CCQM-K137, Nitrogen Monoxide (NO) in nitrogen, 30 µmol mol^{-1} and 70 µmol mol^{-1}
Final Report

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Summary

The key comparison CCQM-K137 was aimed at evaluating the level of compatibility of laboratories' preparative capabilities for gravimetric nitrogen monoxide/nitrogen primary reference mixtures at mole fractions of 30 µmol mol^{-1} and 70 µmol mol^{-1}.

The comparison was organised by the BIPM. It consisted in the simultaneous comparison of a suite of 2n primary gas standards, two standards to be prepared by each of the n participating laboratories at the nominal values of 30 µmol mol^{-1} and 70 µmol mol^{-1}. Two independent analytical methods were used by the BIPM to analyse the amount fraction of nitrogen monoxide (NO) in nitrogen; UV spectrophotometry and chemiluminescence (CLD). The agreement between the results obtained with the two main techniques served to highlight possible issues in the preparation of the standards. During this comparison, standards prepared by two participants appeared to result in a larger bias between the analysers than observed for others. These observations were explained by the analysis of all standards by Fourier Transform Infrared Spectroscopy (FTIR) which identified the presence of a larger amounts of water vapour (H_2O), nitrous oxide (N_2O) and nitrogen dioxide (NO_2) in these standards, which are the three main impurities which can appear in mixtures of NO in nitrogen.

The above observations were used to underpin the selection of standards (at each nominal NO mole fraction) which can be considered as a consistent set, allowing the calculation of a calibration line by a Generalised Least-Square regression. Key

Comparison Reference Values were then proposed for all participants as predicted values from the calibration lines. Interferences caused in the response of the CLD analyser by impurities (verified by FTIR measurements) led to only the results from the UV analyser being proposed for the KCRV and Degrees of Equivalence calculations. Good agreement was observed between all participants who could prepare their standards with minimum levels of impurities.

The key comparison CCQM-K137 is considered to present an analytical challenge at both nominal mole fractions and therefore considered as a Specialised (Track C) comparison in the CCQM nomenclature.

1 Content

2 Purpose

The CCQM-K137 comparison is a Specialised (Track C) comparison designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) preparative capabilities for nitrogen monoxide (NO) in nitrogen primary reference mixtures between 30 µmol mol^{-1} and 70 µmol mol^{-1}, and provide measurement results that can underpin claims over a much wider range.

3 Measurand, quantities and Units

The measurand was the mole fraction of NO in nitrogen, with measurement results being expressed in mol mol^{-1} (or one of its multiples mmol mol^{-1}, µmol mol^{-1} or nmol mol^{-1}).

4 Participants

The comparison included 13 participants listed below:

- Hungarian Trade Licensing Office (BFKH)
- Chemicals Evaluation and Research Institute (CERI)
- Central Office of Measures (Główny Urzad Miar - GUM)
- Korea Research Institute of Standards and Science (KRISS)
- Laboratoire National de métrologie et d’Essais (LNE)
- National Institute of Metrology (NIM)
- National Institute of Standards and Technology (NIST)
- National Measurement Institute, Australia (NMIA)
- National Metrology Institute of South Africa (NMISA)
- National Physical Laboratory (NPL)
- Dutch Metrology Institute (VSL).
- D.I.Mendeleyev Institute for Metrology (VNIIM)

5 Measurement schedule

The comparison was organised by the BIPM following the schedule displayed in Table 1.

Due Date	Event
01 Oct. 2016	Registration
01 Jul. 2017	Shipment of standards to BIPM
30 Oct. 2017	Comparison measurements
16 Mar. 2018	Collection of standards by participants
31 Jul. 2018	Second analysis (optional) and submission of result forms
31 Aug. 2018	Draft A report distributed to participants

Table 1: Schedule of events in CCQM-K137 organisation

6 Standards prepared by participants

Each participant was required to provide two standards of NO in nitrogen: one at the nominal mole fraction of 30 µmol mol^{-1}, the other at 70 µmol mol^{-1}. The mixtures were to be prepared and analysed by participants using their usual procedures.

The comparison protocol required the final mole fraction of NO in each cylinder to be within ± 1 µmol mol^{-1} of the nominal value, a minimum cylinder volume of 5 L and a total pressure between 100 bar to 150 bar.

Participants were asked to report the following information on the standards, in report forms annexed to this document (see Annex 3 – Participants reports):

- The uncertainty budget used to calculate the uncertainty associated with the measurement of the NO mole fraction;
- A description of the measurements performed for the validation of values obtained from the preparation;
- A purity table with uncertainties for the nominally pure NO parent gas;
- A purity table with uncertainties for the nominally pure N_2 gas;
- A brief outline of the dilution series undertaken to produce the final mixtures;
- A purity table for each of the final mixtures, including gravimetric uncertainties;
- A brief outline of the verification procedure applied to the final mixtures;
- A brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

6.1 Issues encountered with the standards

The standard prepared by VNIIM at 70 µmol mol^{-1} arrived empty at the BIPM and could not be measured. No result is presented for this standard in this report.

The standard prepared by VSL at 30 µmol mol^{-1} was found to be anomalous by VSL during the second analysis, after return in their laboratoriesto VSL. VSL decided to withdraw this standard from the comparison and no result is therefore presented.

7 BIPM comparison facility

The analysers used by the BIPM to perform the comparison measurements were of the same technology as during the Pilot Study CCQM−P73[1], namely a UV analyser (model ABB Advance Optima LIMAS 11-UV) connected in series with a Chemiluminescence instrument (model Eco Physics CLD70E).

The input of the UV analyser was connected to the output of an autosampler with a total of 16 entrance ports. The input flow to the UV analyser was controlled at 400 mL min^{-1}. Its output flow pressure was controlled to avoid changes in pressure inside the instrument's gas cell.

In addition to the cylinders to be analysed, a flow of dry air was always connected to the autosampler, as well as a cylinder of BIP® nitrogen (Air Products). To correct for drifts of the analysers, two control standards held at the BIPM, and checked several times prior to the comparison, were selected with a mole fraction close to the target value and connected to the autosampler.

Prior to the comparison measurements, the noise of the two analysers was checked by recording times series of their response to nitrogen and to a control cylinders. From those data, the Allan deviation was calculated and found to be always below 15 nmol mol^{-1} for an averaging time of 2 minutes in the CLD instrument, and always below 35 nmol mol^{-1} for the same averaging time in the UV analyser. This demonstrated the good condition of both analysers.

The BIPM measurement facility also included a Fourier Transform Infrared (FTIR) analyser to detect infrared active impurities in the mixtures, fully described in Annex 2 – FTIR analysis.

8 Measurements at the BIPM

The comparison was performed following the protocol sent to participants on 11 March 2016, described again below. All standards of the same nominal mole fraction were analysed together, starting with the group at 70 μmol mol^{-1}.

8.1 Preparation of cylinders

Cylinders were tracked at the BIPM with their reference as provided by the participants, as well as with a cylinder ID (noted 30.*i* and 70.*i*, *i* being the participant index) used in measurement data files. All pressures were measured upon their arrival and before their return in participant's laboratories. Cylinder references and measured pressures are listed in Table 2 and Table 3 together with the values assigned by participants and their associated uncertainties. It can be seen that participants did prepare their mixtures within ± 1 μmol mol^{-1} of the nominal value, as requested by the protocol, except CERI who prepared standards with lower mole fractions at both nominal values.

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

Each cylinder was equipped with a pressure reducer (Parker−Veriflo Quantum 959) connected to one inlet of a 16-inlet automatic gas sampler connected to the gas analysers.

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

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

NMI	REF	ID	x (µmol mol^{-1})	u (µmol mol^{-1})	P_1 (bar)	P_2 (bar)
BFKH	D521735	30.1	30.100	0.140	118.8	109.8
CERI	CBP18479	30.2	28.510	0.045	96.6	89.1
GUM	D298390	30.3	30.500	0.300	132.9	117.6
KRISS	D557471	30.4	30.014	0.100	97.8	90.9
LNE	1169728	30.5	30.211	0.034	128.3	120.7
NIM	CAL017609	30.6	29.920	0.075	87.6	75.8
NMIA	D248076	30.7	29.980	0.130	133.4	119.9
NMISA	M555689	30.8	30.240	0.085	108.4	94.0
NPL	NPL2238	30.9	29.940	0.030	101.4	94.4
VNIIM	D233917	30.101	30.025	0.006	82.5	69.3
VSL	1005700	30.11	NA	NA	103.6	87.9
NIST	FF58485	30.13	29.854	0.018	92.7	81.0

Table 2: Standards prepared at 30 µmol mol^{-1} NO in N_2: acronym of the participant (NMI), cylinder reference (REF) and internal identification code (ID), mole fraction of NO assigned by participants (x), standard uncertainty (u), pressure measured on arrival of the cylinder (P_1) and before its departure from the BIPM (P_2).

NMI	REF	ID	x (µmol mol^{-1})	u (µmol mol^{-1})	P_1 (bar)	P_2 (bar)
BFKH	D521796	70.1	70.050	0.240	103.4	94.4
CERI	CBP21235	70.2	68.760	0.11	92.6	83.4
GUM	D298384	70.3	71.100	0.550	114.0	96.3
KRISS	D557382	70.4	70.085	0.161	92.9	83.4
LNE	1169715	70.5	69.990	0.080	130.9	115.4
NIM	CAL017455	70.6	69.900	0.175	115.6	95.9
NMIA	D248064	70.7	69.980	0.155	135.4	117.2
NMISA	D958404	70.8	70.090	0.105	107.4	89.7
NPL	NPL2293	70.9	69.890	0.050	114.4	105.2
VNIIM	D249681	70.101	NA	NA	10.3	10.3
VSL	1005700	70.11	70.050	0.105	106.7	89.0
NIST	FF44821	70.13	70.370	0.065	90.9	76.3

Table 3: Standards prepared at 70 µmol mol^{-1} NO in N_2: acronym of the participant (NMI), cylinder reference (REF), internal identification code (ID), mole fraction of NO assigned by participants (x), standard uncertainty (u), pressure measured on arrival of the cylinder (P_1) and before its departure from the BIPM (P_2).

8.2 Series of analysis

Each suite of cylinders was analysed sequentially in series starting with zero air followed by the two control cylinders and five of the standards. Series were repeated in three different orders (increasing, decreasing, and random concentrations), and the entire set further repeated during two additional days. Each analysis step consisted of two minutes of flushing followed by two minutes of analysis, leading to a total sequence time of four hours. On completion of measurements, the cylinder valves were closed and the pressure reducer and connection to the gas sampler left under pressure (typically during the night).

8.3 Calculation of analysers responses and standard uncertainty

The raw response of the analysers to a mixture ($y_{\mathrm{UV,raw}}$ and $y_{\mathrm{CLD,raw}}$) was associated with the Allan variance calculated prior to any measurement (see section 7) as standard uncertainty. Individual measurements were thus associated with typical relative uncertainties between 2×10^{-4} and 10^{-3}.

The raw responses were first interpolated during two measurements of one control cylinder (typically 34 minutes). The second control cylinder was not used in the calculations as no issue was encountered with the first one.

The response to each standard was then normalised with the interpolated response to the control cylinder to provide the normalised drift-corrected responses $y_{\mathrm{c,UV}}$ and $y_{\mathrm{c,CLD}}$, and associated standard uncertainty. As each cylinder was measured three times during a sequence, this led to three corrected responses associated with one standard.

The mean of those three values was calculated to provide one value per standard, per analyser and per day of measurement $\overline{y}_{d,UV}$ and $\overline{y}_{d,CLD}$ (where the measurement day (d) equals 1 to 3). It was associated with the standard deviation on one day.

The mean on three days was finally calculated and used as the final value for each standard $\overline{y}_{UV}$ and $\overline{y}_{CLD}$.

An analysis of variances was performed to detect hidden variances within a day and within the three days. This showed slightly higher variances on three successive runs in a day compared to the day to day variance. The two variances (on three runs in a day and on three days) were combined in quadrature to provide the final uncertainty.

8.4 Measurement results

Detailed results of measurements performed at the BIPM with the CLD and UV analysers are reported in Annex 1 – Detailed measurements results. In this section, results are plotted in different ways to demonstrate the quality of measurements and/or highlight some specific effects.

8.4.1 Agreement between the CLD and UV analysers

The two figures below show the relative difference between the normalised drift−corrected averages obtained with each analyser: $\frac{dy}{y} = (\overline{y}_{CLD} - \overline{y}_{UV})/\,\overline{y}_{UV}$. Because the same control cylinder was chosen to normalise raw measurements of both analyser, the relative difference between the normalised averages is expected to be zero if their response to NO is un−biased (no interferences due to impurities for example).

Considering the expanded uncertainty of the relative difference, the two analysers agree with each other for all standards and mole fraction of NO, except cylinders #30.3 and #70.3. Both standards were prepared by the GUM. The two cylinders #30.1 and #70.1 also show a higher and positive relative difference than others, although covered by the uncertainties. These observations will be clarified in the following section on impurity analysis by FTIR.

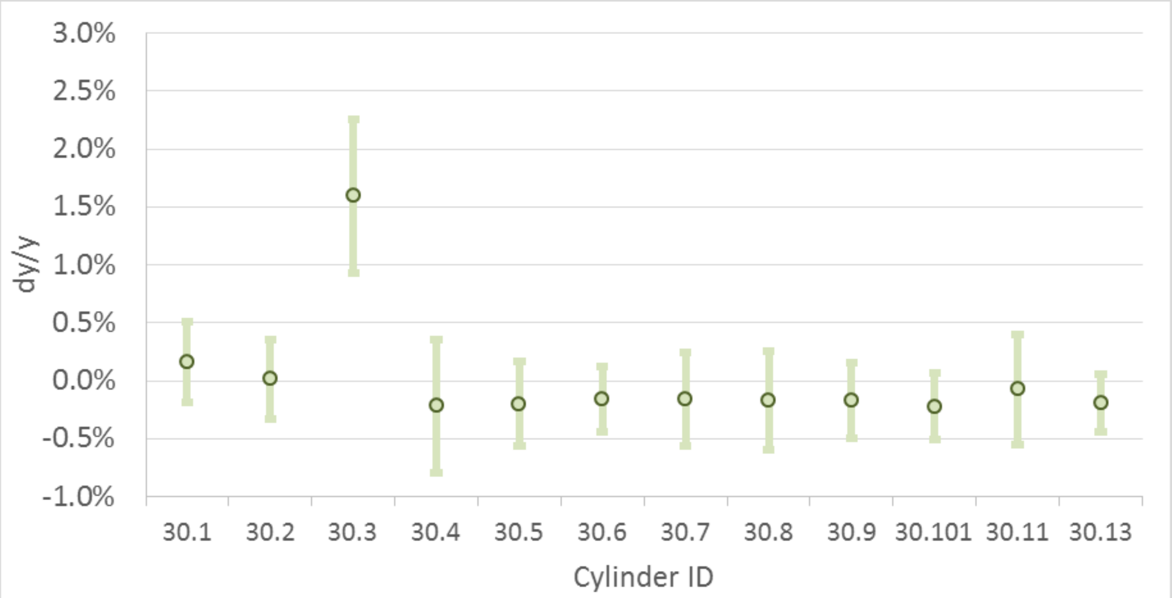

Figure 1: Relative difference between the normalised corrected averages obtained with the CLD and UV analysers for standards prepared at 30 µmol mol⁻¹ (uncertainties at *k* = 2).

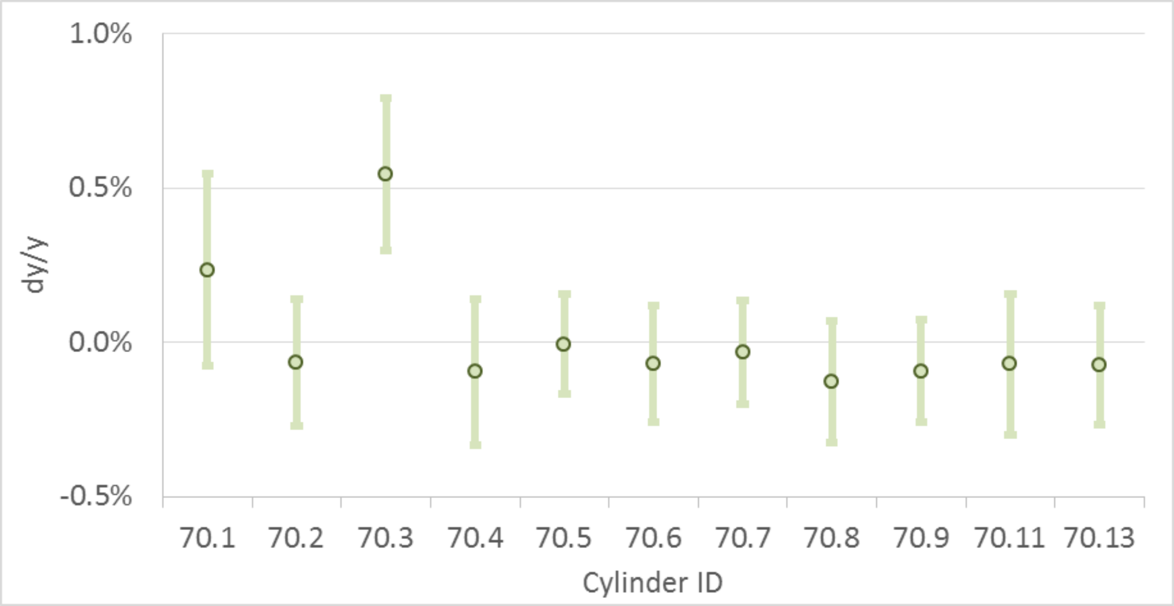

Figure 2: Relative difference between the normalised corrected averages obtained with the CLD and UV analysers for standards prepared at 70 µmol mol⁻¹ (uncertainties at *k* = 2).

8.4.2 Impurity analysis by FTIR

As part of the comparison, the mixtures were analysed by Fourier Transform Infrared Spectroscopy (FTIR). A typical spectrum is displayed in Figure 3. The main absorption peak is due to nitrogen monoxide, and these results could also be used as a quality check in addition to the CLD and UV analysers. Absorption peaks of NO_2, H_2O and N_2O (not shown here) can also be observed when these compounds are present in amounts above their limits of detection in the system. They were considered as the three main probable impurities, as already observed during the pilot study CCQM−P73.

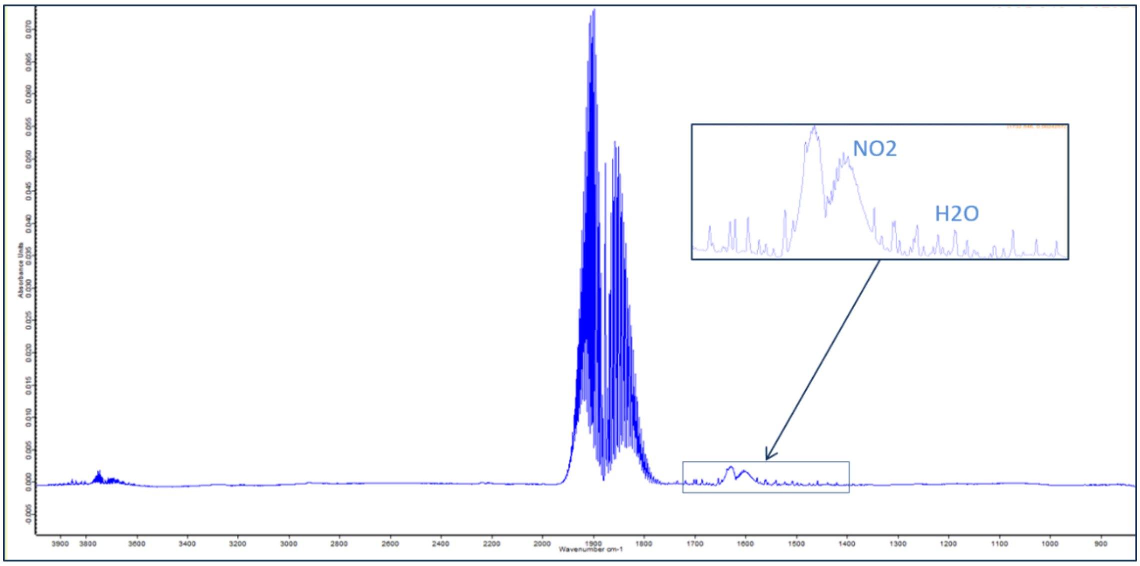

Figure 3: FTIR spectrum recorded on one standard prepared at 70 µmol mol⁻¹, showing the absorption peak of NO in the region 1900 cm⁻¹, as well as NO_2 and H_2O in the region 1500−1700 cm⁻¹ in much smaller amount.

Values of the three main impurities were quantified in all spectra as described in Annex 2 – FTIR analysis. The values are plotted in series of graphs below, together with values provided by participants when appropriate. A number of participants did not report any impurity valuesvalue, as noted in the graphs with the absence of a corresponding bar.

It is noticeable that cylinders #30.3 and #70.3 (GUM), and cylinders #30.1 and #70.1 (BFKH) contain a non-negligible amount of water, about 1.7 µmol mol^{-1} in the standards at 30 µmol mol^{-1}, and 2.2 µmol mol^{-1} in the standards at 70 µmol mol^{-1}.

In addition the FTIR analysis revealed the presence of a non-expected compound in the cylinders #30.3 and #70.3 (GUM), observed as a shoulder on the NO absorption peak. After a search in the literature, the absorption feature corresponds to nitrosyl chloride (NOCl), which could have been introduced in the cylinder if chlorine was used at some point. It can also be noted that after the circulation of the Draft A report, GUM provided results of verification analysis performed just after the gravimetric preparation, which showed NO mole fractions substantially lower than the gravimetric values: 29.6 µmol mol^{-1} instead of 30.5 µmol mol^{-1} and 69.6 µmol mol^{-1} instead of 71.1 µmol mol^{-1}. This would confirm that some of the NO introduced in the cylinder reacted to form another compound. For this comparison, the results of GUM were those submitted before the circulation of the Draft A report and clearly identified in their results form.

A comparison of the FTIR results with similar measurements performed in 2006 during the pilot study CCQM−P73[1] shows that participants who took part in both exercises managed to lower significantly the amount of impurities, and in some cases by a factor of ten.

Excluding the two new participants GUM and BFKH, it is striking to see that on average NO_2 was hardly detected in the participants' standards, and N_2O was found at levels around 20 nmol mol^{-1} in the standards at 30 µmol mol^{-1} of NO, and at 40 nmol mol^{-1} in the standards at 70 µmol mol^{-1} of NO.

NO being also easily detected by FTIR, its mole fraction was measured in all mixtures, including the control standards, and quantified by synthetic calibration using the molecular parameters of NO found in the database Hitran 2012. These results are presented in Annex 2 – FTIR analysis for information as FTIR was not the analytical instrument chosen for the comparison.

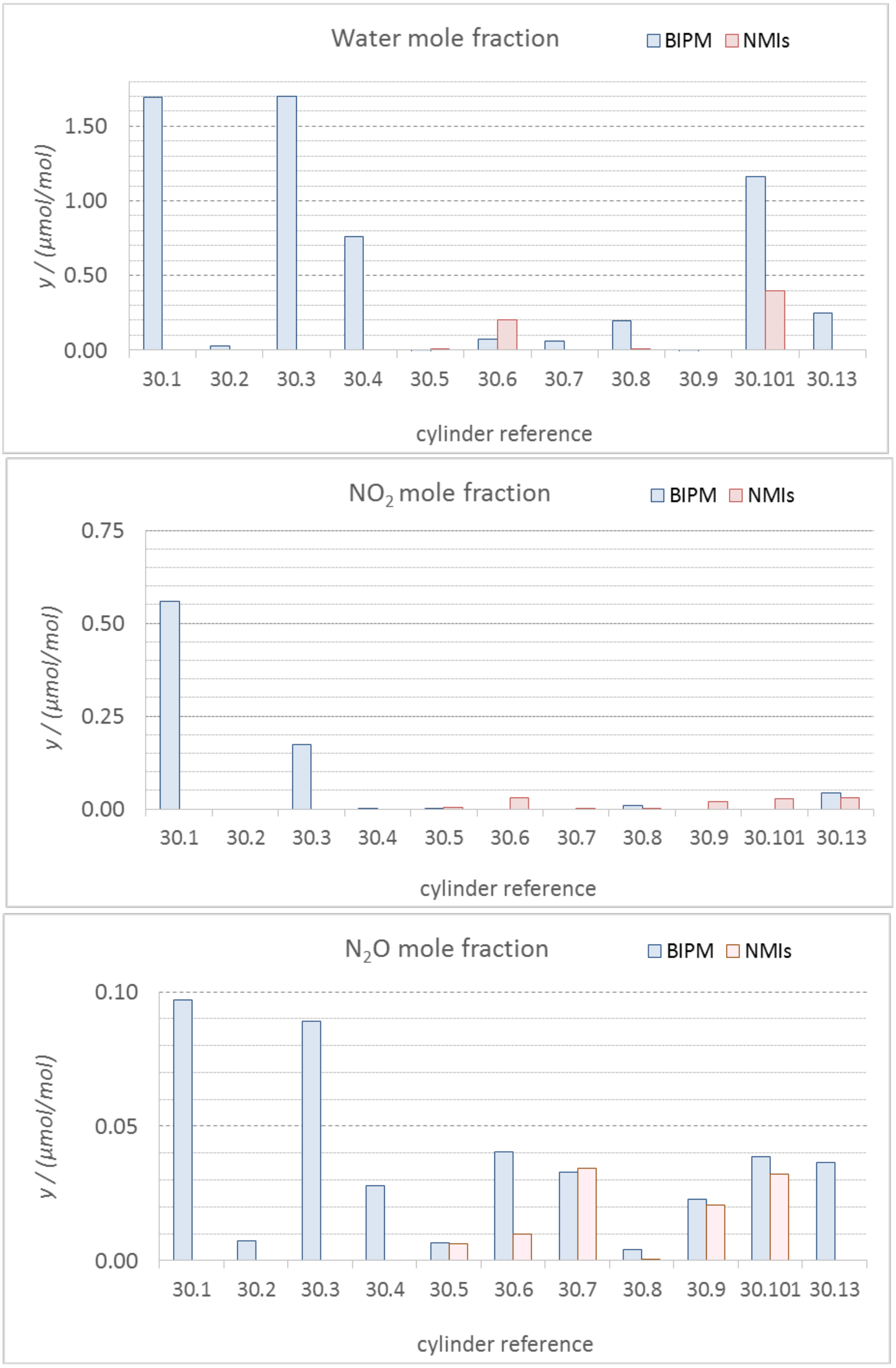

Figure 4: Mole fraction of H_2O, NO_2 and N_2O in standards prepared at 30 µmol mol^{-1}, as measured by FTIR at the BIPM (blue bars) and as reported by participants (pink bars). Absence of a bar indicates that the participant did not report any value.

Figure 5: Mole fraction of H_2O, NO_2 and N_2O in standards prepared at 70 µmol mol^{-1}, as measured by FTIR at the BIPM (blue bars) and as reported by participants (pink bars). Absence of a bar indicates that the participant did not report any value.

9 Stability of the mixtures

After the return of standards in participants' laboratories, they were given the opportunity to perform another verification of the nitrogen monoxide mole fraction. Only two out of twelve participants reported a second value, namely NPL and NIST.
From the values provided by these two participants, interpolated values were calculated with associated uncertainties. The results are reported in the tables below, and were used as the value in the mixture reported by participants at the time of measurements performed at the BIPM.

	NPL		NIST		
days	x (µmol mol^{-1})	u (µmol mol^{-1})	days	x (µmol mol^{-1})	u (µmol mol^{-1})
0	29.94	0.03	0	29.854	0.018
329	29.91	0.03	274	29.720	0.105
			interpolated value		
148	29.93	0.05	154	29.779	0.108

Table 4 : NPL and NIST reported mole fractions of NO (x) and standard uncertainty (u) in their 30 µmol mol^{-1} standard before shipment to the BIPM (day 0) and after their return (360 days). The values during measurements at the BIPM were found by linear interpolation.

	NPL		NIST		
days	x (µmol mol^{-1})	u (µmol mol^{-1})	days	x (µmol mol^{-1})	u (µmol mol^{-1})
0	69.89	0.05	0	70.37	0.06
329	69.83	0.05	316	70.42	0.15
		interpolated value			
148	69.86	0.09	196	70.40	0.18

Table 5 NPL and NIST reported mole fractions of NO (x) and standard uncertainty (u) in their 70 µmol mol^{-1} standard before shipment to the BIPM (day 0) and after their return (360 days). The values during measurements at the BIPM were found by linear interpolation.

10 Key Comparison Reference Values

For each of the two nominal mole fractions, a generalised least–square (GLS) regression was performed on the ensemble of values submitted by participants together with the averaged corrected responses of the analysers and associated standard uncertainties. A linear model was assumed. The software used for that purpose was XLGenline v1.1. The maximum value of the weighted differences between the coordinates of measured and adjusted points (both on the x and the y axes) was observed to judge if the ensemble of values could constitute a consistent calibration set. When this parameter was found to be larger than 2, outliers were identified and rejected from the set. This process was founded on technical reasons, as measurement results clearly demonstrated the presence of biases in values reported by two participants (GUM and BFKH). A disagreement between the CLD and UV analysers was interpreted as a sign of the presence of an interfering compound. FTIR measurements confirmed this assumption and underpinned the selection of standards contributing to the KCRVs calculation.

It was noted that one participant (CERI) prepared its two standards with NO mole fractions noticeably lower than the nominal value, which could constitute a reason of non-inclusion in a GLS regression. The GLS regression was performed with and without this participant, and the agreement between all participants was found to be unchanged. Therefore this value was included in the set.

The inclusion of VNIIM results in the calibration set was discussed during the 40th meeting of the Gas Analysis Working Group of the CCQM. Uncertainties submitted by the VNIIM do not include the component arising from the verification of the NO mole fraction, as was done by all other participants. As a result the uncertainty on the NO mole fraction at 30 µmol mol^{-1} is the lowest with a value of 0.006 µmol mol^{-1}, compared to 0.045 µmol mol^{-1} for the second lowest value submitted by CERI. The working group decided to exclude VNIIM results from the calibration set.

Finally, reference values were calculated by a regression with values and uncertainties submitted by all participants except BFKH, GUM and VNIIM.

The table below displays the results of the Generalised Least–Square regression performed on the four sets of measurement results with XLGenline. In each case the maximum absolute weighted residual shows that the nine chosen standards are consistent with a calibration line.

Nominal mole fraction	30 µmol mol^{-1}	70 µmol mol^{-1}
Number of points	8	9
Gradient *m*:	0.031697	0.013383
Uncertainty associated with *m*:	0.001505	0.001441
Intercept with y-axis *c*:	0.066327	0.064768
Uncertainty associated with *c*:	0.044761	0.100703
Covariance associated with *m* and *c*:	-0.000060	-0.000145
Root mean square residual error:	0.926901	0.934539
Maximum absolute weighted residual:	1.310872	1.335347

Table 6 : Generalised Least–Square parameters calculated with XLGenline at each nominal NO mole fraction on measurement results found with the UV and CLD analysers.

From the above parameters and the measurements results obtained with the UV analyzer, the Key Comparison Reference Values were calculated as follow:

$$x_{\mathrm{R},i} = my_i + \mathrm{c} \qquad (1)$$

And the associated standard uncertainty:

$$u(x_{\mathrm{R},i}) = \sqrt{m^2u(y_i)^2 + y_i^2u(m)^2 + u(\mathrm{c})^2 + u(m,c)} \qquad (2)$$

11 Degrees of Equivalence

The degree of equivalence of the participant *i* at the nominal value x_{nom} is defined as the difference:

$$D_i = x_i - x_{\mathrm{R},i} \qquad (3)$$

and its associated expanded uncertainty:

$$U(D_i) = 2\sqrt{u(x_i)^2 + u\left(x_{\mathrm{R},i}\right)^2} \qquad (4)$$

where

$x_{\mathrm{R},i}$ is the KCRV, calculated as amount of substance fraction in the standard predicted by the linear analysis function (equation 1);

$u(x_{\mathrm{R},i})$ is the standard uncertainty of the KCRV (equation 2);

x_i is the amount of substance fraction reported by the participating laboratory, or the interpolated value at the date of the measurements if a second value was reported;

$u(x_i)$ is the standard uncertainty associated with x_i;

Degrees of equivalences for all participants at the two nominal mole fractions are reported in the two tables below, one per mole fraction. Corresponding graphs of equivalence are plotted in the next section.

	Submitted or interpolated value		***Reference value***		***Degree of equivalence***	
NMI	x_i	$u(x_i)$	$x_{R,i}$	$u(x_{R,i})$	D_i	$U(D_i)$
BFKH	30.100	0.140	30.783	0.066	-0.629	0.314
CERI	28.510	0.045	28.520	0.082	-0.006	0.185
GUM	30.500	0.300	29.852	0.096	0.681	0.630
KRISS	30.014	0.100	29.966	0.094	0.083	0.274
LNE	30.211	0.034	30.286	0.065	-0.032	0.152
NIM	29.920	0.075	29.920	0.045	0.034	0.179
NMIA	29.980	0.130	30.032	0.068	-0.015	0.295
NMISA	30.240	0.085	30.235	0.068	0.047	0.221
NPL	29.927*	0.052	30.049	0.054	-0.085	0.154
VNIIM	30.025	0.006	29.975	0.045	0.086	0.097
NIST	29.779*	0.108	29.745	0.034	0.064	0.229

Table 7 : reference values and degrees of equivalence at the nominal mole fraction 30 µmol mol^{-1}.
*Value interpolated at the date of measurement (see section 9).

	Submitted or interpolated value		***Reference value***		***Degree of equivalence***	
NMI	x_i	$u(x_i)$	$x_{R,i}$	$u(x_{R,i})$	D_i	$U(D_i)$
BFKH	70.050	0.240	70.620	0.123	-0.570	0.539
CERI	68.760	0.110	68.771	0.144	-0.011	0.362
GUM	71.100	0.550	69.785	0.089	1.315	1.114
KRISS	70.085	0.161	69.864	0.069	0.221	0.350
LNE	69.990	0.080	70.020	0.070	-0.030	0.213
NIM	69.900	0.175	69.905	0.064	-0.005	0.372
NMIA	69.980	0.155	69.953	0.052	0.027	0.327
NMISA	70.090	0.105	69.930	0.066	0.160	0.249
NPL	69.863*	0.087	70.007	0.062	-0.144	0.214
VSL	70.050	0.105	70.094	0.087	-0.044	0.272
NIST	70.401*	0.176	70.354	0.076	0.047	0.383

Table 8 : reference values and degrees of equivalence at the nominal mole fraction 70 µmol mol^{-1}.
*Value interpolated at the date of measurement (see section 9).

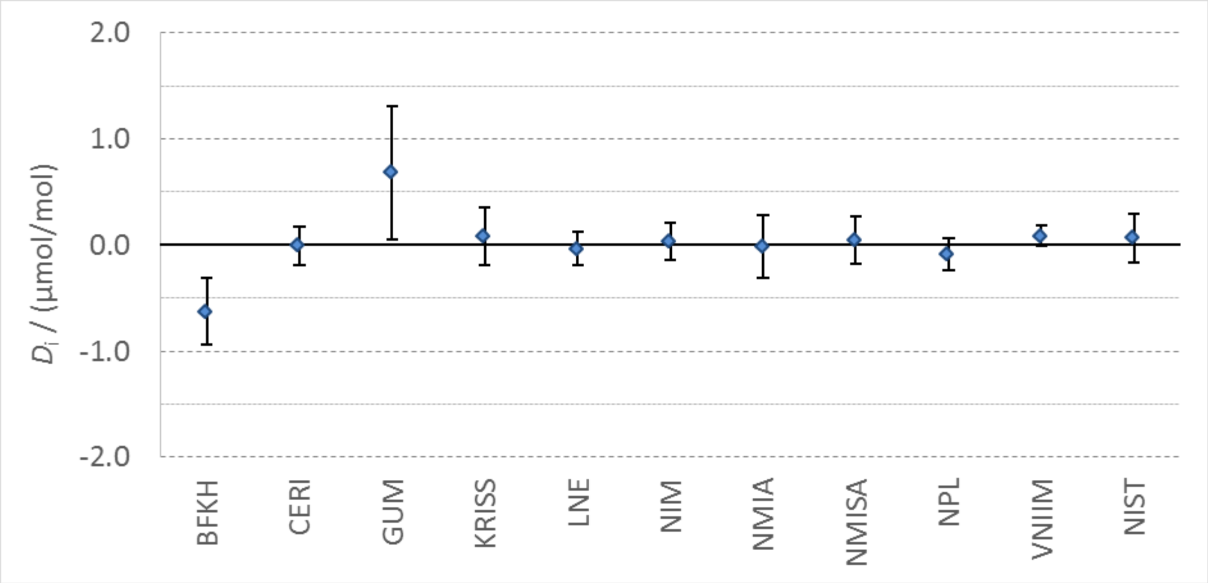

Figure 6: Graph of equivalence at the nominal mole fraction 30 µmol mol^{-1}.

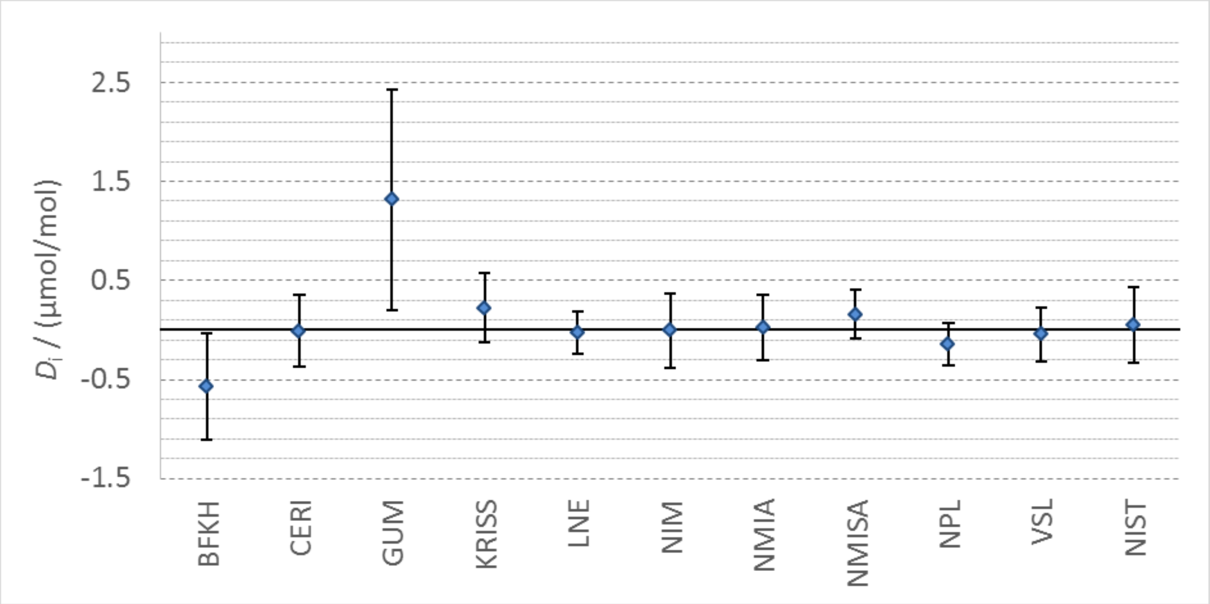

Figure 7: Graph of equivalence at the nominal mole fraction 70 µmol mol^{-1}.

12 Previous comparisons

It is interesting to compare the results of this Key Comparison with the previous exercise organised by the BIPM in 2006 using a very similar protocol, CCQM-P73 [1]. The main difference between the two exercise was the constraint on the nominal NO mole fractions, which had been chosen to span a range between 30 µmol mol^{-1} and 50 µmol mol^{-1} in CCQM-P73. Results displayed in Figure 8 shows that all participants who took part in both comparisons maintained or improved their agreement with the reference value. The improvement is most stricking for LNE, NMIA and NMISA, and this can be explained by an improved quantification of impurities in the mixtures.

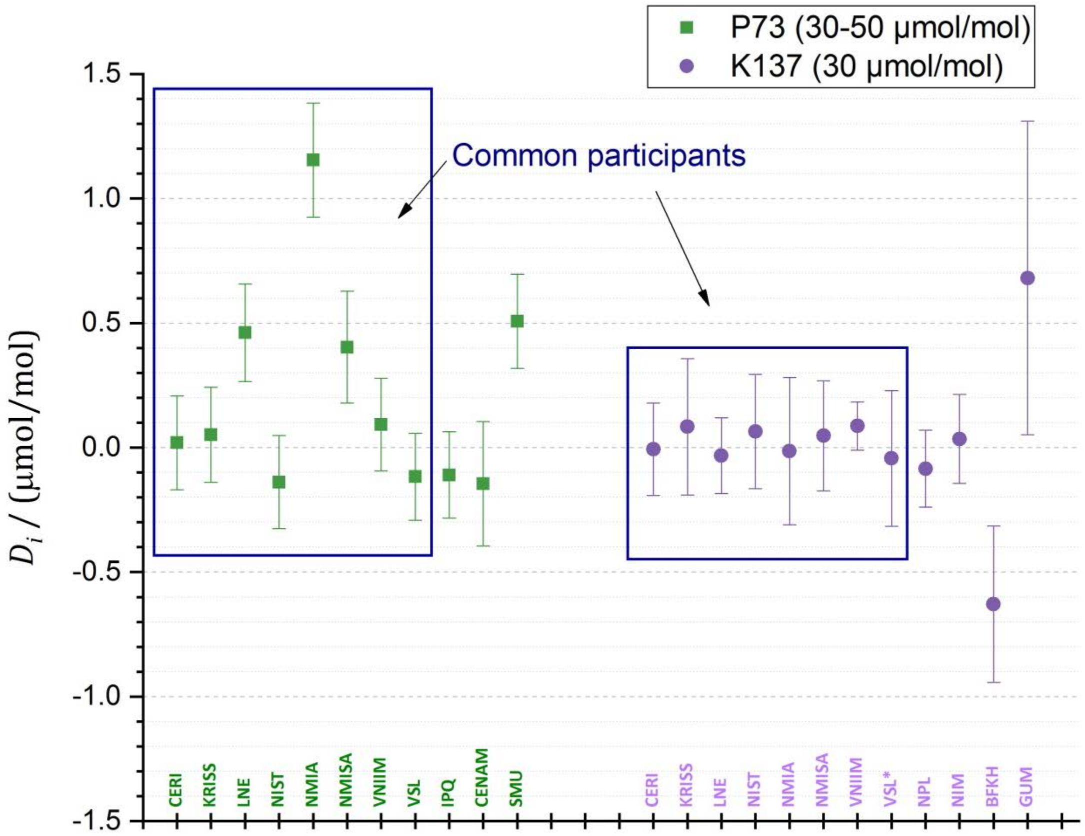

Figure 8: Results of the Pilot Study CCQM−P73 performed in the range 30 µmol mol^{-1} to 50 µmol mol^{-1} and the Key Comparison CCQM−K137 performed at 30 µmol mol^{-1} (except for VSL, result taken at 70 µmol mol^{-1}).

13 Conclusions

The agreement between the measurement results obtained with the two main techniques, CLD and UV, highlighted possible issues in the preparation of standards by two participants. They appeared to result in a larger bias between the analysers than observed for others. These observations were explained by the analysis of all standards by Fourier Transform Infrared Spectroscopy (FTIR) which identified in these standards the presence of a larger amount of water vapour (H_2O), nitrous oxide (N_2O) and nitrogen dioxide (NO_2), the three main impurities which can appear in mixtures of NO in nitrogen. It can be assumed that NO_2 and N_2O impurities were already present in the pure NO gas used during the gravimetric preparation. This highlights the need to choose parent gases of high purity.

The above observations were used to underpin the selection of standards (at the same nominal NO mole fraction) which can be considered as a consistent set, allowing the calculation of a calibration line by a Generalised Least-Square regression. Key Comparison Reference Values are then proposed for all participants as predicted values from the calibration lines. Interferences caused in the response of the CLD analyser by impurities (verified by FTIR measurements) leads to only the results from the UV analyser being proposed for the KCRV and Degrees of Equivalence calculations. Good agreement was observed between all participants who could prepare their standards with minimum levels of impurities. Compared to the results of the previous exercise CCQM−P73, it is striking to see that participants who took part on both comparisons considerably improved their preparative capabilities, minimising the impurities already observed during the Pilot Study.

While all participants were given the possibility to submit a second value after the return of their standards (about a year later), only two participants reported a difference. A loss of NO of about 0.1 % was observed by NPL in its two standards, and of 0.5 % by NIST in the standard at 30 µmol mol^{-1}. This had to be taken into account to calculate an interpolated value in the standards at the date of the measurements at the BIPM. This questions the possibility to reach uncertainties at the nmol mol^{-1} level, as claimed by some participants.

14 Supported claims

Preparing reference mixtures of NO in nitrogen at the µmol mol^{-1} levels is considered to present an analytical challenge by the Gas Analysis Working Group. Therefore, this key comparison is considered as a Specialised (Track C) comparison in the CCQM nomenclature. A detailed table indicating the minimum expanded uncertainty expected to be claimed with the corresponding range of the NO mole fraction will be published as an appendix to this report.

15 Annex 1 – Detailed measurements results

Results of all measurements performed at the BIPM are presented in Table 9 and Table 10 below.

ID	x	u	$\overline{y}_{CLD}$	$u(\overline{y}_{CLD})$	$\overline{y}_{UV}$	$u(\overline{y}_{UV})$
30.1	30.100	0.140	1.03862	0.00114	1.04034	0.00139
30.2	28.510	0.045	0.97005	0.00066	0.97021	0.00154
30.3	30.500	0.300	0.99563	0.00157	1.01150	0.00289
30.4	30.014	0.100	1.01724	0.00071	1.01503	0.00282
30.5	30.211	0.034	1.02699	0.00058	1.02495	0.00179
30.6	29.920	0.075	1.01523	0.00077	1.01361	0.00120
30.7	29.980	0.130	1.01867	0.00061	1.01707	0.00198
30.8	30.240	0.085	1.02509	0.00105	1.02335	0.00191
30.9	29.927	0.052	1.01934	0.00078	1.01761	0.00148
30.101	30.025	0.006	1.01753	0.00090	1.01529	0.00116
30.13	29.779	0.108	1.01016	0.00099	1.00818	0.00077

Table 9: Results of measurements performed at the BIPM on standards prepared at 30 µmol mol^{-1} NO in N_2: cylinder internal reference (ID), mole fraction of NO assigned by participants (x), standard uncertainty (u), average of corrected responses with the CLD analyser ($\overline{y}_{CLD}$) and associated uncertainty $u(\overline{y}_{CLD})$, average of corrected responses with the UV analyser ($\overline{y}_{UV}$) and associated uncertainty $u(\overline{y}_{UV})$.

ID	x	u	$\overline{y}_{CLD}$	$u(\overline{y}_{CLD})$	$\overline{y}_{UV}$	$u(\overline{y}_{UV})$
70.1	70.050	0.240	1.00751	0.00112	1.00988	0.00110
70.2	68.760	0.110	0.98577	0.00040	0.98514	0.00093
70.3	71.100	0.550	0.99330	0.00065	0.99871	0.00104
70.4	70.085	0.161	1.00073	0.00092	0.99977	0.00073
70.5	69.990	0.080	1.00191	0.00038	1.00185	0.00072
70.6	69.900	0.175	1.00100	0.00071	1.00032	0.00063
70.7	69.980	0.155	1.00127	0.00075	1.00095	0.00037
70.8	70.090	0.105	1.00191	0.00071	1.00065	0.00068
70.9	69.863	0.087	1.00260	0.00061	1.00168	0.00057
70.11	70.050	0.105	1.00355	0.00062	1.00284	0.00096
70.13	70.401	0.176	1.00705	0.00085	1.00633	0.00046

Table 10: Results of measurements performed at the BIPM on standards prepared at 70 µmol mol^{-1} NO in N_2: cylinder internal reference (ID), mole fraction of NO assigned by participants (x), standard uncertainty (u), average of corrected responses with the CLD analyser ($\overline{y}_{CLD}$) and associated uncertainty $u(\overline{y}_{CLD})$, average of corrected responses with the UV analyser ($\overline{y}_{UV}$) and associated uncertainty $u(\overline{y}_{UV})$.

16 Annex 2 – FTIR analysis

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 optional), a 40 mm beam diameter, a globar source and CaF_2 beam splitter was used for the study. The spectrometer was configured with a liquid N_2-cooled mid-infrared Indium Antimonide (InSb) detector and a 10.01 m multi-pass White-type gas cell of volume 0.75 L (Gemini Scientific Instruments, USA). The wetted surfaces of the gas cell were electro-polished stainless steel treated with silconert 2000 (Silcotek) and gold (mirror coatings). 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 spectrometer user interface was controlled using a BIPM developed software named B-FOS, that allowed 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. 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 parameters. 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 SFIT1 for ground based solar FT-IR measurements with agreement of better than 0.7 %.

The spectra were constructed by co-adding up to 320 scans recorded in about 5 minutes to provide a single spectrum of a sample. The ratio between this single spectrum and a similar spectrum of ultra-pure N_2 collected under similar conditions was performed to provide an absorbance or transmission spectrum of the gas sample (relative to ultra-pure N_2) in the gas cell. The sample flow rates were kept at ~400 mL min^{-1}. Assuming perfect mixing in the cell it was estimated that 99.9 % of the sample was replaced after 10 min of flow, and 99.998 % replaced after 20 min. In order to ensure the complete exchange of samples, only the measured spectra obtained after flowing the sample through the White-type cell for 40 min (99.99999 % gas replacement) were used for mole fraction determinations. The sample pressure was measured by means of the calibrated barometer Mensor Series 6000. The sample temperature was measured with a calibrated 100 Ω RTD temperature probe introduced into the outlet gas of the White-type gas cell.

The recorded spectra were analysed online by non-linear least squares fitting in the appropriate spectral regions (1770−1980 cm^{-1} for NO, 2100−2300 cm^{-1} for N_2O, 1500−1680 cm^{-1} for NO_2 and H_2O) with modelled spectra calculated by MALT 5.6 using absorption line parameters from the HITRAN database version 2012.

16.1 Impurities

The limit of detection was estimated to be 4 nmol mol^{-1} on NO_2, and N_2O.

Mole fractions of impurities detected by FTIR in all cylinders can be found in Table 11. They are provided for informational purposes only, without an associated uncertainty.

mixture	H_2O	N_2O	NO_2
30.1	1.696	0.097	0.560
30.2	0.028	0.007	
30.3	1.699	0.089	0.174
30.4	0.763	0.028	
30.5		0.007	
30.6	0.071	0.040	
30.7	0.060	0.033	
30.8	0.195	0.004	0.011
30.9		0.023	
30.101	1.160	0.039	
30.13	0.245	0.037	0.044
70.1	2.122	0.228	0.703
70.2	0.179	0.037	
70.3	2.168	0.256	0.551
70.4	0.686	0.079	0.014
70.5	0.042	0.010	
70.6		0.045	
70.7	0.423	0.071	
70.8	0.153		
70.9		0.050	
70.11	0.210	0.022	
70.13	0.393	0.041	0.041

Table 11: amount fractions of impurities detected and calculated by FTIR in standards prepared by participants. All values are in µmol mol^{-1}. Absence of a value means a value below the limit of detection.

16.2 Mole fraction of NO obtained by synthetic calibration

Nitrogen monoxide can easily be detected by FTIR and quantified using synthetic spectra calibration, constructing the synthetic spectra from the molecular parameters found in the Database Hitran 2012. This quantification process was thus performed on all standards in order to check the consistency of these measurements with those performed by CLD and UV. While the accuracy of this method is not as good as with gravimetric preparation, FTIR measurements demonstrated a good precision and linearity if all precautions are taken to avoid the non−linear part of the detector response [2]. In this comparison, it represents an interesting independent method with a different traceability than the gravimetric preparation by participants. Results of the measurements are plotted in Figure 9 and Figure 10, in which the error bars are the standard uncertainties: values submitted by participants on the *x*−axis, and a typical relative uncertainty of 0.5 % on the *y*−axis as representative of the FTIR spectrometer repeatability. Using only a repeatability component is another way to look at the consistency of all standards with a linear model, without using the regression software, and without the introduction of a control cylinder.

The two figures show the same pattern, with all standards except two (from GUM and BFKH) agreeing with a linear response of the FTIR. This is completely consistent with the bias observed between the UV and CLD analysers as well as with the higher amount of impurities for those standards.

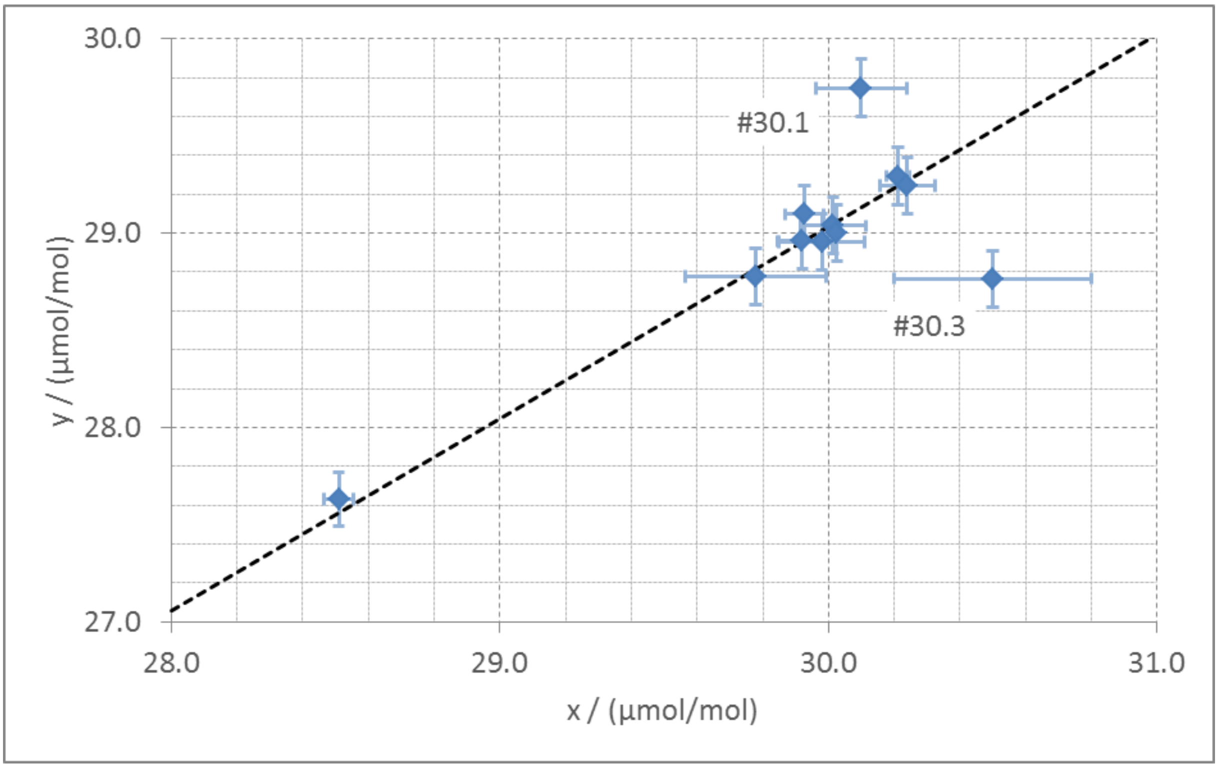

Figure 9: NO mole fractions quantified by FTIR using synthetic calibration against the submitted values by participants, on all standards prepared at 30 µmol mol⁻¹. The dotted line is a linear regression of all standards excluding #30.1 and #30.3. Error bars are standard uncertainties.

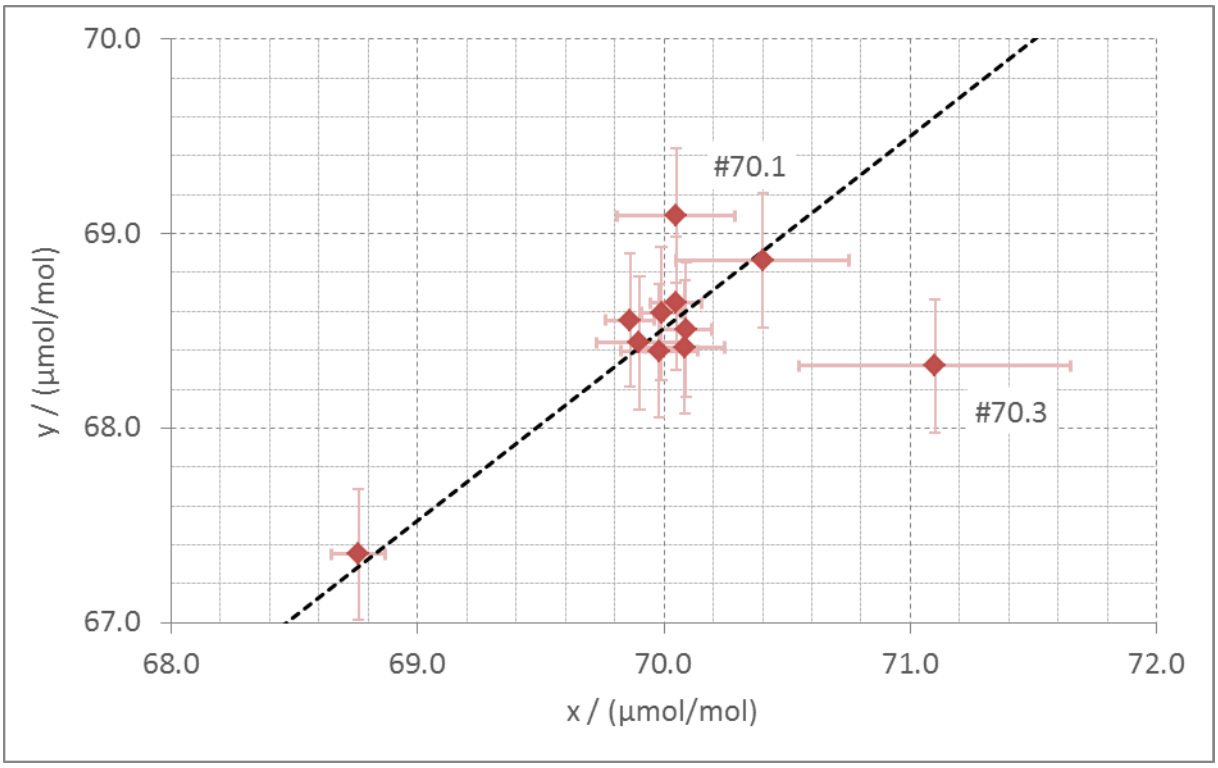

Figure 10: NO mole fractions quantified by FTIR using synthetic calibration against the submitted values by participants, on all standards prepared at 70 µmol mol⁻¹. The dotted line is a linear regression of all standards excluding #70.1 and #70.3. Error bars are standard uncertainties.

17 Annex 3 – Participants reports

All reports are displayed entirely in the following pages (PDF version only).

18 References

[1] Robert I.W., Michael E., Joële V., Philippe M., Sang Hyub O., Byung Moon K., Angelique B., James T., Ipeleng S.M., Masaaki M., Tatiana M., Christophe S., Viliam S., Miroslava V., Stanislav M., Alejandro Pérez C., Victor Serrano C., Francisco Rangel M., Leonid A.K., Yury A.K., Vladimir V.P., Elena V.G., William J.T., Franklin R.G., Damian S., Gonçalo B., Florbela D., Rob M.W., Gerard N. and Adriaan M.H.v.d.V., 2008, Final report on CCQM-P73: International comparison of nitrogen monoxide in nitrogen gas standards (30–70) µmol/mol, *Metrologia*, **45**, 08002,

[2] Flores E., Viallon J., Moussay P. and Wielgosz R.I., 2013, Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO_2) and Nitric Acid (HNO_3) Calibrated with Synthetic Spectra, *Applied spectroscopy*, **67**, 1171-1178,

National Institute of Metrology (NIM), China

Transmission of International Comparison Results

The title of international comparison: Nitrogen monoxide in Nitrogen

Serial number for international comparison: CCQM-K137

Experiment reporter: Hu Shuguo Zhang Tiqiang Han Qiao

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Transmission date: April. 14, 2017

1. Report form

Participant information			
Institute	National Institute of Metrology, China(NIM)		
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Contact person	Shuguo Hu, Tiqiang Zhang, Qiao Han		
Telephone	+086-10-64525337	**Fax**	+086-10-64204601
Email	hushg@nim.ac.cn, zhangtq@nim.ac.cn, hanqiao@nim.ac.cn		

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	2017.3	2017.3
Serial number	CAL017609	CAL017455
Pressure	8.5 MPa	11.5 MPa
Volume	6 L	6 L
Connection type	CGA660	CGA660

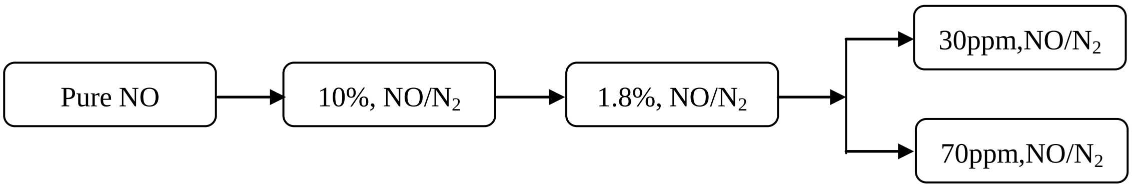
Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty $U(x(\mathrm{NO}))$ / µmol mol^{-1}**	**Coverage factor**
30	29.92	0.15	2
70	69.90	0.35	2

2. Preparation method

The first step: Pure NO and nitrogen were added into cylinder respectively**.**

The second step: The mixture was diluted by nitrogen.

The third step: The mixture was transferred by a small stainless steel cylinder and diluted by nitrogen again.



3. Purity analysis of ‘pure’ components

Purity table for N_2

Component	**Method**	**Mole fraction (µmol/mol)**	**Distribution**	**Uncertainty (µmol/mol)**
O_2	Oxygen Analyzer	0.05	Rectangular	0.03

Ar	GC-PDHID	45.0	Normal	0.90
H_2	GC-PDHID	0.05	Rectangular	0.03
H_2O	CRDs	0.2	Rectangular	0.12
CO	GC-PDHID	0.05	Rectangular	0.03
CO_2	GC-PDHID	0.05	Rectangular	0.03
CH_4	GC-PDHID	0.05	Rectangular	0.03
N_2		999954.40	-	0.92

Purity table for NO

Component	Method	Mole fraction (µmol/mol)	Distribution	Uncertainty (µmol/mol)
N_2O	FTIR	430.0	Normal	43.0
NO_2	FTIR	880.0	Normal	88.0
HNO_3	FTIR	200.0	Normal	100
N_2	GC-PDHID	100.0	Normal	20.0
NO		998390.0	-	141.4

4. Preparation Data

Specification of balance (Model No., Readability, etc.)

1) Metter XP26003L, capacity 26 kg, Readability 1 mg

2) Sartorius-ME614S, capacity 610 g, Readability 0.1 mg

Weighing method (A-B-A, Substitution method, etc.)

Substitution method, reference cylinder (A-B-A)

Concentration’s calculation equation is according to ISO 6142:

$$x_i = \frac{\sum_{A=1}^{P} \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^{n} (x_{i,A} \cdot M_i)} \right)}{\sum_{A=1}^{P} \left(\frac{m_A}{\sum_{i=1}^{n} (x_{i,A} \cdot M_i)} \right)}$$

Components uncertainties are calculated with below equation:

$$u^2(x_i) = \sum_{A=1}^{P} \left(\frac{\partial x_i}{\partial m_A} \right)^2 u^2(m_A) + \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial M_i} \right)^2 u^2(M_i) + \sum_{A=1}^{P} \sum_{i=1}^{n} \left(\frac{\partial x_i}{\partial x_{i,A}} \right)^2 u^2(x_{i,A})$$

Purity table for final mixture

Components	CAL017609		CAL017455	
	Mole fraction (µmol/mol)	Uncertainty (µmol/mol)	Mole fraction (µmol/mol)	Uncertainty (µmol/mol)
H_2	0.05	0.03	0.05	0.03
Ar	45.00	0.09	45.00	0.09
O_2	0.05	0.03	0.05	0.03
CO	0.05	0.03	0.05	0.03
CO_2	0.05	0.03	0.05	0.03
CH_4	0.05	0.03	0.05	0.03
H_2O	0.20	0.12	0.20	0.12
NO	29.92	0.02	69.90	0.02
N_2O	0.01	0.01	0.01	0.01
NO_2	0.03	0.01	0.03	0.01
HNO_3	0.01	0.01	0.01	0.01
N_2	999924.58	0.17	999884.60	0.17

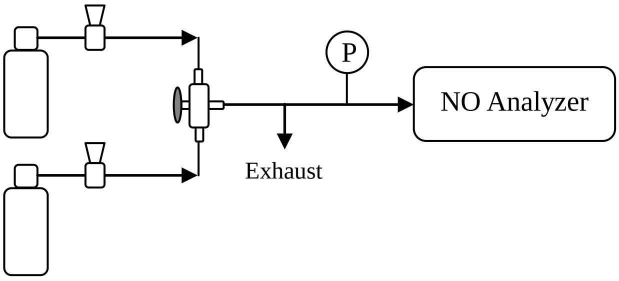
5. Analysis method

5.1 Instrument

Thermo NO analyzer (42i-HL)

5.2 Description of the procedure

Two standard cylinders with similar concentration were connected to pressure regulator. By using the TFA tube(1/4'), two pressure regulators and analyzer were connected to a three-way valve respectively. The sample in two standard cylinders can enter instrument respectively by changing the direction of there-way valve. The sample went through the instrument for analyzing, the inlet pressure of the analyzer was controlled at about 2.0 psi, and the flow rate of the sample was controlled at about 0.5 L/min. The analysis time of each sample was 5 min. When NO were analyzed, ‘A-B-A-B-A’ type calibration was used.



6. Evaluation of uncertainty

The contributions of standard uncertainty were from preparation of gravimetric method, verification in different days and long term stability.

$$u_{rep} = \sqrt{u_{prep}^2 + u_{ver}^2 + u_{st}^2}$$

Here, *u* means relative standard uncertainty.

u_{rep}: Uncertainty of concentration of NO in the comparison gas cylinder.

1. u_{prep}: Uncertainty from gravimetrical preparation and purity.
2. u_{ver}: Uncertainty from verification in different days.
3. u_{st}: Uncertainty of stability.

Source of uncertainty	u_{prep}	u_{ver}	u_{st}
Relative standard uncertainty	0.1%	0.1%	0.2%
Relative expanded uncertainty*	0.5%		

*The coverage factor *k*=2 (95% confidence level)

Key Comparison CCQM-K137
NO in N_2, (30 and 70) µmol mol^{-1}

1. General information

Participant information			
Institute	Government Office of the Capital City Budapest, BFKH Metrological and Technical Supervisory Department Radiation Physics and Chemistry Section		
Address	Németvölgyi út 37-39. Budapest 1124 Hungary		
Contact person	Judit Fükő		
Telephone	+36 1 4585988, +36 1 4585800	Fax	+ 36 1 4585 937
Email*	fuko.judit@bfkh.gov.hu		

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	70 µmol mol^{-1}
Date of preparation	26.05.2017	26.05.2017
Serial number	D521735	D521796
Pressure	125 bar	110 bar
Volume	1250 l	1100 l
Connection type	DIN 1	DIN 1

2. Results of measurements

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	**30.10**	**0.28**	**2**
70	**70.05**	**0.48**	**2**

3. Uncertainty Budget

Uncertainty budget of preparation of NO standard by gravimetry:

D521735	30ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
$NO-N_2$	5380	ppm	Normal	16	ppm	1	0.0030
$NO-N_2$ mass	8.4805	g	Normal	0.0055	g	1	0.00065
O_2	30.10	ppm	Normal	0.07	ppm	1	0.00233
Cylinder	30.10	ppm	Normal	0.05	ppm	1	0.00166
Filling	30.10	ppm	Normal	0.05	ppm	1	0.00166
Stability	100	%	Normal	0.1	%	1	0.001
Variance							0.0092
U (k=2)						ppm:	0.28

D521796	70ppm						
Uncertainty source	Estimate		Assumed distribution	Standard uncertainty		Sensitivity coefficient	Contribution to standard uncertainty
X_I	x_I			$u(x_i)$		c_I	$u_I(y)$
$NO-N_2$	5380	ppm	Normal	16	ppm	1	0.0030
$NO-N_2$ mass	17.015	g	Normal	0.0055	g	1	0.00032
O_2	70.05	ppm	Normal	0.07	ppm	1	0.0010
Cylinder	70.05	ppm	Normal	0.05	ppm	1	0.00071
Filling	70.05	ppm	Normal	0.05	ppm	1	0.00071
Stability	100	%	Normal	0.1	%	1	0.001
Variance							0.0069
U (k=2)						ppm:	0.48

4. Measurement procedure

All the two mixtures measured by using chemiluminescence NO analyser (API, Servomex 1491) in combination with a multimeter (model 2000, Keithley). The measurement method was direct comparison with a BFKH standard.

5. Additional information

SOURCE OF NO, NITROGEN,:

NO	2.0 from SIAD Italy
N_2	5.0 from Messer Hungary
N_2	6.0 from Messer Hungary

5.1 PURITY TABLE OF PURE NO: (38458)

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
NO	specifications	0.990000	0.003000
other	specifications	0.010000	0.003000

5.2 PURITY TABLE OF PURE NITROGEN / 5.0:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
N_2	specifications	0.999990	0.0000120
O_2	measure	0.00000157	0.0000003
H_2O	specifications	0.000003	0.0000035
CH_4	specifications	0.0000001	0.0000001

PURITY TABLE OF PURE NITROGEN / 6.0:

Component	Method	Mole fraction (mol/mol)	Uncertainty (mol/mol)
N_2	specifications	0.999999	0.0000012
O_2	measure	0.00000031	0.00000007
H_2O	specifications	0.0000005	0.0000058
CH_4	specifications	0.0000001	0.0000001
CO	specifications	0.0000003	0.0000004
H_2	specifications	0.0000001	0.0000001

5.3 PREPARATION OF THE MIXTURES:

The hierarchy of gravimetric mixtures prepared by BFKH for this comparison is show Figure 1.

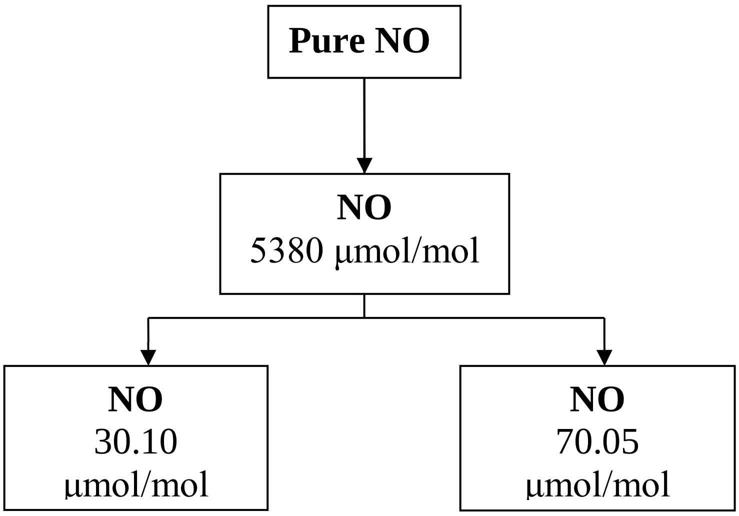


Figure 1. The hierarchy of the gravimetric mixtures of NO/N_2 prepare by BFKH

We used 10 L aluminum cylinder (Luxfer, Aculife 4+3) with stainless steel valves DIN1.
Both mixtures were prepared with dilution series.
First the pure NO was filled into the properly prepared cylinder. After the pure nitrogen gas was filled directly gravimetrically, and the measurement of the gases mass was carried out by a high precision topload balance – Mettler Toledo XP26003L.

5.4 PURITY TABLE OF THE FINAL MIXTURES:

Cylinder Identification Number: D521735

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
NO	0.00003010	mol/mol	0.00000028	mol/mol	2
other	0.00000144	mol/mol			
N_2	0.99996846	mol/mol			

Cylinder Identification Number: D521796

Component	Mole fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
NO	0.00007005	mol/mol	0.00000048	mol/mol	2
other	0.00000187	mol/mol			
N_2	0.99992808	mol/mol			

5.5 VERIFICATION PROCEDURE APPLIED TO THE FINAL MIXTURES:

Mixtures measured by using chemiluminescence NO analyser (API, Servomex 1491) in combination with a multimeter (model 2000, Keithley). The measurement method was direct comparison with a BFKH standard. BFKH's old standard was verified with VSL primery reference materiel.

5.6 STABILITY OF THE MIXTURES:

The stability of the standards were validated by comparison of the old standards which concentration was 97.80 µmol/mol (DC2402).

Stability table 1:

Cylinder	Gravimetric NO (µmol/mol)	Measure1 13.06.2017 NO (µmol/mol)	Measure2 22.06.2017 NO (µmol/mol)
D521735	30.10 ± 0.28	30.16 ± 0.18	30.13 ± 0.17
D521796	70.05 ± 0.48	70.16 ± 0.30	70.12 ± 0.31

All the two mixtures were measured using chemiluminescence NO analyser two times independently between the time they are prepared and the time they are shipped to the BIPM. There wasn't significant difference between the certified values and the measured values.

Second analysis. The two cylinders arrived from BIPM we measured then.

Stability table 2:

Cylinder	Gravimetric NO (µmol/mol)	Measure3 07.03.2018 NO (µmol/mol)
D521735	30.10 ± 0.28	30.18 ± 0.17
D521796	70.05 ± 0.48	70.14 ± 0.30

There wasn't significant difference between the first values and the second values.

5.7 CYLINDERES PRESSURE BEFORE SHIPMENT TO THE BIPM: 100 bar

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.
- Comparison coordinator: Dr Joële Viallon
  Chemistry Department
  Bureau International des Poids et Mesures
  Pavillon de Breteuil
  F-92312 SEVRES CEDEX
  Tel: +33 1 45 07 62 70
  Email: jviallon@bipm.org

Return of result form:

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

Participant information

Institute	LNE		
Address	1 rue Gaston Boissier 75724 Paris Cedex 15		
Contact person	Macé Tatiana		
Telephone	01 40 43 38 53	**Fax**	
Email	tatiana.mace@lne.fr		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	**21/12/2016**	**13/12/2016**
Serial number	**APE1169728-NO/N2 0077**	**APE 1169715-NO/N2 0076**
Pressure	**125**	**130**
Volume	**10**	**10**
Connection type	**C**	**C**

Results of measurements

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	30,211	0,067	2
70	69,99	0,16	2

Uncertainty budget

NO/N2 0076

Uncertainty source	Unit	Value Xi	u(Xi)	Sensitivity coefficient. C(Xi)	C(Xi).u(Xi)	Contribution to the uncertainty
NO Premix Mass	g	142.3222	0.0153	0.4489	6.86e-3	0.82%
N_2 Mass	g	1491.089	0.0184	-4.285e-2	-7.89e-4	0.01%
NO concentration (premix)	mol/mol	803.30e-6	3.25e-7	8.71248e4	2.8316e-2	13.94%
N_2 purity	mol/mol	0.9999749345	1.44e-5	-63.8943	-9.2e-4	0.01%
NO molar mass	g/mol	30.00614	3.1e-4	-1.832e-3	-6e-7	0.00%
N_2 molar mass	g/mol	28.01348	9.9e-5	1.962e-3	2e-7	0.00%
Stability	%	0	0.07	1	7e-2	85.21%

C_{NO}=69.99 ± 0.16 µmol/mol

NO/N2 0077

Uncertainty source	Unit	Value Xi	u(Xi)	Sensitivity coefficient. C(Xi)	C(Xi).u(Xi)	Contribution to the uncertainty
NO Premix Mass	g	61.55914	0.0154	0.4723	7.27e-3	4.80%
N_2 Mass	g	1575.2290	0.0184	-1.8457e-2	-3.4e-4	0.01%
NO concentration (premix)	mol/mol	803.30e-6	3.25e-7	3.76e4	1.22e-2	13.55%
N_2 purity	mol/mol	0.9999749345	1.44e-5	-29.07	-4.19-4	0.02%
NO molar mass	g/mol	30.00614	3.1e-4	-8.34e-4	-3e-7	0.00%
N_2 molar mass	g/mol	28.01348	9.9e-5	8.93e-4	9e-8	0.00%
Stability	%	0	0.03	1	3e-2	81.63%

C_{NO}=30.211 ± 0067 µmol/mol

Measurement procedure

The gas mixtures of NO/N_2 were analysed by an analyser from Thermo fisher model 42i based on a chemiluminescence technique.
The gas mixtures were diluted with very accurate flowmeters (Molbloc) to provide gas mixtures at 10 µmol/mol and then were compared to a gravimetric NO gas mixture at 10 µmol/mol.

Additional information

- Purity table with uncertainties for the nominally pure NO parent gas;

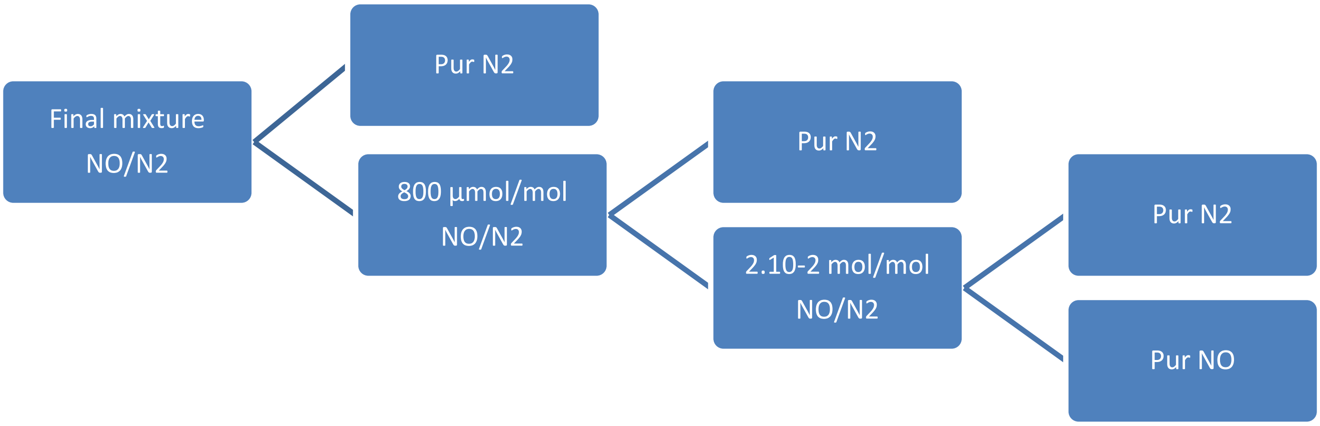
Component	mol/mol	uncertainty (k=1)
'NO'	0.9994833	0.0000666
'NO2'	0.000155	0.000011
'N2O'	0.000210	0.000011
'CO2'	0.0	0.000029
'N2'	0.0001517	0.0000076
'H2O'	0.0	0.0000058

- Purity table with uncertainties for the nominally pure N_2 gas;

°°°°°°°°°° Pur\azote_bip_GQ88DUI.txt °°°°°°°°°°°

Component	mol/mol	uncertainty
N2	0.9999749345	0.0000144338
CO2	0.0000000005	0.0000000003
H2O	0.0000000100	0.0000000058
Ar	0.0000250000	0.0000144338
O2	0.0000000050	0.0000000029
H2	0.0000000250	0.0000000144
CnHm	0.0000000250	0.0000000144

- Brief outline of the dilution series undertaken to produce the final mixtures;



- Purity table for each final mixture, including gravimetric uncertainties;

NO/N2 0076

Component	µmol/mol	uncertainty
N2	999905.0012	13.23072104
NO	69.99101137	0.02922139
Ar	24.91662504	13.23160999
H2	0.02499825	0.01320071
CnHm	0.02491663	0.01320063
N2O	0.01470571	0.00077009
NO2	0.01085422	0.00077013
H2O	0.00999930	0.00533575
O2	0.00499965	0.00266013
CO2	0.00053914	0.00575759
methane	0.00008162	0.00004715
CO	0.00004081	0.00002357

NO/N2 0077

Component	µmol/mol	uncertainty
N2	999944.7485	13.90037295
NO	30.21091	0.01425815
Ar	24.96401205	13.90078409
H2	0.02499924	0.01386825
CnHm	0.02496401	0.01386823
H2O	0.00999970	0.00558916
N2O	0.00634757	0.00033240
O2	0.00499985	0.00279320
NO2	0.00468511	0.00033242
CO2	0.00051690	0.00251297
methane	0.00003523	0.00002035
CO	0.00001762	0.00001018

- a brief outline of any stability testing of the gas mixtures between the time they are prepared and the time they are shipped to the BIPM.

The stability of the gas mixtures were evaluated with the same procedure mentioned for the verification of gas mixtures.
The stability of the gas mixtures were performed during a period of six months. The results are showed below.

NO/N2 0076

Date	analytical concentration µmol/mol	Uncertainty k=2 µmol/mol	Ecart %	Standard used
21/12/2016	70,02	0,47	0,04	NO/N2 0074
05/04/2017	69,43	0,47	-0,80	NO/N2 0074
05/04/2017	69,58	0,47	-0,59	NO/N2 0074
05/04/2017	69,73	0,47	-0,37	NO/N2 0078
29/06/2017	69,41	0,47	-0,83	NO/N2 0078
29/06/2017	69,42	0,47	-0,81	NO/N2 0078

NO/N2 0077

22/12/2016	30,05	0,47	-0,53	0,9
10/04/2017	29,51	0,47	-2,32	
10/04/2017	29,48	0,47	-2,42	
30/06/2017	30,18	0,47	-0,10	0,15
30/06/2017	30,33	0,47	0,39	

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

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

Return of result form:

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

Participant information

Institute	National Measurement Institute, Australia		
Address	36 Bradfield Rd, Lindfield NSW 2070 AUSTRALIA		
Contact person	Damian Smeulders		
Telephone	+61 2 84673534	**Fax**	
Email	gas@measurement.gov.au		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	70 µmol mol^{-1}
Date of preparation	19 April 2017	19 April 2017
Serial number	D248076	D248064
Pressure	130 BAR	130 BAR
Volume	5 LITRE	5 LITRE
Connection type	DIN 1	DIN 1

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	29.98	0.26	2
70	69.98	0.31	2

Uncertainty budget

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

Uncertainty from preparation: including uncertainties from gravimetry and from gas purity.
Uncertainty from verification: verification was performed using FTIR. The verification uncertainty that has been applied also covers long term drift in mixture composition.
Uncertainty contributions were combined using the sum of squares equation.

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

FTIR was used for mixture validation and for purity assessment of the parent gases. For validation a 10m gas cell was used with a Nicolet 6700 FTIR.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
- a purity table with uncertainties for the nominally pure N_2 gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Additional information for CCQM-K137 from NMIA:

Purity tables for nominally pure source gases:

- **Nominally pure nitric oxide**

NO_09A		Conc.	U(Conc.)	Composition Range	Uncertainty Type	Justification of Value
Nitrogen Dioxide	NO_2	0.0024	0.0001	%mol/mol	Normal	NMI analysis
Nitrous Oxide	N_2O	0.114	0.01	%mol/mol	Normal	NMI analysis
Nitric Oxide	NO	0.9988	0.0001	mol/mol	Normal	Nominally pure component

- **Nominally pure nitrogen**

N2_16C_6d0		Conc.	U(Conc.)	Composition Range	Uncertainty Type	Justification of Value
Argon	Ar	32.37	0.09	µmol/mol	Normal	NMI analysis
Oxygen	O_2	0.043	0.043	µmol/mol	Normal	NMI analysis
Water	H_2O	0.25	0.25	µmol/mol	Rectangular	Manufacturer's 'less than' specification
Carbon Monoxide	CO	0.025	0.025	µmol/mol	Rectangular	Below NMI detection limit
Carbon Dioxide	CO_2	0.025	0.025	µmol/mol	Rectangular	Below NMI detection limit
Methane	CH_4	0.025	0.025	µmol/mol	Rectangular	Below NMI detection limit
Nitrogen	N_2	0.999967	3.3E-07	mol/mol	Normal	Nominally pure component

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

NO was cryogenically purified to produce 10% NO in N_2 parent mixtures. This mixture was analysed to determine the NO_x impurities.

Each parent mixture was used to make a 30ppm and 70ppm NO in N_2 mixture by decant using a 10ml transfer vessel.

Purity table for each of the final mixtures, including gravimetric uncertainties:

- 30 ppm mixture: D248076 showing composition and preparation uncertainty (k = 2).

D248076		Conc.	**U**(Conc.)	Composition Range	Uncertainty Type
Nitrogen Dioxide	NO_2	0.000721	0.00003	µmol/mol	Normal
Nitrous Oxide	N_2O	0.0342	0.0030	µmol/mol	Normal
Nitric Oxide	NO	29.988	0.080	µmol/mol	Normal
Nitrogen	N_2	0.9999372		mol/mol	

- 70 ppm mixture: D248064 showing composition and preparation uncertainty (k = 2).

D248064		Conc.	**U**(Conc.)	Composition Range	Uncertainty Type
Nitrogen Dioxide	NO_2	0.00168	0.00008	µmol/mol	Normal
Nitrous Oxide	N_2O	0.0799	0.0070	µmol/mol	Normal
Nitric Oxide	NO	69.993	0.18	µmol/mol	Normal
Nitrogen	N_2	0.9998972		mol/mol	

Outline of the verification procedure applied to the final mixtures; and the stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM

Mixtures were verified on a Nicolet FTIR with 10m gas cell. Verification involved testing the 6 cylinders prepared for this comparison with other NO in nitrogen mixtures prepared at different times. The additional verification mixtures included mixtures made in a separate batch after the completion of these mixtures (4 cylinders at a nominal 30 ppm), plus four cylinders made at 30 and 70 ppm approximately 12 months prior to the manufacture of these mixtures. In addition, historical mixtures made in 2015 that spanned the 10-70 ppm concentration range were also used. Cylinders were analysed 3 times over a one month period.

The verification identified 2 mixtures that contained the lowest concentration of nitrous oxide (N_2O) as an impurity – and it was these mixtures that were selected to be sent to the BIPM. As part of the preparation of the reference gases, NO (~99% pure) was purified cryogenically to remove most N_2O and all NO_2 impurities. The amount of N_2O transferred across during the purification is variable and was estimated by FTIR using a short 10 cm gas cell.

The verification measurements were used to assign a suitable uncertainty to the mixtures. The uncertainty from verification was large enough to cover differences in concentration observed over a 2-year period.

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

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

Return of result form:

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

Participant information			
Institute	NMISA		
Address	Building 5N CSIR Campus Pretoria Meiring Naude Road Brummeria Pretoria		
Contact person	Dr James Tshilongo		
Telephone	+27 12 841 2589	**Fax**	
Email	Jtshilongo@nmisa.org		

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	30 May 2017	13 June 2017
Serial number	M55 5689	D95 8404
Pressure	110 bar	112 bar
Volume	5L	5L
Connection type	BS 341	BS 341

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	30,24	0,17	2
70	70,09	0,21	2

Uncertainty budget

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

$$\mathrm{u(NO)} = \sqrt{ugravimetric^2 + u\ verification^2}$$

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

- The measurements were performed on the ABB Limas UV spectroscopy using multipoint standard ranging from 10- 100 µmol/mol. The measurements were performed over three weeks period in the month of June 2017.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
    - The purity of NO used contained approximately 2,3 % NO in nitrogen purchased from Takachiho in Japan. The NO with 99,99% could not be shipped between South Africa and Japan between 2015 and early 2017. The purity of cylinder CPE10044 is shown below in table 1 and that of CPB30758 is in table 2

Table 1: Purity of CPE10044 used to prepare D95 8404

CPE10044		
N2'	0.976981007	2.05546E-05
NO'	0.023017902	2.0548E-05
NO2'	3.45285E-07	1.9934E-07
N2O'	3.45285E-07	1.9934E-07
H2O'	2.55755E-07	1.40842E-07
CH4'	3.5934E-08	1.52097E-08
CO2'	3.5934E-08	1.52097E-08
CO'	2.44245E-08	1.36777E-08
H2'	2.44245E-08	1.36777E-08
O2'	2.44245E-08	1.36777E-08

Table 2: Purity of CPE10044 used to prepare M55 5689

CPB30758		
N2'	9.769727E-01	2.106427E-05
NO'	2.302616E-02	2.105777E-05
NO2'	3.454085E-07	1.994116E-07
N2O'	3.454085E-07	1.994118E-07
H2O'	2.557568E-07	1.408414E-07
CH4'	3.593794E-08	1.521068E-08
CO2'	3.593794E-08	1.521067E-08
CO'	2.442432E-08	1.367762E-08
H2'	2.442432E-08	1.367762E-08
O2'	2.442432E-08	1.367762E-08

- a purity table with uncertainties for the nominally pure N_2 gas;

Table 3: Purity table of nitrogen BIP

Nitrogen BIP		
'Ar'	5.3900E-05	2.70E-06
'C2H6'	6.3000E-09	3.64E-09
'CH4'	4.2900E-09	2.48E-09
'CO'	6.8500E-09	3.96E-09
'CO2'	9.7500E-09	1.13E-09
'H2'	9.0000E-09	5.20E-09
'H2O'	1.0000E-08	5.75E-09
'O2'	5.0000E-09	2.89E-09
'N2'	9.9995E-01	2.70E-06

- a brief outline of the dilution series undertaken to produce the final mixtures;
  - the dilution steps for each mixture is as follows: for cylinder D95 8404, two dilution steps were taken and for cylinder M55 5689 it is three step dilutions.

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

  The purity table for mixture M55 5689 is shown in table 4 below:

Table 4: purity table of M55 5689

M55 5689		
N2	9.99915881E-01	2.5028E-06
Ar	5.38292195E-05	2.50268E-06
NO	3.02375458E-05	3.0071E-08
H2O	1.03227200E-08	5.333E-09
CO2	9.78439000E-09	1.04761E-09
H2	9.02025000E-09	4.82002E-09
CO	6.87308000E-09	3.67065E-09
C2H6	6.29173000E-09	3.37399E-09
O2	5.02551000E-09	2.67886E-09
CH4	4.33156000E-09	2.29885E-09
NO2	4.53580000E-10	2.6186E-10
N2O	4.53580000E-10	2.6186E-10

The purity table for mixture D95 8404 is shown in table 5 below:

Table 5: Purity table for D95 8404

D95 8404		
N2	9.99876123E-01	2.4905E-06
Ar	5.37358805E-05	2.48985E-06
NO'	7.00869505E-05	6.11414E-08
H2O	1.07483000E-08	5.31976E-09
CO2	9.82973000E-09	1.04308E-09
H2	9.04697000E-09	4.79544E-09
CO	6.90351000E-09	3.65201E-09
C2H6	6.28082000E-09	3.35668E-09
O2	5.05915000E-09	2.66538E-09
CH4	4.38635000E-09	2.28744E-09
NO2	1.05135000E-09	6.0697E-10
N2O	1.05135000E-09	6.0697E-10

- a brief outline of the verification procedure applied to the final mixtures;
    - The verification measurements were performed on the ABB Limas UV spectroscopy using multipoint calibration with primary reference gas mixtures ranging from 10-100 µmol/mol prepared at NMISA. The measurements were performed over three weeks period in the month of June 2017.

- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.
    - The mixtures were prepared and verified within a month prior to shipping, no stability was observed in that period

Participant submission form
CCQM-K137, NO in N_2 (30 and 70 µmol mol^{-1})

Comparison Coordinator: Dr. Joële Vialon
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email: jviallon@bipm.org

Participant information			
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Contact person	Leonid Konopelko		
Telephone	+7 812 315 11 45	Fax	+7 812 315 15 17
Email*	**fhi@b10.vniim.ru**		

Information on Standards sent to BIPM		
	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	13.06.2017	09.06.2017
Serial number	D233917	D249681
Pressure	8 MPa	8 MPa
Volume	5 dm^3	5 dm^3
Connection type	DIN-6	DIN-1

Results of measurements

Table 1

Nominal mole fraction/ µmol mol^{-1}	NO mole fraction/ x (NO) µmol mol^{-1}	Expanded uncertainty* U (x (NO)) / µmol/mol^{-1}	Coverage factor
30	30.025	0.012	2
70	70.028	0.023	2

*****The values of expanded uncertainty do not include the component due to verification

Uncertainty Budgets

Table 2: Uncertainty budget (only gravimetry) for NO mole fraction for the cylinder D249681 (70 µmol/mol^{-1})

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.6720 µmol/mol	B	Rectangular	0.2003 µmol/mol	0.000025	0.000005
Purity of NO		998010.0000 µmol/mol	B	Rectangular	81,6175 µmol/mol	0.000070	0.005725
Weighing* 1 stage premixture (3.2 %)	NO	28.73093149 g	A,B	Normal	0.00209180 g	-2.353488	-0.004923
	N_2	805.91566679 g	A,B	Normal	0.01409150 g	0.083902	0.001182
Weighing* 2 stage premixture (980 µmol/mol^{-1})	1 pre-mixture	18.10624579 g	A,B	Normal	0.00204611 g	-3.748888	-0.007671
	N_2	571.58631086 g	A,B	Normal	0.00936699 g	0.118754	0.001112
Weighing* final mixture	2 pre-mixture	42.24202050 g	A,B	Normal	0.00278699 g	-1.539791	-0.004291
	N_2	551.21421736 g	A,B	Normal	0.01099118 g	0.118001	0.0012969
Combined standard uncertainty							**0.0117**
Expanded uncertainty k=2							**0.023**

Table 3: Uncertainty budget (only gravimetry) for NO mole fraction for the cylinder D233917 (30 µmol/mol^{-1})

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.6720 µmol/mol	B	Rectangular	0.2003 µmol/mol	0.000011	0.000002
Purity of NO		998010.0000 µmol/mol	B	Rectangular	81,6175 µmol/mol	0.000031	0.002453
Weighing* 1 stage premixture (3.2 %)	NO	28.73093149 g	A,B	Normal	0.00209180 g	-1.3009054	-0.002111
	N_2	805.91566679 g	A,B	Normal	0.01409150 g	0.0835973	0.000507
Weighing* 2 stage premixture (980 µmol/mol^{-1})	1 pre-mixture	18.10624579 g	A,B	Normal	0.00204611 g	-1.607329	-0.003289
	N_2	571.58631086 g	A,B	Normal	0.00936699 g	0.050916	0.000477
Weighing* final mixture	2 pre-mixture	17.96297847 g	A,B	Normal	0.00211215 g	-1.620460	-0.003423
	N_2	570.6332347 g	A,B	Normal	0.01069176 g	0.051011	0.000545
Combined standard uncertainty							**0.00581**
Expanded uncertainty k=2							**0.012**

*Uncertainty due to weighing includes constituents related to accuracy of balance, buoyancy effect resulting from change of cylinder volume during filling, mass pierces used, drift of balance, residual gas in cylinder.

Measurement procedure

1) Measurement for the 1-st stage (3.2 %) and 2-nd stage (980 µmol/mol^{-1}) premixtures were carried out by means of FTIR spectrometer FSM 1201 (Russia):
Spectral resolution - 4 cm^{-1},
Accumulation time -20 s,
Optical path length - 0,1 m for gas mixtures of the 1-st stage;
4.8 m for lower concentrations.
2) Measurements for the final mixtures were carried out
2.1) for 30 µmol/mol^{-1} by chemiluminescence technique with the help of Gas analyzer “AC-30M” (Environnement S.A., France):
settling time – 3 min,
zero control with pure N_2,
gas flowrate – 1.7 dm^3/min.

2.2) for 70 µmol/mol^{-1}
by UV absorbtion spectroscopy with the help of Cary-5000 Spectrofotometer (Agilent, US) with gas cell:
gas flowrate – 0.3 dm^3/min,
settling time – 10 min,
data averaging - 5 s,
reading time –last 3 minutes.

by FTIR spectrometer FSM 1201 (Russia)
Spectral resolution - 4 cm^{-1},
Accumulation time -20 s,
Optical path length -4.8 m.

Additional information

a) Purity table with uncertainties for the nominally pure NO parent gas
Table 4

Cylinder N 77485 Main component NO Mole fraction 99,8010 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
N_2O	1070	62
NO_2	920	53
CO_2	5	2.9

b) Purity table with uncertainties for the nominally pure N_2 parent gas
Table 5:

oblock Main component N_2 Mole fraction 99.9998672 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
Ar	0.916	0.011
O_2	0.0015	0.0009
CO_2	0.0025	0.0014
H_2	0.0025	0.0014
CH_4	0.0025	0.0014
CO	0.0025	0.0014
H_2O	0.40	0.23

c) Brief outline of the dilution series undertaken to produce the final mixtures
Preparation of final mixtures (NO in nitrogen) was carried out from pure substances in 3 stages:
1-st stage – 3 mixtures NO/N_2 –level 3.2 %;
2-nd stage –3 mixtures NO/N_2. – level 980 µmol/mol;
3-nd stage – 2x3 target mixtures NO/N_2 - 30 and 70 µmol/mol.

All the final mixtures were prepared in Luxfer cylinders with Aculife III and Aculife IV coating (V= 5 dm^3)
d) Purity tables for the final mixtures with gravimetric uncertainties

Table 6: Purity table for the final mixture 70 μmol/mol^{-1} (cylinder D249681)

Component	Mole fraction, μmol/mol	Expanded uncertainty (k=2), μmol/mol
NO	70.028	0.023
N_2O	0.075	0.009
NO_2	0.065	0.007
Ar	0.916	0.022
H_2O	0.40	0.46
N_2	balance	

Table 6: Purity table for the final mixture 30 μmol/mol^{-1} (cylinder D233917)

Component	Mole fraction, μmol/mol	Expanded uncertainty (k=2), μmol/mol
NO	30.025	0.012
N_2O	0.032	0.004
NO_2	0.028	0.003
Ar	0.916	0.022
H_2O	0.40	0.46
N_2	balance	

e) brief outline of the verification procedure applied to the final mixtures

Verification within each group of cylinders (each concentration level) was performed by checking consistency between 3 freshly prepared nominally similar PSMs using regression analysis (FTIR technique and UV absorbtion spectroscopy) or direct comparison method (chemiluminescence technique).

Standard uncetainty of verification for NO/N_2 mixture 70 μmol/mol^{-1} u_{ver}=0,03 %

2 measurement series in 2 days (UV absorbtion spectroscopy) were carried out, each series consisted of 3 measurements in a sequence X_{ref}-X_1-X_{ref}-X_2-X_{ref} (with zero control with pure N_2)

Standard uncetainty of verification for NO/N_2 mixture 30 μmol/mol^{-1} u_{ver}=0,24 %

2 measurement series in 2 days (chemiluminescence technique) were carried out, each series consisted of 4 measurements in a sequence X_{ref}-X_1-X_{ref}-X_2-X_{ref} (with zero control with pure N_2)

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 and submitted at the same time as standards are sent to the BIPM

- Comparison coordinator:

Dr Joële Viallon
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Tel: +33 1 45 07 62 70
Email: jviallon@bipm.org

Return of result form:

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

Participant information

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Email	d.cieciora@gum.gov.pl; gas@gum.gov.pl		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	15.07.2016	28.07.2016
Serial number	D298390	D298384
Pressure	140 bar	140 bar
Volume	5 l	5 l
Connection type	DIN-1	DIN-1

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	30,5	0,6	2
70	71,1	1,1	2

Uncertainty budget

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

Uncertainty budget for the cylinder no. D298390

Uncertainty source	Estimate (µmol/mol)	Standard uncertainty (µmol/mol)	Distribution	Sensitivity coefficient	Contribution (µmol/mol)
gravimetric	30,5	0,12	normal	1	0,12
verification	-	0,3	normal	1	0,3
systematic error	-	0,5	rectangular	1	0,5

Uncertainty budget for the cylinder no. D298384

Uncertainty source	Estimate (µmol/mol)	Standard uncertainty (µmol/mol)	Distribution	Sensitivity coefficient	Contribution (µmol/mol)
gravimetric	71,1	0,28	normal	1	0,28
verification	-	0,7	normal	1	0,7
systematic error	-	0,9	rectangular	1	0,9

Measurement procedure

The verification according to ISO 6143. The measurements were repeated 10 times for the standards and the sample. The curve was calculated from ratios by the software B_least.exe (linear case).
The standards were prepared by gravimetric method according to ISO 6142. The standards were prepared from separate premixtures and were diluted according ISO 6145-9.

Additional information

The final mixtures were prepared according ISO 6142: the cylinders evacuated on turbo molecular pump, filled up an weighted on the verification balance. The mixtures were prepared in aluminium (with coated layers) cylinders. The mixtures were prepared with used pure nitrogen and threer steps premixture of nitrogen oxide. The purity of pure gases used for preparation was taken from the certificates of producer.

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

- Comparison coordinator: Dr Joële Viallon
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Return of result form:
- Please complete and return the form by email to jviallon@bipm.org

Participant information

Institute	NIST		
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Contact person	Jerry Rhoderick		
Telephone	301-975-3937	**Fax**	301-977-8392
Email	George.rhoderick@nist.gov		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	05/08/17	03/27/17
Serial number	FF58485	FF44821
Pressure	9.5MPa	10.8MPa
Volume	$0.53m^3$	$0.63m^3$
Connection type	CGA660	CGA660

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	29.854	0.035	2
70	70.37	0.13	2

Uncertainty budget

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

$$U_{exp} = 2 * Conc.\sqrt{\left(\frac{u_{total\ mol}}{total\ mol}\right)^2 + \left(\frac{u_{NO\ mol}}{NO\ mol}\right)^2}$$

FF58485

		Standard	Sensitivity	Contribution
	Value	Uncertainty	Coefficient	to Uncertainty
Major Component MW	28.01340	0.00016	0.0053	0.00000
Minor Component MW	30.00610	0.00021	0.0059	0.00000
Mass Parent Gas	60.08572	0.00271	0.0193	0.00005
Mass Balance Gas	648.09001	0.00338	0.0002	0.00000
Minor Component Wt Fraction	0.000376870	0.000000220	71953.4439	0.01582
Mass minor component - Parent	0.02264448	0.00001325	1244.8851	0.01649
Mass minor component - Bal	0.00000069	0.00000069	34.5089	0.00002
Total mass minor component	0.02264518	0.00001327	1288.0081	0.01709
Moles of minor component	0.00075469	0.00000044	38773.5450	0.01714
Balance gas wt fraction (purity)	0.999961495	0.00000850	0.1814	0.00000
Mass balance gas - parent	60.05794800	0.00291419	0.0001	0.00000
Mass balance gas - balance	648.06505699	0.00646323	0.0003	0.00000
Total mass balance gas	708.12300498	0.00708984	0.0004	0.00000
Moles of balance gas	25.27800999	0.00029286	0.0117	0.00000
Moles impurities from parent	0.00012832013	0.00000551689	0.0002	0.00000
Moles impurities from balance	0.0006247	0.0000463	0.0018	0.00000
Total Moles of gas	25.2795177	0.0002965	0.0118	0.00000
Conc minor component (ppm)	29.854	0.017		
	Relative uncert	0.059%		0.06663

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

This cylinder was part of a 5-cylinder suite of new primary standard materials from (13-30) µmol/mol NO. They were analysed using a Thermo Model 42H chemiluminescent process analyser. SRM Lot Standard 50-HL-01 (nominal 20 µmol/mol NO) was used as the control cylinder to monitor detector performance. Standards or Control cylinder selection was made using a computer-operated gas analysis system (COGAS # 17). Sample flow was controlled by an MKS mass flow controller. For each reading, the measurement system was flushed for 180 seconds followed by a 60-second data acquisition. The voltage output from the detector was downloaded to a spreadsheet and ratios of the standards to the control were plotted against the gravimetric value of each primary standard. Measurements were taken over a three-day period. The instrument function was linear and the R^2 of the best straight line was 0.99996.

GENLINE - Linear (y=b0+b1*x)

	Value	Std Error
b0	0.302939	0.024619
b1	19.772973	0.026216
cov(b0,b1)		-0.000624
rms residual error		1.083775

New PSM	X	Y	X-Solution	Y-Solution	uTest	Y-Difference	% Diff (Y)
FF58485	1.49633	29.854	1.49523	29.868	PASS	0.014	0.05
FF58497	1.23581	24.743	1.23587	24.740	PASS	-0.003	-0.01
FF58483	0.98793	19.851	0.98797	19.838	PASS	-0.013	-0.07
FF58449	0.80344	16.186	0.80341	16.189	PASS	0.002	0.02
FF58517	0.63794	12.910	0.63786	12.915	PASS	0.005	0.04

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;

Cylinder: CQB11167 (99.99% NO)

Compound	mol/mol	Uncert.
NO (difference)	0.99827	0.00015
N2 (measured)	0.00012	0.000005
N2O (measured)	0.00082	0.000040
NO2 (measured)	0.00079	0.000035

Cylinder: ALM024286 (1.548% NO)

Compound	mol/mol	Uncert.
NO (measured)	0.0154800	0.0000090
N2 (difference)	0.9844564	0.0000093
Ar (measured)	0.0000485	0.0000020
NO2 (measured)	0.0000151	0.0000015

Cylinder: FF44778 (3456.4ppm NO)

Compound	mol/mol	Uncert.
NO (measured)	0.0034654	0.0000020
N2 (difference)	0.9963753	0.0000163
Ar (measured)	0.0001560	0.0000039
NO2 (measured)	0.0000034	0.0000003

Cylinder: FF44822 (351.86ppm NO)

Compound	mol/mol	Uncert.
NO (measured)	0.00035186	0.00000021
N2 (difference)	0.99958831	0.00001605
Ar (measured)	0.00005948	0.00000257
NO2 (measured)	0.00000034	0.00000003

- a purity table with uncertainties for the nominally pure N_2 gas;

BIP N2 balance AIRPRO-271826

Compound	mol/mol	Uncert
N2 (difference)	0.999972998	0.000002000
NO (measured)	0.000000001	0.000000001
Ar (measured)	0.000027000	0.000002000
NO2 (measured)	0.000000001	0.000000001

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

Mass measurements of NIST Primary Standards are made using a Toledo-Mettler Model XP26003L balance (S/N # 13220934568). This balance has a capacity of 26.1 kg and a resolution of 0.001 g. The reproducibility is typically ± 0.002 g. Candidate cylinders are purged and evacuated four times with BIP N_2. The cylinder is evacuated to less than 10 µHg pressure prior to mass determination. The cylinder is placed on the balance and, after one-minute settling time, six readings are acquired over a 1-minute time period. The average of the six readings is downloaded to a spreadsheet along with the ambient temperature, humidity and barometric pressure. The primary standard cylinder is alternated with measurements of a 10-kg calibration control mass. This alternation is repeated at least seven times.
A pre-determined amount of parent mix is then introduced into the cylinder and the mass measurement procedure is repeated. Likewise, the balance gas is added to the cylinder contents and the mass measurement procedure is repeated. Finally, the cylinder is placed on a cylinder roller and rolled for five hours.

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

FF58485

Compound	mol/mol	Uncert
NO	0.000029854	0.000000017
N2	0.999940360	0.000016486
Ar	0.000029756	0.000001843
NO2	0.000000030	0.000000003

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

  This cylinder was part of a 5-cylinder suite of new primary standard materials from (13-30) µmol/mol NO. They were analysed using an Thermo 42H chemiluminescent process analyser. SRM Lot Standard 50-HL-03 (nominal 20 µmol/mol NO) was used as the control cylinder to monitor detector performance. Standards or Control cylinder selection was made using a computer-operated gas analysis system (COGAS # 17). Sample flow was controlled by an MKS mass flow controller. The voltage output from the detector was downloaded to a spreadsheet and ratios of the standards to the control were plotted against the gravimetric value of each primary standard. Measurements were taken over a three-day period. The instrument function was linear and the R^2 of the best straight line was 0.99996.

- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

  None.

Results of measurements performed after the return of cylinders in the participant's institute

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	29.72	0.21	2
70	70.42	0.30	2

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

- Comparison coordinator: Dr Joële Viallon
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Return of result form:

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

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Email	paul.brewer@npl.co.uk		

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	21/03/2017	09/06/2017
Serial number	2238	2293
Pressure (MPa)	10	11
Volume (L)	10	10
Connection type	BS341 No. 14	BS341 No. 14

Results of measurements

Measurements performed before despatch of cylinders

Nominal mole fraction / µmol mol^{-1}	NO mole fraction x(NO) / µmol mol^{-1}	Expanded uncertainty U(x(NO)) / µmol mol^{-1}	Coverage factor
30	29.94	0.06	2
70	69.89	0.10	2

Measurements performed after the return of cylinders

Nominal mole fraction / µmol mol^{-1}	NO mole fraction x(NO) / µmol mol^{-1}	Expanded uncertainty U(x(NO)) / µmol mol^{-1}	Coverage factor
30	29.91	0.06	2
70	69.83	0.10	2

Matrix compositions: Component mole fractions and uncertainties (for each standard submitted):

(Standard 1) Cylinder Identification Number: **2238**

Component	Amount fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.9999543	mol/mol	0.0000015	mol/mol	2
Ar	15.667	µmol/mol	1.475	µmol/mol	2
NO_2	18.707	nmol/mol	0.934	nmol/mol	2
N_2O	20.666	nmol/mol	2.065	nmol/mol	2

Table 1 Composition of standard 1

(Standard 2) Cylinder Identification Number: **2293**

Component	Amount fraction Value	Unit	Expanded Uncertainty	Unit	Coverage Factor
N_2	0.9999143	mol/mol	0.0000014	mol/mol	2
Ar	15.666	µmol/mol	1.363	µmol/mol	2
NO_2	43.658	nmol/mol	2.181	nmol/mol	2
N_2O	48.239	nmol/mol	4.819	nmol/mol	2

Table 2 Composition of standard 2

Uncertainty budget

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

The estimated uncertainty for the measurement contains the following components:
- Purity analysis of NO and nitrogen
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analytical validation

Table 3 details the uncertainty analysis. The preparation component includes estimated uncertainty from purity analysis, weighing and atomic weights.

		Relative Uncertainty (%)		
Identifier	**Component**	**Preparation (*k*=1)**	**Validation (*k*=1)**	**Total (*k*=2)**
2238	NO	0.022	0.10	0.20
2293	NO	0.021	0.07	0.15

Table 3: Uncertainty contributors

To calculate the combined uncertainty, the uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of k=2, providing a level of confidence of approximately 95%.

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

An Eco Physics CLD 822M chemiluminescence spectrometer and an ABB A02020 non-dispersive ultraviolet spectrometer were used to validate the amount fraction of NO in mixtures 2238 and 2293. The analyser response to the matrix gas was recorded. The analyser response to a reference mixture was then recorded for a five minute period followed by either 2238 or 2293 for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of 2238 and 2293 were then determined by multiplying the ratio of the analyser response to each mixture and the reference mixture (both were corrected for the analyser response to matrix gas) with the amount fraction of the reference mixture. These measurements were used to validate the gravimetric amount fractions submitted.
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.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
- a purity table with uncertainties for the nominally pure N_2 gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Description of the procedure

Two gas mixtures were prepared for this comparison (2238 and 2293) at NPL in nitrogen from sources of NO (Air Liquide speciality gases) and N_2 (Air Products, BIP$^+$). The mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. Three further sets of two reference standards were prepared and these were used to validate the comparison mixtures. The scheme below shows the gravimetric dilutions with nominal NO amount fractions.

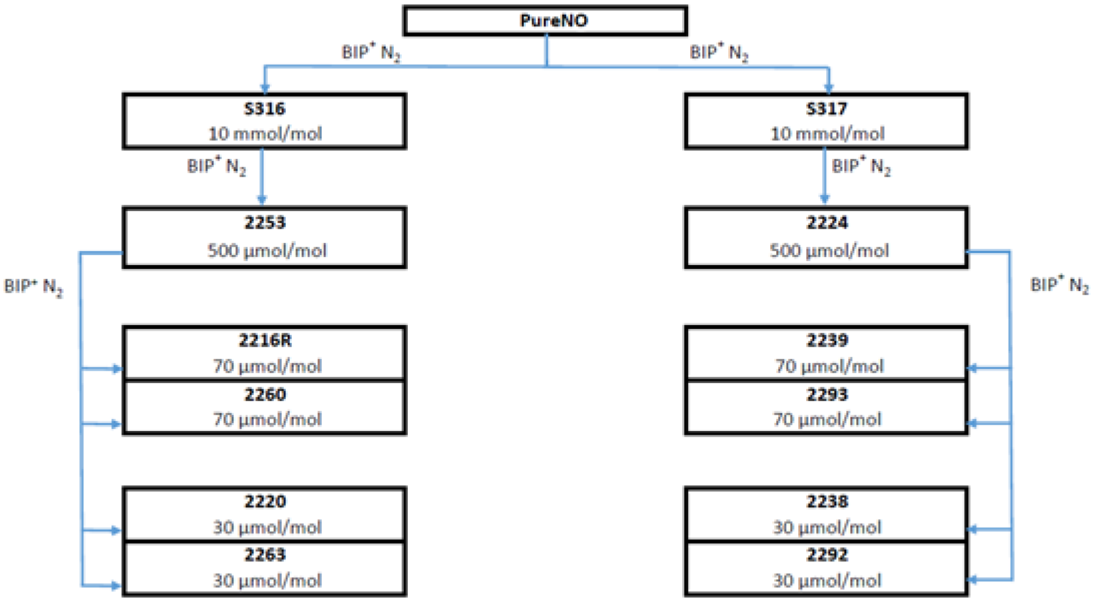

Figure 1 Dilution scheme for gravimetric preparation

Purity tables for the NO and N_2 are provided below.

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
NO	998533.17	57.74
N_2	150.369	5.818
NO_2	623.71	31.19
N_2O	689.16	68.92
O_2	2.554	0.737
Ar	1.041	0.301

Table 4: NO purity table

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
N_2	999984.3	1.6
O_2	0.015	0.009
Ar	15.67	1.57
CO_2	0.00085	0.00049
CO	0.00058	0.00033
NO	0.00050	0.00014
CH_4	0.00080	0.00046
NO_2	0.00050	0.00014
N_2O	0.00050	0.00014

Table 5: N_2 purity table

The mixtures were prepared during the period 21st March to 9th June 2017. Measurements to study the stability of the mixtures were carried out over a 6 week period.
The cylinder pressure of mixtures 2238 and 2293 prior to shipping was > 10 MPa.

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 and submitted at the same time as standards are sent to the BIPM

- Comparison coordinator: Dr Joële Viallon
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Email: jviallon@bipm.org

Return of result form:

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

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Address	Center for Gas Analysis (Chemistry Building 306 Office 203) Division of Metrology for Quality of Life Korea Research Institute of Standards and Science(KRISS) 267 Gajeong-ro, Yuseong-gu, Daejeon 34113 REPUBLIC of KOREA		
Contact person	Dr. Sang Hyub, Oh		
Telephone	+82 42 868 5341	**Fax**	+82 42 868 5042
Email	shoh@kriss.re.kr		

Information on Standards sent to the BIPM		
	30 µmol mol^{-1}	70 µmol mol^{-1}
Date of preparation	27 May. 2017	26 May. 2017
Serial number	D55 7471	D55 7382
Pressure	9 MPa	9 MPa
Volume	10.2 L	10.2 L
Connection type	JIS B 8246 V2 Type (W22.0 14 TPI RH-EXT)	JIS B 8246 V2 Type (W22.0 14 TPI RH-EXT)

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	NO mole fraction x(NO) / µmol mol^{-1}	Expanded uncertainty $U(x(\mathrm{NO}))$ / µmol mol^{-1}	Coverage factor
30	30.014	0.199	2
70	70.085	0.321	2

Uncertainty budget

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

Nominal mole fraction / µmol mol^{-1}	Relative standard uncertainties / %			Expanded uncertainty / %	Coverage factor
	Gravimetry	Analysis	Stability		
30.014	0.10	0.30	0.10	0.66	2
70.085	0.05	0.20	0.10	0.46	2

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

- NO analyser : Chemiluminescent NO/NOx analyser (Thermo 42i-HL)
- Samples : 4 PRMs (4 cylinders of 30 µmol/mol and 4 cylinders of 70 µmol/mol)
- Gas feeding system : Gas feeding system was used to control the flow rate, gas feeding time and to get data. This system is composed of MFC (Bronkhorst), 5 multi-position valves (Valco), regulator, and vacuum pump, and controlled by LabVIEW program.

  In this work, flow rate was 400 ml/min, and feeding time of sample and zero gas were 7 minutes and 0.5 minutes, respectively. Feeding tube line was evacuated after each measurement, and sample was analysed 4 times in succession as follow.

S1 - Zero - S1 - Zero - S1 - Zero - S1 - Zero - S2- Zero - S2 - Zero - S2 - Zero - S2 …

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
- a purity table with uncertainties for the nominally pure N_2 gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

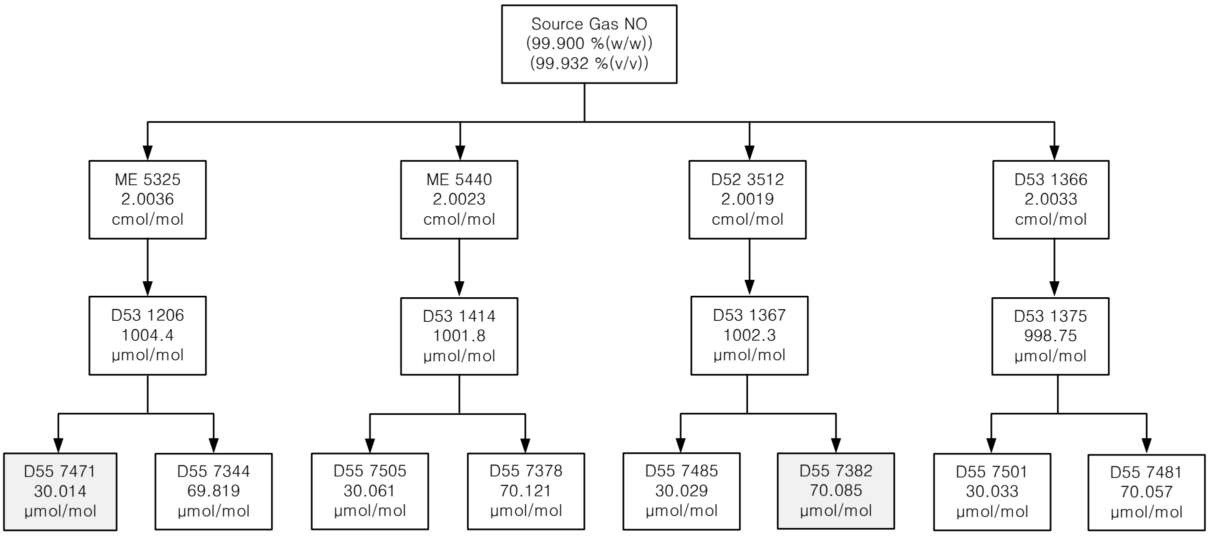
Table 1. Purity table for NO.

Component	Mole fraction µmol/mol	Uncertainty µmol/mol
NO_2	351.8	3.5
N_2O	285.9	2.9
H_2	0.05	0.014
O_2	1.00	0.01
N_2	40.9	0.6
CO	0.1	0.03
CO_2	1.4	0.1
H_2O	1.0	0.1
NO	**999 318**	**4.6**

Table 2. Purity table for N_2.

Component	Mole fraction µmol/mol	Uncertainty µmol/mol
H_2	0.05	0.014
O_2	0.18	0.05
Ar	0.17	0.05
CO	0.1	0.03
CO_2	0.01	0.003
CH_4	0.0013	0.0003
H_2O	1.20	0.29
NO	0.01	0.003
N_2	**999 998**	**0.3**

Table 3. Dilution series undertaken to produce the final mixtures



Verification procedure applied to the final mixtures

4 cylinders of same concentration level were analysed 3 times and sensitivities of each cylinder were compared. In calculation of sensitivity, instrument drift with time was corrected.

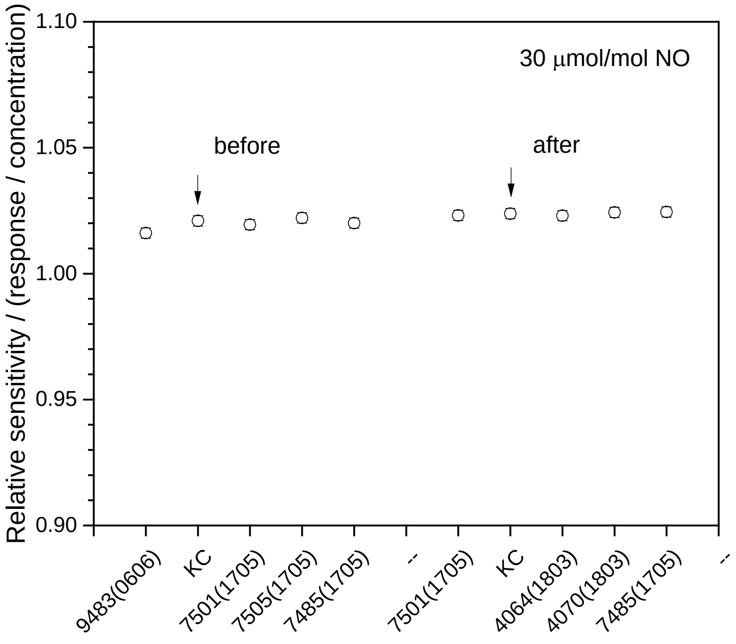
Stability testing

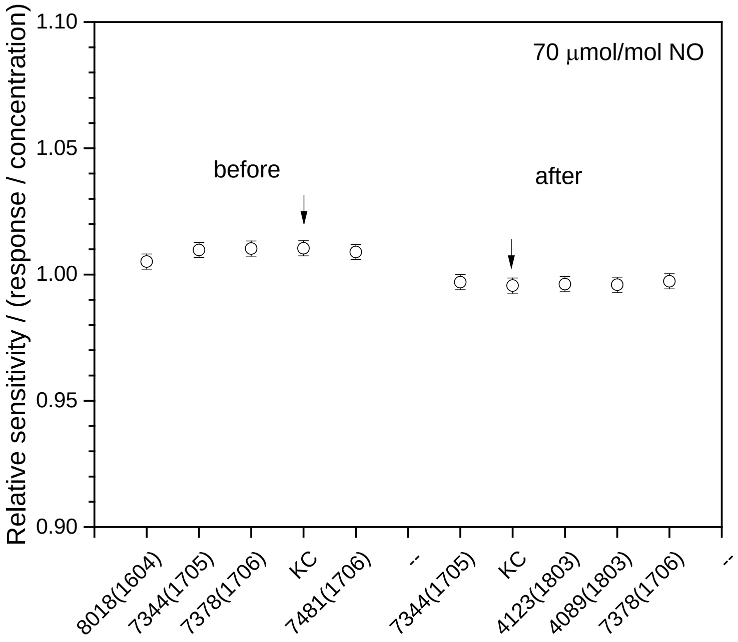
3 cylinders of 50 µmol/mol were tested. One cylinder (reference in this test) was prepared March 2016 and two cylinders were prepared May 2017. In this test, sensitivity differences were 0.13% and 0.07% respectively, therefore NO 50 µmol/mol cylinders were stable for over a year.

Results of second analysis.

We confirmed that concentrations of KRISS KC cylinders were not changed during KC periods.

In figures, sample name means cylinder number and preparation date. For example, 9483(0606) was prepared in June 2006, and 7501(1705) was prepared in May 2017.





Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K137 in two steps: the first page only is to be submitted at the same time as standards are sent to the BIPM, and the complete form after the return of the standards in participant's laboratories and evaluation of participant's final results.

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

Return of result form:

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

Participant information

Institute	Chemicals Evaluation and Research Institute, Japan		
Address	1600 Shimotakano, Sugito-machi, Kitakatsushika-gun, Saitama 345-0043, Japan		
Contact person	Shinji UEHARA		
Telephone	+81-480-37-2601	**Fax**	+81-480-37-2521
Email	uehara-shinji@ceri.jp		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	**15 Nov 2016**	**14 Nov 2016**
Serial number	**CPB-18479**	**CPB-21235**
Pressure	**10 MPa**	**10 MPa**
Volume	**950 L**	**950 L**
Connection type	Plated brass valve (G-12) made by the Hamai industries ltd.	Plated brass valve (G-12) made by the Hamai industries ltd.

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
30	28.51	0.09	$k = 2$
70	68.76	0.22	$k = 2$

Uncertainty budget

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

"30 µmol mol^{-1} sample"

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty	Contribution to standard uncertainty
Gas standards for measurements	0.001030	Normal	0.001030	0.001030
Impurities in nitrogen	-	-	-	Negligible
Impurities in NO	0.000018	Normal	0.000018	0.000018
Stability	0.015 µmol mol^{-1}	Rectangle	0.00866 µmol mol^{-1}	0.00030
Measurement	0.00101	Normal	0.00101	0.00101

Combined uncertainty:0.001474

Expanded uncertainty:0.002948

Expanded uncertainty:0.09 µmol mol^{-1}

"70 µmol mol^{-1} sample"

Uncertainty source	Estimate $u(x_i)$	Assumed distribution	Standard uncertainty	Contribution to standard uncertainty
Gas standards for measurements	0.001030	Normal	0.001030	0.001030
Impurities in nitrogen	-	-	-	Negligible
Impurities in NO	0.000018	Normal	0.000018	0.000018
Stability	0.075 µmol mol^{-1}	Rectangle	0.04330 µmol mol^{-1}	0.00063
Measurement	0.00101	Normal	0.0010	0.00101

Combined uncertainty: 0.001574

Expanded uncertainty: 0.003148

Expanded uncertainty: 0.22 µmol mol^{-1}

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

All gas standards were prepared by gravimetric method. Chemiluminescence analyser was calibrated using three gravimetrically prepared PRMs(JCSS PRMs) ranging in concentration from 20 µmol mol^{-1} to 50 µmol mol^{-1} for “30 µmol mol^{-1} sample” and from 50 µmol mol^{-1} to 100 µmol mol^{-1} for “70 µmol mol^{-1} sample”.
After preparation, cylinders were left at laboratory temperature for at least 48 hours.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;
  Purity and impurities of NO are determined by NMIJ.

Pure NO gas sample
Container: 10L aluminum cylinder
Purity in catalogue: >99.99%
Initial inner pressure: 1.97 MPa
Analysis was carried out within 1 month after its filling date

Select of analytes for purity analysis
Impurities to be measured are N_2O, NO_2, N_2, H_2O, CH_4 and CO_2. As nitrogen monoxide (NO) has a nature of self-reaction and poor long-term stability, N_2O and NO_2 are expected to be major impurities in the pure NO gas.

Purity table
Purity of NO was determined by a subtraction method in accordance with ISO-6142:2015

i	**Mole fraction (µmol/mol)**	**Standard uncertainty (µmol/mol)**	**Analytical method**	**Remarks**
N_2O	58.2	0.5	FT-IR	Detected more than detection limit
NO_2	58.9	7.7	FT-IR	Detected more than detection limit
N_2	12.5	7.2	GC-TCD	Lower than detection limit of 25 µmol/mol
H_2O	21.8	12.6	FT-IR	Lower than detection limit of 43.7 µmol/mol
CH_4	2.1	1.2	FT-IR	Lower than detection limit of 4.2 µmol/mol
CO_2	10	5.8	FT-IR	Lower than detection limit of 20 µmol/mol

Purity table of NO

Component	Purity (certified value) µmol mol^{-1}	Standard uncertainty µmol mol^{-1}
NO	999836	18

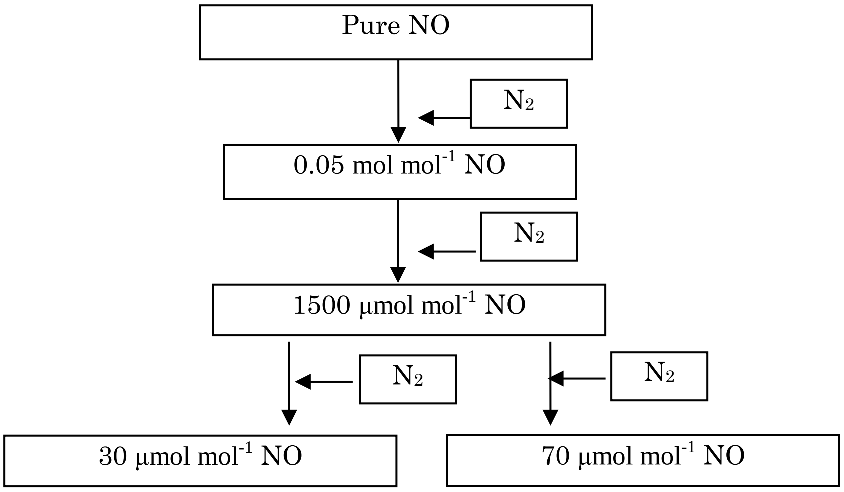
- a purity table with uncertainties for the nominally pure N_2 gas;

Purity table of N_2

Component	Analytical value µmol mol^{-1}	Distribution	Mole fraction µmol mol^{-1}	Uncertainty µmol mol^{-1}
O_2	≤ 0.1	Rectangular	0.05	0.02890
Ar	≤ 1	Rectangular	0.5	0.2890
CO	≤ 0.01	Rectangular	0.005	0.002890
CO_2	≤ 0.01	Rectangular	0.005	0.002890
Total hydro carbon (THC)	≤ 0.01	Rectangular	0.005	0.002890
SO_2	≤ 0.005	Rectangular	0.0025	0.001443
NOx	≤ 0.005	Rectangular	0.0025	0.001443
N_2	-	-	999 999.43	0.2905

Each mole fraction of impurity in nitrogen is adequately low. Therefore, the molar mass of dilution gas wasn't affected from the impurities.

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



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

"30 µmol mol^{-1} sample"

Component	Analytical value µmol mol^{-1}	Distribution	Mole fraction µmol mol^{-1}	Uncertainty µmol mol^{-1}
O_2	≤ 0.1	Rectangular	0.05	0.02890
Ar	≤ 1	Rectangular	0.5	0.2890
CO	≤ 0.01	Rectangular	0.005	0.002890
CO_2	≤ 0.01	Rectangular	0.005	0.002890
Total hydro carbon (THC)	≤ 0.01	Rectangular	0.005	0.002890
SO_2	≤ 0.005	Rectangular	0.0025	0.001443
N_2	-	-	999 970.92	0.2905
NO	28.51	-	28.51	0.0100 (Gravimetric uncertainty)

"70 µmol mol^{-1} sample"

Component	Analytical value µmol mol^{-1}	Distribution	Mole fraction µmol mol^{-1}	Uncertainty µmol mol^{-1}
O_2	≤ 0.1	Rectangular	0.05	0.02890
Ar	≤ 1	Rectangular	0.5	0.2890
CO	≤ 0.01	Rectangular	0.005	0.002890
CO_2	≤ 0.01	Rectangular	0.005	0.002890
Total hydro carbon (THC)	≤ 0.01	Rectangular	0.005	0.002890
SO_2	≤ 0.005	Rectangular	0.0025	0.001443
N_2	-	-	999 930.66	0.2905
NO	68.81	-	68.81	0.0241 (Gravimetric uncertainty)

- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Samples for CCQM were measured at several terms, at the time they were prepared, before shipped to BIPM and after shipped back to CERI (procedure is written in "Measurement procedure").

"30 µmol mol^{-1} sample"

・Gravimetric value and measured value before shipped to BIPM

There wasn't obvious difference between the measured value and the gravimetric value.

・Gravimetric value and measured value after shipped back to CERI

There wasn't obvious difference between the measured value and the gravimetric value.

Uncertainty of stability was estimated as half of 0.03 µmol mol^{-1}, 0.015 µmol mol^{-1}.

"70 µmol mol^{-1} sample"
・Gravimetric value and measured value before shipped to BIPM
There wasn't obvious difference between the measured value and the gravimetric value.
・Gravimetric value and measured value after shipped back to CERI
There was a slight difference between the measured value and the gravimetric value.

Uncertainty of stability was estimated as half of 0.15 µmol mol^{-1}, 0.075 µmol mol^{-1}.

Nominal mole fraction / µmol mol^{-1}	**Gravimetric value x(NO) / µmol mol^{-1} (15/Nov/2016)**	**Measured value before shipped to BIPM x(NO) / µmol mol^{-1} (12/Apr/2017)**	**Measured value after shipped back to CERI x(NO) / µmol mol^{-1} (25/Jun/2018)**
30	28.51	28.51	28.48
70	68.81	68.76	68.61

Author ship:

Mr. Shinji Uehara, Mr. Dai Akima

Participant Submission Form
CCQM-K137, NO in N_2, (30 and 70) µmol mol^{-1}

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

Return of result form:

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

Participant information

Institute	VSL		
Address	Thijsseweg 11 2629 JA Delft The Netherlands		
Contact person	Gerard Nieuwenkamp		
Telephone	+31 15 2691682	**Fax**	
Email	gnieuwenkamp@vsl.nl		

Information on Standards sent to the BIPM

	30 µmol mol^{-1}	**70 µmol mol^{-1}**
Date of preparation	**18 May 2017**	**11May 2017**
Serial number	**# 289198**	**# 1005700**
Pressure	**10.7 MPa**	**10.7 MPa**
Volume	**5 L**	**5 L**
Connection type	**DIN-1**	**DIN-1**

Results of measurements

Please indicate below the value and associated expanded uncertainty of the NO mole fraction in each of the two standards.

Nominal mole fraction / µmol mol^{-1}	**NO mole fraction x(NO) / µmol mol^{-1}**	**Expanded uncertainty U(x(NO)) / µmol mol^{-1}**	**Coverage factor**
~~30~~	~~30.00~~		~~2~~
70	70.05	0.21	2

Uncertainty budget

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

The relative standard uncertainty as computed by the formulae of ISO 6142-1 is 0.04 %. An analysis of the long-term behaviour of PSMs of nitrogen monoxide in nitrogen has shown that the relative standard uncertainty $\tau = 0.14$ %. These two contributions are combined in accordance with the law of propagation of uncertainty to obtain the standard uncertainty for the assigned value in this key comparison.

$$u(x) = x\sqrt{u_{\mathrm{rel}}^2\left(x_{\mathrm{grav}}\right) + \tau^2}$$

Measurement procedure

Please provide below a description of the measurements performed for the validation of values obtained from the preparation.

The NO in N_2 mixtures have been validated by comparison to a suite of VSL's NO in N_2 PSMs in the range of 10 µmol/mol - 100 µmol/mol. The measurements were performed with an ABB Limas 11 analyzer, with a measurement principle that is based on UV absorption. Calibration curves are obtained in accordance with ISO 6143. For the verification measurements, a 2nd order curve has been used. Two series of measurements have been performed on the dates 20 and 26 June 2017, before shipment of the cylinders to BIPM.

After arrival back at VSL, two more analyses have been performed on 5 February and 16 April 2018 to confirm the stability of the mixtures.

Additional information

Please include in this section the following information:

- a purity table with uncertainties for the nominally pure NO parent gas;

Table 1. Purity table of pure NO parent gas (AL8234), expressed as amount fractions

Component	x (mol/mol)	$u(x)$ (mol/mol)
Nitrogen	0.000122130	0.000002500

Nitrous oxide	0.000331810	0.000051958
Nitrogen monoxide	0.999025089	0.000097089
Nitrogen dioxide	0.000255526	0.000007040
Nitrous acid (HNO_2)	0.000210621	0.000079215
Nitric acid (HNO_3)	0.000032937	0.000022430
Water	0.000020000	0.000004492
Carbon dioxide	0.000001887	0.000000221

- a purity table with uncertainties for the nominally pure N_2 gas;

Table 2. Purity table of nitrogen (APN26B), expressed as amount fractions

Component	*x* (mol/mol)	*u*(*x*) (mol/mol)
Argon	0.000005000	0.000003000
Methane	0.000000008	0.000000005
Carbon monoxide	0.000000015	0.000000009
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000025	0.000000015
Water	0.000000010	0.000000006
Nitrogen	0.999994927	0.000006000
Oxygen	0.000000005	0.000000003

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

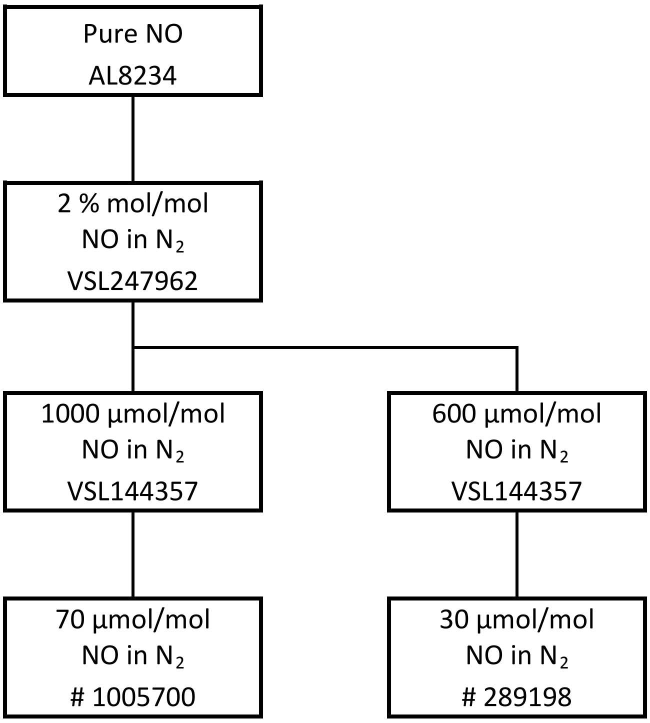

Figure 1. Schematic overview of the dilution series

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

Table 3. Purity table of mixture # 289198, nominally 30 µmol/mol NO in nitrogen

Component	*x* (mol/mol)	*u*(*x*) (mol/mol)
Argon	0.000005000	0.000002854
Methane	0.000000008	0.000000005
Carbon monoxide	0.000000015	0.000000009
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000025	0.000000014
Water	0.000000011	0.000000006
Nitrogen monoxide	0.000030005	0.000000014
Nitrogen	0.999964806	0.000005708
Nitrogen dioxide	0.000000008	0.000000002
Oxygen	0.000000095	0.000000028
Nitrous oxide	0.000000010	0.000000002
Nitrous acid (HNO_2)	0.000000006	0.000000003
Nitric acid (HNO_3)	0.000000001	0.000000001

Table 4. Purity table of mixture # 1005700, nominally 70 µmol/mol NO in nitrogen

Component	*x* (mol/mol)	*u*(*x*) (mol/mol)
Argon	0.000005000	0.000002797
Methane	0.000000008	0.000000005
Carbon monoxide	0.000000015	0.000000008
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000025	0.000000014
Water	0.000000011	0.000000006
Nitrogen monoxide	0.000070046	0.000000029
Nitrogen	0.999924727	0.000005594
Nitrogen dioxide	0.000000018	0.000000005
Oxygen	0.000000100	0.000000028
Nitrous oxide	0.000000023	0.000000004
Nitrous acid (HNO_2)	0.000000015	0.000000006
Nitric acid (HNO_3)	0.000000002	0.000000002

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

The NO in N_2 mixtures are validated by comparison to a suite of VSL 's NO in N_2 PSM's in the range of 10-100 µmol/mol. The measurements are performed with an ABB Limas 11 analyzer, with a measurement principle that is based on UV absorption. Calibration curves are obtained in accordance with ISO 6143. For these measurements, a 2nd order curve has been used. Two series of measurements have been performed before the measurement at BIPM, on the dates 20 and 26 June 2017. Also, two series of measurements have been performed after the measurement at BIPM, on the dates 5 February and 16 April 2018.

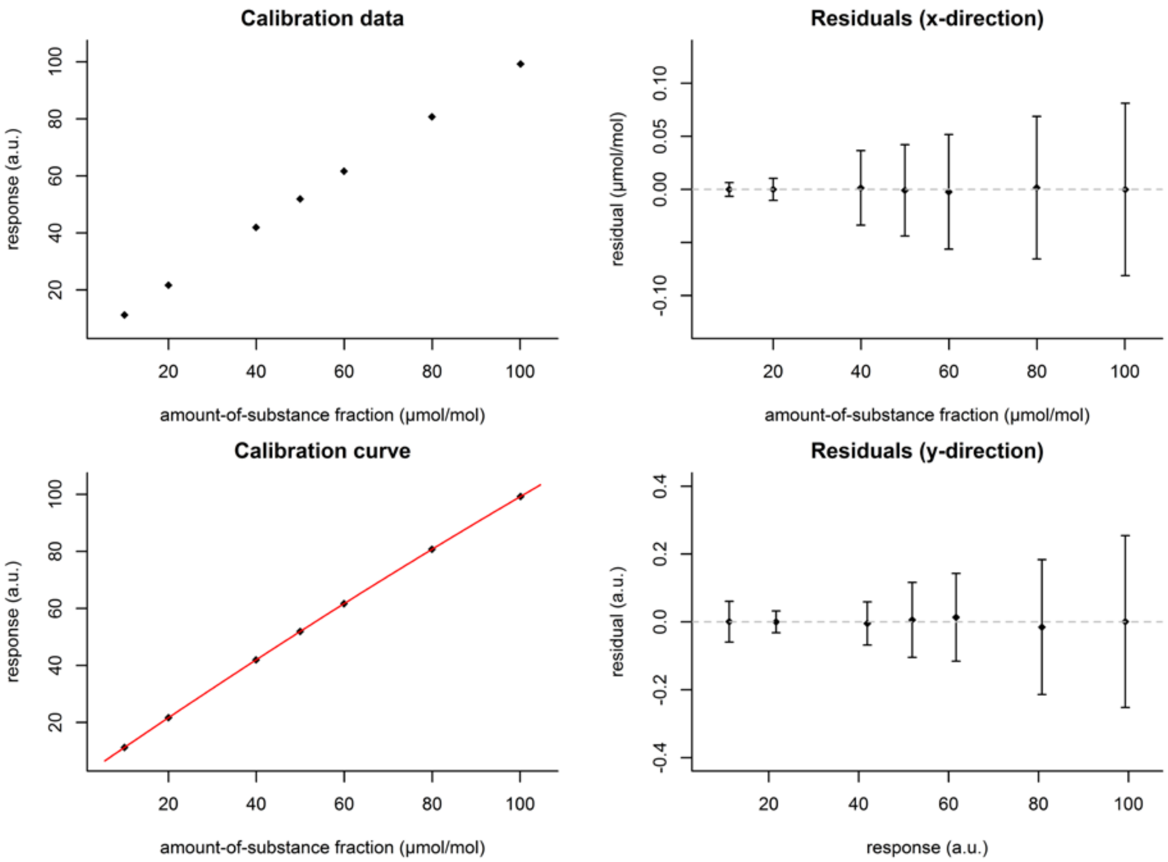

Figure 1: Calibration of the NO analyser for the third verification

- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Stability testing of these type of mixtures in similar cylinders has been performed. Evidence is found that no significant instability can be expected within the time frame of this key comparison. The results of the verification measurements are summarised in tables 1 and 2. The standard uncertainty of the amount fractions is obtained by propagating the uncertainties associated with the amount fractions of the PSMs and those of the responses. No allowance is made for other sources of uncertainty.
However, to VSL's surprise and disappointment, the measurement results for the 30 µmol mol^{-1} NO mixture appear to be significantly lower than the gravimetric value (-0.5% relative, table 1). Therefore, this mixture cannot be qualified as a representative mixture for the work VSL is doing for this type of mixtures. Consequently, VSL must withdraw this mixture from the comparison and can only participate with the 70 µmol mol^{-1}.

Table 1: Responses (y) and amount fractions (x) obtained during the fourth verification; Δx denotes the difference between the amount fractions from verification and gravimetry; the amount fractions are given in ppm

Mixture	***y***	***u*(*y*)**	***x***	***u*(*x*)**	***u*(*x*)/*x***	**Δ*x***	**Δ*x*/*u*(*x*)**	**Δ*x*/*x***
VSL389198	31.43	0.02	30.02	0.02	0.07%	0.01	0.66	0.04%
VSL389198	31.48	0.01	29.99	0.02	0.06%	-0.01	-0.81	-0.05%
VSL389198	31.76	0.04	29.86	0.05	0.15%	-0.15	-3.18	-0.49%
VSL389198	31.46	0.04	29.75	0.05	0.17%	-0.25	-5.12	-0.84%

Table 2: Responses (y) and amount fractions (x) obtained during the fourth verification; Δx denotes the difference between the amount fractions from verification and gravimetry; the amount fractions are given in ppm

Mixture	***y***	***u*(*y*)**	***x***	***u*(*x*)**	***u*(*x*)/*x***	**Δ*x***	**Δ*x*/*u*(*x*)**	**Δ*x*/*x***
VSL205700	70.94	0.04	70.00	0.04	0.06%	-0.05	-1.09	-0.07%
VSL205700	71.14	0.03	70.02	0.04	0.06%	-0.02	-0.55	-0.03%
VSL205700	71.37	0.09	70.05	0.10	0.14%	0.01	0.05	0.01%
VSL205700	71.42	0.05	70.06	0.08	0.12%	0.02	0.19	0.02%