acid, $u(x_{HNO3})$, are calculated by means of the software GUM Workbench V.2.3⁷. An example of the uncertainty budget is listed below:

Quantity	Estimate	Assumed	Standard	Sensitivity	Uncertainty	Index
		distribution	uncertainty	coenicient	contribution	%
			$u(x_i)$	<i>ci=∂x</i> N02/∂x	$u_i(\gamma)$	
	Xi				mol·mol ⁻¹	
Р	1500	Normal	8.3	0.067	0.55	1.9
	10 ⁻⁹ g min ⁻¹		10 ⁻⁹ g min ⁻¹		10 ⁻⁹	
$V_{\rm m}$	22.4038	Normal	340.00	4.5	1.5	0.0
	$L \text{ mol}^{-1}$		10 ⁻⁶ L mol ⁻¹		10^{-12}	
$q_{v { m molbloc1}}$	5.332	Normal	80	-19	-1.5	0.0
	$L \min^{-1}$		10 ⁻⁶ L min ⁻¹		10^{-12}	
M _{NO2}	46.0055	Normal	1.40	-1.06	-2.2	0.0
	$g mol^{-1}$		$10^{-3} \mathrm{g} \mathrm{mol}^{-1}$	10^{-3}	10 ⁻⁶	
$M_{\rm HNO3}$	63.013	Normal	1.17	-1.4	-2.4	0.0
	$g mol^{-1}$		$10^{-3} \text{ g mol}^{-1}$		10^{-12}	
M _{H2O}	18.0153	Normal	1.4	-0.68	-0.950	0.0
	$g mol^{-1}$		10^{-3} g mol ⁻¹		10 ⁻⁶	
$x_{\rm NO2_Allan}$	0	Normal	3.00	-0.73	-2.2	29.3
	$10^{-9} \text{ mol mol}^{-1}$		10^{-9} mol mol ⁻¹		10 ⁻⁹	
$x_{\rm NO2_BIPM}$	0.1	Normal	0.09	-0.73	-0.06	0.0
	$10^{-9} \text{ mol mol}^{-1}$		$10^{-12} \text{ mol mol}^{-1}$		10 ⁻⁹	
$x_{\rm H2O_sys}$	50	Rectangular	11.5	0.29	3.3	66.5
	$10^{-9} \text{ mol mol}^{-1}$		10^{-9} mol mol ⁻¹		10 ⁻⁹	
$x_{\rm H2O_Cal}$	92.70	Normal	1.39	-0.29	-0.40	1.0
	$10^{-9} \text{ mol mol}^{-1}$		10^{-9} mol mol ⁻¹		10 ⁻⁹	
$x_{\rm H2O_std}$	0	Normal	1.64	-0.29	-0.47	1.3
	$10^{-9} \text{ mol mol}^{-1}$		10^{-9} mol mol ⁻¹		10 ⁻⁹	

Quantity	Value	Standard Uncertainty
XHNO3	87.7 nmol∙mol ^{−1}	4.05 nmol·mol ⁻¹

11. Uncertainty budget for a HNO₃ /N₂ primary mixture generated with the BIPM facility.

The uncertainty components for P, $V_{\rm m}$, q_{ν} , $M_{\rm NQ}$, and $M_{\rm HNQ}$ are fully described elsewhere⁸.

The amount fraction of NO₂ into the HNO₃ mixture was calculated using the HITRAN data base parameters and the methodology described elsewhere¹ summarised here for completeness reasons.

The synthetic spectra used to analyze NO₂ were created using integrated line strengths and other line parameters extracted from HITRAN 2012 (unchanged in version 2016) of the v_3 band located around 6.2 µm. According to Rothman et al.⁹ those parameters have an uncertainty of 3% that is based on the agreement between experimental studies done

by Benner et al.¹⁰ In the absence of other experimental evidence challenging this value, 3% was retained as the "global" uncertainty component for HITRAN 2012, $u_{HITRAN_NO2} = 3\%$.

The uncertainty in the NO₂ amount fraction determination by MALT_{4.4}+CLS, u_{calc_NO2} , was assessed by varying MALT-CLS input parameters, as suggested in the GUM and studying the effect on the predicted amount fraction. This method is defined as a sensitivity study. Each MALT_{4.4}+CLS input parameter variation was chosen according to a range delimited by its standard uncertainty $x_i - u(x_i)$ to $x_i + u(x_i)$. The contribution to the total standard uncertainty was considered equal to half the variation (ΔY) observed in the amount fraction. Details are fully described elsewhere¹.

$$u(x_{\text{NO2}_\text{BIPM}}) = \sqrt{\left(u_{\text{HITRAN}_\text{NO2}}\right)^2 + \left(u_{\text{Calc}_\text{NO2}}\right)^2} \tag{6}$$

and in a numerical equation with results expressed in μ mol mol⁻¹ by:

$$u(x_{\text{NO2}_\text{BIPM}}) = \sqrt{(0.03x)^2 + (0.015x)^2}$$
(7)

The noise of the FTIR response, u_{NO2_Allan} , was also considered. This contribution was equal to 20 nmol/mol. These parameters are only valid for amount fractions in the range of 5 µmol mol⁻¹ to 15 µmol mol⁻¹.

12.1 Correlations

Non-zero covariances, $u(x_{HNO_3,i}, x_{HNO_3,j})$ were included in the uncertainty calculations because all dynamic mixtures were derived from the same BIPM facility and an error in the analyte content of the one gas is considered to propagate to all gas mixtures in a positive correlated fashion. The covariance between two calibration gas mixtures *i* and *j* is described as follows:

$$u(x_{HNO_{3,i}}, x_{HNO_{3,j}}) = \gamma \left[u(x_{HNO_{3,i}}) \right]^2,$$
(8)

Where $u(x_{HNO_3,i})$ is the standard uncertainty of the more concentrated mixture as given by equation 4,

$$\gamma = \frac{q_j}{q_i} \tag{9}$$

is the dilution factor of the total gas flows q_j and q_i (with $q_j < q_i$). Note that as the HNO₃ calibration gas mixtures generated with the facility are distributed in a small range of amount fractions (typically 30 nmol/mol to 990 nmol/mol), the dilution factor is often close to 1, and the covariances often close to the variances $u(x_{\text{HNO3},i})^2$.

12.2 Regression analysis

The procedure outlined in ISO 6143:2001 (Gas analysis-Comparison methods for determining and checking the composition of calibration gas mixtures) was used for the calibration of HNO₃ amount fractions in participants standards by the dynamic standards generated with the BIPM facility.

All calculations were performed with B_LEAST, a computer program which implemented the methodology of ISO 6143:2001, and takes into consideration uncertainties in both axes for regression analysis.

12.3 FTIR analysis of gas standards

Analysis of all gas standards was undertaken to quantify nitrogen dioxide and moisture within the gas standards, and to compare these with the impurities and their uncertainties reported by the participating laboratories.

12.3.1 FTIR Spectra acquisition

A vacuum Bruker Vertex 70v FTIR Spectrometer equipped with a RockSolid interferometer (vacuum better than 0.2 hPa), with 1 cm⁻¹ resolution (0.16 cm⁻¹ optional), a 40 mm beam diameter, a globar source and CaF₂ beam splitter was used for the study. The spectrometer was configured with a MCT-high D* liquid N2-cooled mid-infrared detector and a multi-pass White-type gas cell of volume 8 L (Gemini Scientific Instruments, USA) with an optical path of 45.3 ± 2.1 m. The wetted surfaces of the gas cell were electro-polished stainless steel treated with silconert 2000 (Silcotek) and gold (mirror coatings) to minimize surface adsorption and desorption effects for NO₂ and HNO₃. The interferometer was scanned at 64 scans min⁻¹ and spectra co-added for five minutes to obtain an acceptable signal-to-noise ratio. The transmission spectra of gas reference standards obtained following this procedure had a very high signal to noise ratio of typically ~1 x 10⁴ peak-peak from 2400 cm⁻¹ - 4700 cm⁻¹. By comparison the main NO₂ peak had absorbance in the range 0.04 $abs_{10} - 0.16 abs_{10}$.

In order to prevent nonlinear responses produced by excess photon flux reaching the detector special care was put into adjusting the instrument parameters of the software to ensure that the apparent intensity from the detector was zero at 700 cm⁻¹.

The spectrometer user interface was controlled using a BIPM developed software named B-FOS, that allows the automatic setting of all instrument parameters into Bruker's proprietary OPUS software for control, spectral acquisition and on-line analysis through the use of MALT (Multiple Atmospheric Layer Transmission)¹¹ spectrum analysis software, version 5.56. MALT retrieves concentrations of each trace gas in the sample from a least-squares fit to the measured spectrum based on a model calculation and Hitran line parameters⁹. This code is the basis for quantitative analysis of open and closed path FTIR trace gas measurements and has been compared with other codes such as SFIT¹²

for ground based solar FTIR measurements with agreement of better than 0.7% (Griffith et al.¹³).

The gas sample, from either the permeation system or from a high pressure cylinder, flows from the HNO₃ facility sampling manifold through the White cell, and then to waste. The sample pressure and temperature are measured in real time by means of a calibrated barometer (Series 6000 Digital Pressure Transducer, Mensor, USA) and a calibrated 100 Ω RTD temperature probe attached to the White cell.

The White cell has a volume of ~8 L and the sample flows at ~2 L·min⁻¹. Assuming perfect mixing in the cell we estimate that an initial sample at time t = 0 s has been 99.9 % replaced after 100 min of flow, and 99.9999 % replaced after 120 min. Accordingly, to ensure complete exchange of sample, spectrum acquisition started at t = 0 but only the measured spectra obtained after flowing the sample through the White cell for 100 min were used for the amount fraction determination. We also empirically verified that after 100 min of flow, the sample was completely exchanged, within the bounds of measurement uncertainty.

Calculations were performed using the HNO₃ v_2 band at 1709 cm⁻¹.

12.3.1 HNO₃ signal stability uncertainty contribution

Due to the sticky nature of HNO₃¹⁴ two components were considered as contributors to the uncertainty of the HNO₃ measurements by FTIR. The first was a component related to the passivation¹⁵ period necessary to reduce the effect of HNO₃ sticking to the cell walls and the second due to the instrument noise when measuring a constant amount fraction of HNO₃. In the previous work this uncertainty component due to the passivation period was determined by sampling the gas mixtures generated by the facility with the FTIR gas cell until the instrument response to HNO₃ was stable, which took typically 15 hours¹.

A flow rate of $2 \text{ L} \cdot \text{min}^{-1}$ was used in this work for replacing 99.9999 % of the gas in the cell in 120 minutes meaning 240 L of gas were flushed into the cell for each measurement (30 times the gas cell volume). Measurements were performed after 100 minutes and the uncertainty for these measurements took into account the maximum difference in concentration that would have been achieved with 15 hours of flushing.

This difference on average was calculated to be 35 nmol mol⁻¹. Considering this as the upper (b_+) and lower (b_-) boundaries for HNO₃ differences, the uncertainty due the passivation period was evaluated using the equation:

$$u_{\text{pass}}^{2}(x_{\text{HNO3}}) = \frac{(b_{+} + b_{-})^{2}}{(12)}$$
(10)

resulting in $u_{\text{pass}}(x_{\text{HNO3}}) = 20 \text{ nmol mol}^{-1}$.

The second uncertainty source, instrument noise at a constant HNO₃ amount fraction, was estimated to result in an uncertainty contribution of only $u_{\text{noise}}(x_{\text{HNO3}}) = 4 \text{ nmol mol}^{-1}$. The combination of both contributions was then equivalent to u_{stab} HNO₃ = 20 nmol mol⁻¹.

12.3.2 H₂O determination by CRDS

The determination of moisture amount fractions in the dynamic mixtures was performed by means of the trace water analyser (Tiger Optics HALO⁺) calibrated by NPL in July 2017. Table 12 lists the amount fractions measured in each of the participant mixtures as indicative measurements.

NMI	Cylinder	Measurement	<i>X</i> H2O(1)	$u(x_{\rm H2O(1)})$	Measurement	<i>X</i> H2O(2)	$u(x_{\mathrm{H2O}(2)})$
		date	(nmol/mol)	(nmol/mol)	date	(nmol/mol)	(nmol/mol)
CENAM	DT0020739	31/07/2018	644.08	19.32	05/12/2018	648.82	19.46
KRISS.3	D634058	17/07/2018	811.17	24.34	19/07/2018	823.49	24.70
KRISS.4	D634074	19/07/2018	655.34	19.66	31/07/2018	697.31	20.92
NMISA	D626420	17/07/2018	33.93	1.02	13/12/2018	102.91	3.09
NPL	NPL2451	03/08/2018	1277.84	38.34	20/12/2018	1304.14	39.12
VSL	VSL105805	31/07/2018	75.56	2.27	06/12/2018	60.42	1.81

BIPM H₂O Measurements

Table 12. H_2O amount fraction measured in cylinder gas standards by the BIPM using the HALO+ analyser.

13 Bibliography

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14 ANNEX II - Measurement reports of participants

CENAM

Before shipping to the BIPM

(No report)

Post BIPM measurements

Result form CCQM-P172-R

A1. General information

Institute	Centro Nacional de Metrología			
Address	Carretera a los Cués km 4,5, El Marqués, Qro., Mexico.			
Contact person	Manuel de Jesús Ávila Salas / Jorge Koelliker Delgado			
Telephone	442 211 0500	Fax		
Email*	mavila@cenam.mx / jkoellik@cenam.mx			
Serial number of cylinder	DT0020739			
Cylinder pressure as received	1200 psi			

A2. Results

Description of measurement	Date of measurement	Nitric acid mole fraction X _{HNO3} / µmol/mol	Expanded uncertainty <i>U</i> (x _{HNO3}) / µmol/mol	Coverage factor
(Preparation)	-	-	-	-
(Stability 1)	08/02/2018	7.6x10 ⁻³	1.5x10 ⁻³	2
(Stability 2)	23/03/2018	2.6x10 ⁻²	3.6x10 ⁻³	2
(Stability 3)	19/04/2018	5.0x10 ⁻²	6.8x10 ⁻³	2

Cylinder 1 – Before shipping to the BIPM

Cylinder 1 – Post BIPM measurement

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

Description of measurement	Date of measurement	Nitric acid mole fraction X _{HNO3} / µmol/mol	Expanded uncertainty <i>U</i> (<i>x</i> _{HNO3}) / µmol/mol	Coverage factor
(Preparation)	-	-	-	-
(Stability 1)	21/05/2020	1.3x10 ⁻²	2.7x10 ⁻³	2
(Stability 2)	25/06/2020	5.9x10 ⁻²	8.1x10 ⁻³	2
(Stability 3)	24/07/2020	1.5x10 ⁻²	2.8x10 ⁻³	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The mathematical model used to calculate the uncertainty in the composition of mixture analyzed is:

$$u = \sqrt{(u(x)Hitran)^2 + (u(x)rep)^2 + (u(x)calcMalt)^2}$$

Were the uncertainty components considered are the following:

- u(x)rep; Uncertainty of the repeatability of the measurement day, the standard deviation of six measurements made by means of the automatic adjustment of MALT is considered, in the measurement time interval that is considered stable.
- u(x)Hitran; Uncertainty due to the consideration of synthetic spectra from the HITRAN database for HNO₃, data were taken from reference [1].
- *u*(*x*)*calcMalt*; Uncertainty due to quantification by MALT, the value was taken from reference [1].

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis¹.

The mixture was analyzed by means of a Thermo Scientific Nicolet 6700 FT-IR spectrometer configured with a mercury cadmium telluride (MCT-high D*) liquid nitrogen cooled mid infrared detector.

To isolate the spectrometer of any interference species from the environment, this FT-IR was placed in a stainless-steel enclosure that was constantly purged with extra dry air produced from a generator flowing at 10 L/min.

The path length of the gas multipass cell of 10 m was measured using two reference materials of methane. The 10 m cell had a volume of 2 L, and the sample flow rates were kept at 0.75 mL/min, in order to ensure the complete exchange of the sample inside of the gas cell the sample were replace after 35 min of flowing.

Before the measurement, the cylinder was rolled for 30 minutes to ensure homogeneity of the mixture, after that the cylinder was allowed to equilibrate at laboratory conditions. Two-stage regulators of stainless steel with CGA-660 were connected to the sample cylinder.

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

The pressure and temperature of the sample is measured in real time using a program developed by CENAM, which takes data from the Mensor barometer and the calibrated 100 Ω RTD temperature probe connected to the gas cell.

The B_FOS software was used to configure the instrument parameters in OMNIC and perform the measurement and capture of spectrographic data.

Measurement were made at continuous flow supplying the sample from the high-pressure cylinder, the sample flow is controlled before entering the cell at 0.75 L/min, using the two stage regulator connected to the cylinder and the mass flow controller.

For the acquisition of high-quality spectra suitable for quantitative analysis, 32 scans are added together over a period of approximately 1 minute to provide a single beam spectrum of the sample. This single beam spectrum was compared to a similar spectrum of ultra-high purity nitrogen grade 6.0 collected under similar conditions to provide an absorbance spectrum of the sample (background).

A5. Complementary information on the cylinder

Please report the value of the pressure let in the cylinder before shipment to the BIPM:

1700 psi approximately.

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Any juts those of HNO3 spectra calculated with MALT+HITRAN+BFOS.

A6. Reference

[1]. E. Flores, J. Viallon, P. Mousay R. Wielgosz. "Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO₂) and Nitric Acid (HNO₃) Calibrated with Synthetic Spectra."

¹ The choice of the procedure used for gas analysis is the responsibility of the participating laboratory.

Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixture have been prepared is reported to the coordinators

KRISS

Before shipping to the BIPM

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

 Project name:
 CCQM-P172.

 Comparison:
 Comparability study of laboratories' capabilities to value assign the amount of HNO3 in mixtures of NO2 in nitrogen by spectroscopic methods.

 Proposed dates:
 2018.

Coordinating laboratory: Bureau International des Poids et Mesures Chemistry Department Pavillon de Breteuil 92312 Sevres Cedex, France.

Study Coordinator: Edgar Flores BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92 Eav: +33 (0)1 45 34 20 21

Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

Protocol A

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	KRISS
Address	Center for Gas Analysis (Chemistry Building 230 Office 209) Division of Chemical and Medical Metrology Korea Research Institute of Standards and Science(KRISS)
	267 Gajeong-ro, Yuseong-gu, Daejeon 34113 REPUBLIC of KOREA
Contact person	Sang-Hyub Oh

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

Telephone	+82 42 868 5341	Fax	+82 42 868 5042
Email*	shoh@kriss.re.kr		
Serial number of cylinder received			
Cylinder pressure as received	8 MPa		

A2. Results

Cylinder 1(D63 4058) - Before shipping to the BIPM

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO:}$ / nmol/mol	$U(x_{\rm HNO})/$	
(Preparation)		11.3	3.4	2
(Stability 1)				
(Stability 2)				
(Stability 3)				

Cylinder 2(D63 4074)- Before shipping to the BIPM

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Preparation)		11.3	3.4	2
(Stability 1)				
(Stability 2)				
(Stability 3)				

Cylinder 1(D63 4058): 11.3 nmol/mol HNO₃ (U = 3.4 nmol/mol) Cylinder 2(D63 4074): 11.3 nmol/mol HNO₃ (U = 3.4 nmol/mol)

Cylinder 1- Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget. Uncertainty budget for high purity NO₂ source gas

HNO₃ concentration: 1,130 μ mol/mol Combined standard uncertainty: $u = 150 \mu$ mol/mol

Expanded uncertainty: U =300 µmol/mol

Contributions to uncertainty:

Gravimetric uncertainty from permeation tube: 100 µmol/mol Mixture stability: 50 µmol/mol Repeatability of FT-IR measurement: 100 µmol/mol

A4. Description of the procedure used during the gas analysis Please describe in detail the analytical method(s) used for gas analysis^{iv}.

^{iv} The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Instrument and analysis conditions: FT-IR(Bruker, Alpha, 5 m gas cell, sample gas flow rate 1,000 ml/min, resolution 1 cm⁻¹)

1 % NO₂/Nitrogen mixture gas was analysed using FT-IR, and HNO₃ permeation tube (KIN-TEK, LFHA-0357.00-2022/30) was used as reference. NO₂ concentration produced by permeation tube at 30 °C and 500 ml/min nitrogen flow rate was 6.97 μ mol/mol which was determined by gravimetric method. Pressure difference in the FT-IR gas cell of 500 ml/min and 1,000 ml/min was about 1 % and was ignored.

HNO₃ concentration in 1 % NO₂ mixture gas was about 11.3 µmol/mol, so HNO₃ concentration in NO₂ source gas was estimated to be 1130 µmol/mol. Therefore, it is estimated that HNO₃ concentration of KC sample cylinders diluted by 100,000 times is about 11.3 nmol/mol.

The wave number range used in the HNO₃ quantitative analysis was 1322.6 cm⁻¹ – 1327.2 cm⁻¹, and it was determined by HNO₃ and NO₂ absorption images from HITRAN.





So, NO₂ 200 µmol/mol gas mixture could not be used for quantitative analysis.

The following figure shows HNO₃ absorption spectrums of NO₂ in nitrogen, converted NO₂ in air gas mixtures and permeation tube.



A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

 $\sim 8 \text{ MPa}$

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

```
10 \mu mol/mol~NO_2 and {\sim}1000~\mu mol/mol~Oxygen
```

Cylinder 1

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Cylinder 2

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Post BIPM measurements

(Not available –the cylinder was empty during stability measurements)

NMISA

Before shipping to the BIPM

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

 Project name:
 CCQM-P172.

 Comparison:
 Comparability study of laboratories' capabilities to value assign the amount of HNO3 in mixtures of NO2 in nitrogen by spectroscopic methods.

Proposed dates: 2018.

Coordinating laboratory: Bureau International des Poids et Mesures Chemistry Department Pavillon de Breteuil 92312 Sevres Cedex, France.

Study Coordinator:

Edgar Flores BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

Protocol A

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	National Metrology Institute of South Africa				
Address	CSIR Campus Building 5 Meiring Naude Road Brummeria Pretoria 0182				
Contact person	Dr. James Tshilongo				
Telephone	+27 12 841 2589	Fax	+27 12 841 2131/4458		
Email*	jtshilongo@nmisa.org	9			
Serial number of cylinder received	D62 6420				
Cylinder pressure as received	10.5 MPA				

A2. Results

Cylinder 1 (D62 6420) – Before shipping to the BIPM

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	x _{HNO3} / nmol/mol	<i>U</i> (x _{HNO3}) / nmol/mol	
(Preparation)	12 March 2018			
(Stability 1)	15 March 2018	26,28	5,86	k=2
(Stability 2)	11 April 2018	21,95	2,53	k=2
(Stability 3)	08 May 2018	24,40	3,54	k=2

Result (Cylinder 1: D62 6420)

Expanded uncertainty	Coverage factor
U(x _{HNO3}) / nmol/mol	
8,4	k=2
	Expanded uncertainty U(X _{HNO3}) / nmol/mol 8,4

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The parameters that were considered for the uncertainty were the pathlength of the gas cell, the HITRAN database HNO_3 line parameters, the standard deviation of the mean of repeated measurements.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis^v.

For HNO₃ measurements NICOLET iS50 FT-IR was used. A fixed optical path length gas cell of 10 m from Gemini-Mars was used. The cell was flushed with BIPTM N₂ (6.0) with flow of 500ml/min, for background spectrum. The cell was flushed for 20 minutes prior to obtaining spectra. The similar conditions were used for the analysis of NO₂ gas mixtures containing HNO₃.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

The amount oxygen in the cylinder is 1000 µmol/mol nominal.

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
15 March 2018	NO ₂	10,026	0,674	k=2	FT-IR
11 April 2018	NO ₂	9,911	0,666	k=2	FT-IR
08 May 2018	NO ₂	9,888	0,664	k=2	FT-IR

Cylinder 1: D62 6420

^v The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Post BIPM measurements

(Not available -the cylinder was empty during stability measurements)

NPL

Before shipping to the BIPM

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

CCQM-P172. Project name: Comparison: Comparability study of laboratories' capabilities to value assign the amount of HNO₃ in mixtures of NO₂ in nitrogen by spectroscopic methods. Proposed dates: 2018. Coordinating laboratory: Bureau International des Poids et Mesures **Chemistry Department** Pavillon de Breteuil 92312 Sevres Cedex, France. Study Coordinator: Edgar Flores **BIPM** Chemistry Department Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to <u>edgar.flores@bipm.org</u> **Protocol A**

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	National Physical Laboratory				
Address	National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK				
Contact person	Michael Ward/Dave Worton				
Telephone	+44 (0)20 8943 6909 Fax -				
Email*	michael.ward@npl.co.uk/dave.worton@npl.co.uk				
Serial number of cylinder sent	2451				

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

	0.5 D
Cylinder pressure before sending	95 Bar

A2. Results

The below measurements were collected using FT-IR spectroscopy and the amount fractions are traceable to the HITRAN database.

Cylinder 1 – Before shipping to the BIPM

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / µmol/mol	$U(x_{ m HNO3})$ / μ mol/mol	
(Stability 1)	06/03/2018	0.47	0.07	2
(Stability 2)	29/03/2018	0.69	0.09	2
(Stability 3)	17/04/2018	0.81	0.10	2

Cylinder 1- Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / µmol/mol	$U(x_{ m HNO3})$ / μ mol/mol	
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The uncertainty in the determination of the amount fraction of HNO₃ can be described by the following equation, similar to Flores *et al.* 2013:*

$$u(x) = \{(u_{\text{noise HNO3}})^2 + (u_{\text{HITRAN HNO3}})^2 + (u_{\text{calc HNO3}})^2 + (u_{\text{pass HNO3}})^2\}^{0.5}$$
Eq.I

 u_{noise_HNO3} : Is the uncertainty from the noise of the measurement system. It is taken from the Allan variance of spectra averaged over 22 seconds (spectra averaged over 10 scans) to determine the high frequency noise (result of 2 nmol/mol for 180 scans *i.e.* ~5 mins of averaging) and the low frequency noise which was taken from the standard deviation of the average of the last 15 minutes of data collection (3 nmol/mol). Combining these sources of high and low frequency noise gives a standard uncertainty of 4 nmol/mol for the noise component.

 $u_{\text{HITRAN_HNO3}}$: The HITRAN 2012 standard uncertainty for HNO₃ is taken to be 5 %, as described in Flores *et al.* 2013. The version of HITRAN used in Flores *et al.* 2013 uses HITRAN 2008, however it seems no significant changes were made to the 2012 database over the region used in this analysis and is considered the same in this analysis.

 u_{calc} HNO3: Is the combined uncertainty in the calculated amount fraction resulting from the fitting of the MALT software. This was determined by conducting a sensitivity analysis of the MALT software. This was performed by changing each input parameter within the MALT software by its assigned uncertainty and then running the software. The variation in x_{HNO3} was noted and the standard uncertainty for x_{HNO3} from a given parameter was calculated as half the variation in x_{HNO3} . However, in the case where a given input parameter has not been constrained by experiment, a conservative \pm 50% uncertainty has been assumed for the most part. Despite the large relative uncertainty of these parameters, the effect on the returned variation on the amount fraction of HNO₃ was small. For the transmission layer parameters *i.e.* the gas cell conditions p, T and L, these have been constrained by measurement and therefore have the lowest uncertainties. However, the calculated amount fraction of HNO₃ was most sensitive to these parameters. For HNO₃ the combined standard uncertainty in the calculated amount fraction from MALT was 2.36 %.

 $u_{pass HNO3}$: Due to the sticky nature of HNO₃ the system takes a long time to stabilise within the measurement system and the limited measurement time. Therefore considering the time that HNO₃ is first introduced into the system and when the measurements are taken, the uncertainty is based on the difference in HNO₃ measurements made between 2 and 5 hours of passivation of the system, of another mixture similar to 2451. Using this difference as the lower and upper boundaries for HNO₃ differences, the uncertainty due to the system passivation was calculated as follows, as in Flores *et al.* 2013*:

$$u_{\text{pass HNO3}} = \{(b_+ + b_-)^2 / 12\}^{0.5}$$
 Eq II

giving a result of 24 nmol/mol.

The numerical form of Eq I for the absolute standard uncertainty of the measured amount fraction of HNO_3 (in $\mu mol/mol$) is therefore:

$$u(x) = \{(0.004)^2 + (0.05x)^2 + (0.024x)^2 + (0.024)^2\}^{0.5}$$
 Eq III

The uncertainties in the results section for each HNO₃ stability measurement have been calculated as above and then multiplied by a coverage factor k = 2, to give the expanded uncertainty.

*E. Flores, J. Viallon, P. Moussay, R. Wielgosz. "Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO₂) and Nitric Acid (HNO₃) Calibrated with Synthetic Spectra". Applied Spectroscopy. 2013. 67(10): 1171-1178. 10.1366/13-07030.

A4. Description of the procedure used during the gas analysis Please describe in detail the analytical method(s) used for gas analysis^{vi}.

Gas Mixture Preparation:

Mixtures containing nominal amount fractions of 10 μ mol/mol NO₂ and 2 μ mol/mol H₂O and 1000 μ mol/mol of O₂ were prepared by gravimetry from parent mixtures of 500 μ mol/mol NO₂ in nitrogen and 100 μ mol/mol H₂O in nitrogen and 5 % O₂ in nitrogen. HNO₃ was formed from the reaction:

 $2NO_2 + H_2O \rightarrow HNO_3 + HONO$

Gas Analysis by FT-IR Spectroscopy:

A Thermo Scientific Nicolet 6700 FT-IR spectrometer was used to measure the single beam spectra used in the analysis. Gas mixtures were passed through a heated gas cell (Specac, Cyclone C5) and both gas cell and spectrometer are housed in a box, which is purged continuously during measurements with nitrogen at a flow rate of 10 L/min. The spectrometer was operated using BFOSv1.1, which controls the FT-IR proprietary operating software OMNIC, allowing the automatic collection of spectra. Spectra were quantified using MALT version 5.5.9, which used the HITRAN 2012 database to produce the synthetic spectra that were used to assign the reported HNO₃ amount fractions of cylinder 2451. In the absence of any standards for HNO₃ for quantification, the reported values are traceable to the HITRAN 2012 database.

For each measurement run of 2451 and 2399 (a sister of 2451 kept at NPL for the duration of P172 for stability measurements), the following typical procedure was performed:

- 1. The MCT detector was cooled with liquid nitrogen and allowed to stabilise for a minimum of 1 hour prior to performing any FT-IR measurements.
- 2. While the detector stabilised, the heated gas cell was purged with BIP Nitrogen (the background gas) at a flow rate of 1 L/min, for a minimum of 1 hour.
- 3. The spectrometer signal was checked and the spectrometer parameters were verified in OMNIC before launching BFOS, where a background was collected and then several blank measurements were made.
- A flow of a purge gas mixture from a cylinder (BOC, UK) containing an estimated 11 µmol/mol of NO₂ and 1 µmol/mol of HNO₃ was then introduced to the gas and the gas cell was passivated for approximately 90 mins.
- 5. 2451 was then introduced to the gas cell at a flow rate of 1 L/min for approximately 1 hour. The last 15 minutes of the measurement run were used in the analysis of HNO₃ and the other components measured.

Cylinders were maintained at a laboratory temperature of 20 ± 3 °C throughout the period of analysis. Samples were introduced into the analyser at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

Spectrometer Acquisition Parameters (Omnic Input)

Range: Min (cm⁻¹) = 0, Max (cm⁻¹) = 4000 Gain: 8 Optical Velocity: 1.8988 Aperture: 12 No. of Scans: 180 Resolution (cm⁻¹): 1.0 Final Format: Single Beam Correction: None Zero Filling: None

vi The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Apodization: Blackman-Harris Phase Correction: Mertz

MALT parameters

amplitude 1=0

Below is a copy of the BFOS input file "NO2-HNO3_P172.ini", that was used as the input parameters for MALT for fitting the spectra to obtain mole fractions of the components of 2451:

[Spectrum calculation] MGI RWA Section Options=2.0.1 %04Y%02m%02d %02H%02M%S%25u*~|.%d*~|.,*~|.%#_13g Comments=Window 1400-1800 Fitfile=T:\GPM\Laboratories\FT-IR\Nicolet\FT-IR data\2018\April 2018\2018 04 17\nexus 20180417 171408.SPC bgndfile=T:\GPM\Laboratories\FT-IR\Nicolet\FT-IR data\2018\April 2018\2018 04 17\bkg 20180417 125118.SPC Abscof file= linelist file=C:\Malt5\Hitran\HITRAN2012.par molecule def file=C:\Malt5\Hitran\hitran.dat Scratch directory=C:\Malt5\workfolder #iter=20 low=1400 hiah=1800 ext=10 outspacing=0 snr=0 weight=0 HKP files=FALSE _xs.spc files=FALSE [ILS] MGI RWA Section Options=2.0.1 %04Y%02m%02d %02H%02M%S%25u*~|.%d*~|.,*~|.%#_13g #=2 a=1 b=0 c=0 d=0 Shift=0.016915966 resoln=1 apod=Blackmann Harris fitshift=FALSE fitres=FALSE fov=32.41288 fap=-0.056592196 phase=-0.1990887 sym1=0 sym2=0 malign=0 PBadj=0 zoffset=0 fitfov=FALSE fitfap=FALSE fitphase=FALSE fitsym1=FALSE fitsym2=FALSE fitmalign=FALSE fitpbadj=FALSE fitzoffset=FALSE period 1=0 phase 1=0

delay 1=0 fitc1period=FALSE fitc1phase=FALSE fitc1amp=FALSE fitc1delay=FALSE period 2=0 phase 2=0 amplitude 2=0 delay 2=0 fitc2period=FALSE fitc2phase=FALSE fitc2amp=FALSE fitc2delay=FALSE [Components] MGI RWA Section Options=2.0.1 %04Y%02m%02d %02H%02M%S%25u*~|.%d*~|.,*~|.%#_13g Ytype=1 #layers=1 laver 1.tvpe=1 laver 1.Press=1064.3 layer 1.Press unit=mb laver 1.fitL1press=FALSE layer 1.Temp=31.1 layer 1.Temp unit=1 layer 1.fitL1temp=FALSE layer 1.Path=7.76 layer 1.Path unit=1 layer 1.Broad=0 layer 1.isoscale=0 #components=3 #library spectra=0 components=<3> components 0.Component params.comp=10 components 0.Component params.amount=15 components 0.Component params.unit=ppm components 0.Component params.linefile= components 0.Component params.type= components 0.Component params.fit=TRUE components 0.Component params.display=TRUE components 1.Component params.comp=1 components 1.Component params.amount=1 components 1.Component params.unit=ppm components 1.Component params.linefile= components 1.Component params.type= components 1.Component params.fit=TRUE components 1.Component params.display=TRUE components 2.Component params.comp=12 components 2.Component params.amount=1 components 2.Component params.unit=ppm components 2.Component params.linefile= components 2.Component params.type= components 2.Component params.fit=TRUE components 2.Component params.display=TRUE Libraries=<0> [Other parameters]

MGI RWA Section Options=2.0.1 %04Y%02m%02d %02H%02M%S%25u*~|.%d*~|.,*~|.%#_13g Spectra Path=C:\B-FOS\Batch Test configuration file path=T:\GPM\Laboratories\FT-IR\B-FOS\K74 NO2 HNO3\NO2-HNO3_P172.ini Final wave number=4000 Link to FT-IR=OMNIC Experiment Method File=

Information on the supplied example spectra:

Background: bkg_20180417_125118.SPC

Gas: BIP Nitrogen

T: 31.1 ± 1.5 °C P: 1066 ± 5 mbar OPL*: 7.76 ± 0.12m

Sample: nexus_20180417_171408.SPC

Cylinder: 2451

T: 31.1 ± 1.5 °C P: 1064 ± 5 mbar OPL: 7.76 ± 0.12 m

*Optical Path Length

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

95 Bar

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1

Two other components were measured and quantified alongside nitric acid: nitrogen dioxide and water vapour. These components were quantified using FT-IR spectroscopy and are traceable to the HITRAN database unless indicated otherwise.

NO₂ Component

		Nitrogen Dioxide amount fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{NO2}^{}/\ \mu mol/mol$	$m{U}(m{x_{NO_2}})$ / µmol/mol	
(Preparation) ^a	01/03/2018	9.63	0.07	2
(Stability 1)	06/03/2018	9.73	0.76	2
(Stability 2)	29/03/2018	9.37	0.74	2
(Stability 3)	17/04/2018	9.24	0.73	2

^aMeasured by NDUV as described in the CCQM-K74.2018 NPL report.

H ₂ O Component				
		Water amount fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m H_2O}$ / µmol/mol	U (x_{H20})U(x _{H20})U(x /μmol/mol	
(Stability 1)	06/03/2018	1.64	0.51	2
(Stability 2)	29/03/2018	1.29	0.41	2
(Stability 3)	17/04/2018	1.07	0.34	2

Post BIPM measurements

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

Project name:	CCQM-P172.
Comparison:	Comparability study of laboratories' capabilities to value assign the amount of HNO ₃ in mixtures of NO ₂ in nitrogen by spectroscopic methods.
Proposed dates: 2018.	
Coordinating laborat	ory:
Bureau International des F Chemistry Department Pavillon de Breteuil 92312 Sevres Cedex, Fra	Poids et Mesures
Study Coordinator:	Edgar Flores BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

Protocol A

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	National Physical Laboratory		
Address	National Physical Laboratory, TW11 0LW, UK	Hampto	on Road, Teddington,
Contact person	Michael Ward / Dave Worton		
Telephone	+44 (0)20 8943 6909	Fax	-
Email*	michael.ward@npl.co.uk / day	ve.wortc	n@npl.co.uk
Serial number of cylinder sent	2451		

Cylinder pressure before	9.5 MPa
sending	

A2. **Results**

The below measurements were collected using FT-IR spectroscopy and the amount fractions are traceable to the HITRAN database.

Before shipping to the BIPM

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / µmol/mol	$U(x_{ m HNO3})$ / μ mol/mol	
(Stability 1)	06/03/2018	0.47	0.07	2
(Stability 2)	29/03/2018	0.69	0.09	2
(Stability 3)	17/04/2018	0.81	0.10	2

Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / µmol/mol	$U(x_{ m HNO3})$ / μ mol/mol	
(Stability 4)	16/04/2019	0.93	0.11	2
(Stability 5)	22/05/2019	0.94	0.11	2
(Stability 6)	21/06/2019	0.98	0.12	2

A3.

Uncertainty Budget Please provide a complete uncertainty budget.

The uncertainty in the determination of the amount fraction of HNO_3 can be described by the following equation, similar to Flores *et al.* 2013:

$$u(x) = \{(u_{\text{noise}_\text{HNO3}})^2 + (u_{\text{HITRAN}_\text{HNO3}})^2 + (u_{\text{calc}_\text{HNO3}})^2 + (u_{\text{pass}_\text{HNO3}})^2\}^{0.5}$$
Eq.I

 u_{noise_HNO3} : Is the uncertainty from the noise of the measurement system. It is taken from the Allan variance of spectra averaged over 22 seconds (spectra averaged over 10 scans) to determine the high frequency noise (result of 2 nmol/mol for 180 scans *i.e.* ~5 mins of averaging) and the low frequency noise which was taken from the standard deviation of the average of the last 15 minutes of data collection (3 nmol/mol). Combining these sources of high and low frequency noise gives a standard uncertainty of 4 nmol/mol for the noise component.

 $u_{\text{HITRAN_HNO3}}$: The HITRAN 2012 standard uncertainty for HNO₃ is taken to be 5 %, as described in Flores *et al.* 2013. The version of HITRAN used in Flores *et al.* 2013 uses HITRAN 2008, however it seems no significant changes were made to the 2012 database over the region used in this analysis and the uncertainty is considered the same in this analysis.

 $u_{calc \text{ HNO3}}$: Is the combined uncertainty in the calculated amount fraction resulting from the fitting of the MALT software. This was determined by conducting a sensitivity analysis of the MALT software. This was performed by changing each input parameter within the MALT software by its assigned uncertainty and then running the software. The variation in x_{HNO3} was noted and the standard uncertainty for x_{HNO3} from a given parameter was calculated as half the variation in x_{HNO3} . However, in the case where a given input parameter has not been constrained by experimental data, a conservative \pm 50 % uncertainty has been assumed for the most part. Despite the large relative uncertainty of these parameters, the effect on the returned variation on the amount fraction of HNO₃ was small. For the transmission layer parameters *i.e.* the gas cell conditions *p*, *T* and *L*, these have been constrained by measurement and therefore have the lowest uncertainties. However, the calculated amount fraction of HNO₃ was most sensitive to these parameters. For HNO₃ the combined standard uncertainty in the calculated amount fraction from MALT was 2.4 %.

 $u_{\text{pass HNO3}}$: Is the uncertainty due to the passivation of the system. Due to the sticky nature of HNO₃ the response of HNO₃ takes time to stabilise within the measurement system, depending on the time for this and the measurement time. Therefore, considering the time that HNO₃ is first introduced into the system and when the measurements are taken, the uncertainty is based on the difference in HNO₃ measurements made between 2 and 5 hours of passivation of the system, of another mixture similar to cylinder 2451. Using this difference as the lower and upper boundaries for HNO₃ differences, the uncertainty due to the system passivation was calculated as follows, similar to Flores *et al.* 2013:

$$u_{\text{pass HNO3}} = \{(b_+ + b_-)^2 / 12\}^{0.5}$$
 Eq II

This gave a result of 24 nmol/mol.

The numerical form of Eq I for the absolute standard uncertainty of the measured amount fraction of HNO₃ (in μ mol/mol) was calculated for each measurement point and then multiplied by a coverage factor k = 2, to give the expanded uncertainty.

Reference

E. Flores, J. Viallon, P. Moussay, R. Wielgosz. "Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO₂) and Nitric Acid (HNO₃) Calibrated with Synthetic Spectra". Applied Spectroscopy. 2013. 67(10): 1171-1178. 10.1366/13-07030.

A4. Description of the procedure used during the gas analysis Please describe in detail the analytical method(s) used for gas analysis^{vii}.

^{vii} The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Gas Mixture Preparation:

Mixtures containing nominal amount fractions of 10 μ mol/mol NO₂ and 2 μ mol/mol H₂O and 1000 μ mol/mol of O₂ were prepared by gravimetry from parent mixtures of 500 μ mol/mol NO₂ in nitrogen and 100 μ mol/mol H₂O in ntirogen and 5 % O₂ in nitrogen. HNO₃ was formed from the reaction:

 $2NO_2 + H_2O \rightarrow HNO_3 + HONO$

Gas Analysis by FT-IR Spectroscopy:

A Thermo Scientific Nicolet 6700 FT-IR spectrometer was used to measure the single beam spectra used in the analysis. Gas mixtures were passed through a heated gas cell (Specac, Cyclone C5) and both gas cell and spectrometer are housed in a box, which is purged continuously during measurements with nitrogen at a flow rate of 10 L/min. The spectrometer was operated using BFOSv1.1, which controls the FT-IR proprietary operating software OMNIC, allowing the automatic collection of spectra. Spectra were quantified using MALT version 5.5.9, which used the HITRAN 2012 database to produce the synthetic spectra that were used to assign the reported HNO₃ amount fractions of cylinder 2451. In the absence of any standards for HNO₃ for quantification, the reported values are traceable to the HITRAN 2012 database.

For each measurement run of 2451 and 2399 (a sister of 2451 kept at NPL for the duration of P172 for stability measurements), the following typical procedure was performed:

- The MCT detector was cooled with liquid nitrogen and allowed to stabilise for a minimum of 1 hour prior to performing any FT-IR measurements.
- 7. While the detector stabilised, the heated gas cell was purged with BIP Nitrogen (the background gas) at a flow rate of 1 L/min, for a minimum of 1 hour.
- 8. The spectrometer signal was checked and the spectrometer parameters were verified in OMNIC before launching BFOS, where a background was collected and then several blank measurements were made.
- A flow of a purge gas mixture from a cylinder (BOC, UK) containing an estimated 11 µmol/mol of NO₂ and 1 µmol/mol of HNO₃ was then introduced to the gas and the gas cell was passivated for approximately 90 mins.
- 10. 2451 was then introduced to the gas cell at a flow rate of 1 L/min for approximately 1 hour. The last 15 minutes of the measurement run were used in the analysis of HNO₃ and the other components measured.

Cylinders were maintained at a laboratory temperature of 20 ± 3 °C throughout the period of analysis. Samples were introduced into the analyser at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

Spectrometer Acquisition Parameters (Omnic Input)

Range: Min (cm⁻¹) = 0, Max (cm⁻¹) = 4000 Gain: 8 Optical Velocity: 1.8988 Aperture: 12 No. of Scans: 180 Resolution (cm⁻¹): 1.0 Final Format: Single Beam Correction: None Zero Filling: None Apodization: Blackman-Harris Phase Correction: Mertz

Information on the supplied example spectra:

Background: bkg_20180417_125118.SPC Gas: BIP Nitrogen T: 31.1 ± 1.5 °C P: 1066 ± 5 mbar Optical path length: 7.76 ± 0.13 m Sample: nexus_20180417_171408.SPC

Cylinder: 2451 T: 31.1 ± 1.5 °C P: 1064 ± 5 mbar Optical path length: 7.76 ± 0.13 m

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

9.5 MPa

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Two other components were measured and quantified alongside nitric acid in cylinder 2451: nitrogen dioxide and water vapour. These components were quantified using FT-IR spectroscopy and are traceable to the HITRAN database unless indicated otherwise.

		Nitrogen Dioxide amount fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{NO2}^{}/\ \mu mol/mol$	$m{U}(m{x_{NO_2}})$ / µmol/mol	
(Preparation) ^a	01/03/2018	9.63	0.07	2
(Stability 1)	06/03/2018	9.73	0.68	2
(Stability 2)	29/03/2018	9.37	0.66	2
(Stability 3)	17/04/2018	9.24	0.65	2

NO2 Component - Before shipping to the BIPM

^aMeasured by NDUV as described in the CCQM-K74.2018 NPL report.

NO2 Component - Post measurement at BIPM

Description of	Date of measurement	Nitrogen Dioxide amount fraction / µmol/mol	Expanded uncertainty $U(x_{ m NO_2})$ / µmol/mol	Coverage factor
measurement			-	
(Stability 4)	16/04/2019	8.82	0.19	2
(Stability 5)	22/05/2019	8.85	0.19	2
(Stability 6)	21/06/2019	8.81	0.19	2

H₂O Component - Before shipping to BIPM:

		Water amount fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m H_2O}$ / µmol/mol	U (x_{H20})U(x _{H20})U(x /μmol/mol	
(Stability 1)	06/03/2018	1.64	0.50	2
(Stability 2)	29/03/2018	1.29	0.40	2
(Stability 3)	17/04/2018	1.07	0.34	2

H₂O Component - Post measurement at BIPM:

		Water amount fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m H_2O}$ / µmol/mol	U (x _{H20})U(x _{H20})U(x / μmol/mol	
(Stability 4)	16/04/2019	1.36	0.04	2
(Stability 5)	22/05/2019	1.43	0.04	2
(Stability 6)	21/06/2019	1.47	0.12	2

VSL

Before shipping to the BIPM

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

Project name: CCQM-P172. Comparison: Comparability study of laboratories' capabilities to value assign the amount of HNO₃ in mixtures of NO₂ in nitrogen by spectroscopic methods. Proposed dates: 2018. Coordinating laboratory: Bureau International des Poids et Mesures **Chemistry Department** Pavillon de Breteuil 92312 Sevres Cedex, France. Study Coordinator: Edgar Flores **BIPM** Chemistry Department Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

Protocol A

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	VSL
Address	Thijsseweg 11
	2629 JA Delft The Netherland
Contact person	Stefan Persijn

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment
Telephone	0031 15 269 1756	
Email*	spersijn@vsl.nl	
Serial number of cylinder received	VSL105805	
Cylinder pressure as received	110 bar	

A2. Results

Cylinder 1 – Before shipping to the BIPM (VSL105805)

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Preparation)				
(Stability 1)	17-1-2018	75	7	k = 2
(Stability 2)	28-2-2018	81	7	k = 2
(Stability 3)	29-3-2018	102	9	k = 2

Cylinder 1- Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget Please provide a complete uncertainty budget.

A4. Description of the procedure used during the gas analysis Please describe in detail the analytical method(s) used for gas analysis^{viii}.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

^{viii} The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
5-1-2018	NO ₂	9.922	0.1	k=2	UV
1-3-2018	NO ₂	9.889	0.1	k=2	UV
28-3-2018	NO ₂	9.807	0.1	k=2	UV

Cylinder 1

Note: preparation date 11-12-2017

Gravimetry: NO₂ = $10.003 \pm 0.0023 \mu mol/mol$

Post BIPM measurements

Pilot Study CCQM-P172 – Spectroscopic methods for value assignment of HNO₃ in NO₂ in nitrogen gas mixtures

Result form CCQM-P172-R

Project name: CCQM-P172. Comparison: Comparability study of laboratories' capabilities to value assign the amount of HNO3 in mixtures of NO₂ in nitrogen by spectroscopic methods. Proposed dates: 2018. Coordinating laboratory: Bureau International des Poids et Mesures **Chemistry Department** Pavillon de Breteuil 92312 Sevres Cedex, France. Study Coordinator: Edgar Flores **BIPM Chemistry Department** Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

Protocol A

This protocol aims to evaluate the level of compatibility of laboratories' spectroscopic methods for trace gas quantification using nitric acid (HNO₃) as a model system. Participation in this protocol is primarily intended for laboratories that are not yet designated to participate in the CIPM-MRA.

A1. General information

Institute	VSL		
Address	Thijsseweg 11		
	2629 JA Delft The Netherland		
Contact person	Stefan Persijn, Iris de Krom, Adriaan van der Veen		
Telephone	0031 15 269 1756		
Email*	spersijn@vsl.nl		
Serial number of cylinder received	VSL105805		
Cylinder pressure as received	110 bar		

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

A2. Results

Cylinder 1 – Before shipping to the BIPM (VSL105805)

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ /nmol/mol	
(Preparation)	-	-	-	-
(Stability 1)	17-1-2018	83	15	k = 2
(Stability 2)	28-2-2018	90	16	k = 2
(Stability 3)	29-3-2018	113	20	k = 2

Cylinder 1- Post BIPM measurements

		Nitric acid mole fraction	Expanded uncertainty	Coverage factor
Description of measurement	Date of measurement	$x_{ m HNO3}$ / nmol/mol	$U(x_{ m HNO3})$ / nmol/mol	
(Stability 4)	31-5-2019	133	24	k = 2
(Stability 5)	23-8-2019	124	22	k = 2
(Stability 6)	28-8-2019	104	19	k = 2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

To quantify the HNO₃ amount fraction in the NO₂ gas mixture the PNNL infrared database was used [1,2]. HITRAN database does not provide data for the used v₁ absorption band. The accompanying meta data of the PNNL database states for the uncertainty of the absorption values: '*type A* = 2.5%, Type B "Best effort"'.

To obtain an estimate of the uncertainty the literature was checked. The PNNL data for HNO₃ is based on Chackerian et al. [1]. This reference states a band strength uncertainty of 2.6% for the v₁ band. Comparing their results for the band strength of other fundamental HNO₃ absorption bands with literature (including HITRAN) they found differences up to 6.4%. Based on this, here we apply a standard uncertainty of $(6.4^2 + 2.5^2)^{\frac{1}{2}} = 6.9\%$ for the absorption coefficients of the v₁-band.

Within the v₁-band a wavelength region was selected around 3541 cm⁻¹ with high HNO₃ and negligible NO₂ absorption. PNNL database provides HNO₃ absorption spectra at temperatures of 5, 25 and 50 °C (see Figure 19) [2]. The absorption spectra have a weak, nearly linear, temperature dependence for the spectral region around 3541 cm⁻¹ (about -0.15%/°C). As the measurements were performed at 20 °C, a linear interpolation of the spectra at 5 °C and 25 °C was made.



Figure 19 Spectra from the PNNL database at 5 °C, 25 °C and 50 °C. Also depicted is the ratio of the absorption at 25°C and 5°C showing on average a 3% lower absorption at 25°C.

As the spectra in PNNL database were obtained at atmospheric pressure, also our measurements were made at atmospheric pressure in order to have the same pressure broadening as the PNNL HNO_3 absorption data.

The data in PNNL database have been recorded by FT-IR at a spectral resolution of 0.112 cm⁻¹. The CRDS spectrometer has a much higher resolution (about 0.001 cm⁻¹). The HNO₃ spectrum is highly congested at atmospheric pressure as can be seen in Figure 19. This results in the region around 3541 cm⁻¹ in a broad background with on top of this peaks with a relative amplitude of about 30% of this background. A standard uncertainty contribution of 3% was estimated to account for the difference in spectral resolution.

Except for traces of water no other spectral interferents were observed (including HNO₂) in the analyzed mixture.

 HNO_3 readily adsorbs on cylinder valve, pressure regulator and all parts of the sampling system even though only polymer and SilcoNert 2000 coated materials are used in the sampling system. The strong adsorption manifests itself by the long period of time (30 minutes or more) to obtain relatively stable readings. As final readings ('infinitive waiting') are likely higher we include a standard uncertainty of 5% for adsorption and the derived amount fractions of HNO₃ are multiplied by a factor 1.1 to account for this.

Table 13 shows an overview of the main uncertainty sources of the analysis. The expanded uncertainty (coverage factor k=2) is 18%.

Uncertainty source	Contribution to standard uncertainty $u_l(y)$		
Absorption coefficients PNNL database	6.9 %		
Resolution	3 %		
Adsorption & reproducibility analysis	5 %		
Temperature	0.2 %		
Pressure	0.5 %		
Combined standard uncertainty	9.0 %		

Table 13 Overview of the main uncertainty sources of the analysis

Figure 20 shows an example of one of the measurements taken. The recorded spectrum matches the HNO₃ data from the PNNL database well confirming that spectral interferences by other components is small in the used wavelength region.



Figure 20 Measurement of HNO₃ from cylinder VSL105805 on 29 March 2018. Data of the PNNL database are also plotted.

A4. Description of the procedure used during the gas analysis

International comparison CCQM-P172, Spectroscopic methods for HNO3 value assignment

Please describe in detail the analytical method(s) used for gas analysisix.

The measurements were performed using the CRDS-facility developed at VSL [4,5]. HNO₃ readily adsorbs on many parts of the sampling system. For example, in the BIPM FT-IR facility a response time of 15 hours has been observed for HNO₃ [Erreur ! Source du renvoi introuvable.]. Use of polymer materials is mostly advised for HNO₃ analysis [3]. Here, a FEP sampling line was used in combination with SilcoNert 2000 coated materials (mass flow controller, pressure regulator and CRDS measurement cell). The strong adsorption of HNO₃ is evidenced by both a slow build-up of the HNO₃ amount fraction when analysing for the first time a sample containing HNO₃ and by the slow HNO₃ decrease observed when switching to pure nitrogen after sample analysis. In a typical analysis 30 minutes (in some cases even more) is needed to reach a relatively stable signal at the applied flow rate of 30 L/h (for comparison, for a non-reactive gas like methane it takes less than 1 minute). To limit gas consumption experiments lasted typically maximum 1 hour. For longer measurement times it might be possible that the measured HNO₃ amount fraction increases somewhat further.

The laser was scanned around 3541 cm⁻¹ over a range of 2-3 cm⁻¹. Here an effective absorption path length of 3-4 km is obtained. Spectra were recorded and later averaged. For the recording of the background spectrum, high purity nitrogen was used. The high purity nitrogen spectrum was fitted using a linear fit. From these two spectra, the absorption spectrum $\alpha(v)$ is calculated. The HNO₃ amount fraction was directly determined by comparing the measured absorption spectrum from the measurements with the HNO₃ reference spectrum from PNNL database. The HNO₃ amount fraction was calculated as

$$x_{HNO3} = \frac{10^4 \cdot k_{\rm B} \cdot T}{C_f \cdot c \cdot \sigma_{PNNL}(\nu) \cdot p} \left(\frac{1}{\tau(\nu)} - \frac{1}{\tau_0(\nu)}\right)$$

with

$$\begin{split} \tau(v) \text{ is the recorded decay time of the NO}_2 \text{ mixture at wavenumber } v \\ \tau_0(v) \text{ the (fitted) decay time of the pure nitrogen measurement at wavenumber } v \\ c \text{ the speed of light} \\ k_\text{B} \text{ the Boltzmann constant} \\ T \text{ the temperature of the gas sample} \\ p \text{ the pressure inside the measurement cell} \\ C_t \text{ the conversion factor of the PNNL decadic absorbance units as described in [Erreur ! Source du renvoi introuvable.]} \\ \sigma_{\text{PNNL}}(v) \text{ the data as listed in the PNNL database} \end{split}$$

The derived HNO_3 amount fractions were multiplied with a factor 1.1 to account for the HNO_3 adsorption.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

If any other component other than HNO₃, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1

^{ix} The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
5-1-2018	NO ₂	9.914	0.14	<i>k</i> =2	ND-UV (actually the NO ₂ absorption in the visible region is used by the analyzer)
1-3-2018	NO ₂	9.885	0.14	<i>k</i> =2	UV
28-3-2018	NO ₂	9.804	0.14	<i>k</i> =2	UV
21-5-2019	NO ₂	9.844	0.14	<i>k</i> =2	UV
25-6-2019	NO ₂	9.900	0.14	<i>k</i> =2	UV
25-7-2019	NO ₂	9.914	0.14	<i>k</i> =2	UV

- Gravimetry: NO₂ = 10.003 ± 0.0023 µmol/mol
- Preparation date NO₂ gas mixture: 11-12-2017
- Cylinder treatment: AlphaTech (Air Liquide)
- Cylinder number: VSL105805
- After the final HNO₃ measurement (i.e., stability measurement 6 on 25 July 2019) the remaining pressure in the cylinder was 34 bar.

References

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7. Brauer, C. S., Blake, T. A., Guenther, A. B., Sharpe, S. W., Sams, R. L., & Johnson, T. J. (2014). Quantitative infrared absorption cross sections of isoprene for atmospheric measurements. Atmospheric Measurement Techniques, 7(11), 3839-3847.