International Comparison CCQM-P73: Nitrogen Monoxide Gas Standards (30-70) µmol/mol

Final Report

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Field: Amount of Substance, Gas Standards

Subject: Comparison of primary standards of nitrogen monoxide (NO) in nitrogen.

Participants:

Institute	Acronym	Country
Korean Research Institute of Standards and	KRISS	Korea, republic of
Science		
CSIR National Metrology Laboratory*	CSIR-NML*	South Africa
Chemicals Evaluation and Research Institute	CERI	Japan
Laboratoire national de métrologie et	LNE	France
d'essais		
Slovensky metrologicky ustav	SMU	Slovakia
Centro Nacional de Metrologia	CENAM	Mexico
D.I. Mendeleyev All-Russian Institute for	VNIIM	Russian
Metrology		Federation
National Institute of Standards and	NIST	USA
Technology		
National Measurement Institute, Australia	NMIA	Australia
Instituto Portuges da Qualidade	IPQ	Portugal
Nederlands Meetinstituut	NMi-VSL	The Netherlands
Bureau International des Poids et Mesures	BIPM	

* The CSIR National Metrology Laboratory (CSIR NML) became The National Metrology Institute of South Africa (NMISA) on 1 May 2007.

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Organizing Body: CCQM

Rationale for Comparison:

The aim of the pilot study was to evaluate the level of comparability of laboratories' preparative capabilities for gravimetric nitrogen monoxide/nitrogen primary reference mixtures in the range (30-70) μ mol/mol. Such primary gas reference mixtures are prepared and maintained by a number of NMIs in order to provide NO_x calibration services in the areas of environmental and emissions analysis at the national level. The comparison was designed so that measurements would be performed at a central laboratory (the BIPM) and measurement results compared to values assigned by each National Metrology Institute (NMI) based on gravimetry. It had already been demonstrated that measurement uncertainties achievable for stable gas mixture standards

using such a comparison protocol could be considerably smaller than reported for comparison in which gas standards were distributed from one laboratory for measurement by all participating laboratories. CCQM-P73 would be the first comparison organized within the CCQM in which reactive gas standards would be compared against each other at a central measurement facility, with the additional complication that the stability of gas concentration within cylinders could be a limiting factor to the level of comparability achievable.

Measurement Standards:

The study was organised as a comparison of a suite of 2n primary gas standards, two standards prepared by each of the *n* participating laboratories. The reference value for a given gas standard was to be determined from a regression line calculated from all standards, or from a self consistent subset of the standards. Measurement results were based on two independent analytical methods, notably UV spectrophotometry and chemiluminescence.

Each participating laboratory was asked to provide:

- one high pressure cylinder containing a NO/N $_2$ mixture in the range (30-50) $\mu mol/mol$
- one high pressure cylinder containing a NO/N₂ mixture in the range (50-70) μ mol/mol;

together with the following information:

- a purity table with uncertainties for the nominally pure NO parent gas; or
- in the case that the highest level parent gas was not nominally pure NO, a purity table with uncertainties for the highest level parent NO/N₂ mixture;
- a purity table with uncertainties for the nominally pure N₂ parent 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 were prepared and the time they were shipped to the BIPM.

Information submitted by participating laboratories is listed in Appendix 3.

The total number of different gas mixtures analysed in the study was twenty-eight, and consisted of:

- the twenty-two gravimetric mixtures provided by the eleven participating laboratories;
- three gravimetric mixtures (referred to as VALCRM1,2,3) provided by an NMI that did not participate in the CCQM-P73, but had participated successfully in CCQM-K1.c and EUROMET-K1.c. These gas standards had been used in the validation studies performed at the BIPM in preparation for the coordination of CCQM-P73. These gas mixture were contained in aluminium cylinders passivated with the BOC Spectraseal process. They were not pre-treated with nitrogen monoxide.

- two gas standards from a speciality gas company used as control mixtures for instrument drift monitoring and correction;
- and N_2 (6.0 grade, Messer) used as the zero gas.

A description of the gas mixtures, the autosampler port to which they were attached, and the pressure reducer assigned to each mixture, is summarised in Table 1.

Mixture Label	Source	Cylinder #	Range (µmol/mol)	NMI Assigned <i>x</i> _{NO} (µmol/mol)	NMI Assigned <i>u</i> (x _{NO}) (µmol/mol)	Autosampler Port #	Pressure Reducer #
M1	KRISS	CPB29491	30-32	31.020	0.007	1	16
M2	CSIR- NML	3775	32-34	33.149	0.062	2	20
M3	CERI	CPB10283	34-36	34.93	0.02	3	17
M4	VALCRM1	-	-	37.17	0.027	4	11
M5	LNE	SMG1391	38-40	39.839	0.040	5	23
M6	SMU	MY9744	38-40	40.419	0.031	6	27
M7	CENAM	FF39556	40-42	40.777	0.088	7	47
M8	VNIIM	MS7351	42-44	42.18	0.03	8	40
M9	NIST	CAL016209	42-44	43.081	0.062	9	46
M10	NMIA	MK0787	44-46	44.844	0.074	10	35
M11	VALCRM2	-	-	46.98	0.028	11	14
M12	IPQ	PSM103453	46-48	47.001	0.004	12	25
M13	NMI-VSL	VSL174481	46-48	47.011	0.011	13	38
M14	CERI	CPB03542	50-52	50.91	0.02	14	19
M15	KRISS	ME5305	52-54	52.984	0.009	15	15
M16	CSIR- NML	3770	54-56	55.111	0.104	16	20
M17	VALCRM3	-	-	56.95	0.031	17	13
M18	SMU	MY9741	58-60	59.576	0.044	18	43
M19	LNE	AA7060C	58-60	60.580	0.065	19	26
M20	CENAM	FF39527	60-62	60.690	0.104	20	31
M21	NMI-VSL	VSL174455	62-64	63.012	0.023	21	37
M22	VNIIM	MS7340	62-64	63.32	0.04	22	39
M23	NMIA	MK0781	64-66	64.84	0.11	23	36
M24	NIST	CAL016177	66-68	67.082	0.087	24	28
M25	IPQ	PSM103406	68-70	69.700	0.007	25	24
R ₁	Control 1	5901234	-	(~45)	-	26	33
R ₂	Control 2	5901165	-	(~65)	-	27	32
N ₂	Messer		-	(0.000)	-	31	Х

Table 1: Gas standards and mixtures analysed as part of CCQM-P73

Schedule:

Measurements on gas standards received by the BIPM were carried out on the following dates:

Measurement	Date of measurement	Data/results reference
Series		
	28/08/06	2808a
	28/08/06	2808b
1	29/08/06	2908a
	30/08/06	3008a
	30/08/06	3008b
	31/08/06	3108a
	11/09/06	1109f
	12/09/06	1209a
2	12/09/06	1209b
	13/09/06	1309a
	13/09/06	1309b
	14/09/06	1409a
	03/10/06	0310c
	04/10/06	0410b
3	04/10/06	0410c
	05/10/06	0510a
	06/10/06	0610b

Description of measurement systems used at the BIPM:

Two analysers, the ABB Advance Optima LIMAS 11-UV analyser and the Thermo Environmental Instruments Model 42C Chemiluminescence $NO-NO_2-NO_x$ analyser, were used for the comparison of nitrogen monoxide gas standards. The two analysers were connected in series, with the 42C downstream of the LIMAS. A sample flow of 500 ml_n/min was sufficient to supply both analysers when connected in series.

To avoid *post hoc* correction for changes in pressure within the measurement cells of the 42C and LIMAS analysers, arising from changes in ambient pressure, the BIPM NO Facility was designed so that it was isolated from the effects of ambient pressure changes. In the case of the LIMAS, a software-controlled electronic pressure controller (EPC) immediately downstream of the measurement cell, in combination with the MFC-controlled sample flow, actively regulated the pressure within the LIMAS measurement cell at approximately 1050 hPa with a typical variation (1 σ) over several hours of 0.01 hPa (0.001% relative). In the case of the 42C analyser a capillary tube in the sample stream immediately upstream of the measurement cell and a diaphragm vacuum pump immediately downstream of the reaction chamber, ensured pressure stability within the measurement cell. With this configuration, in combination with the MFC- and EPC-controlled sample flow, the pressure within the 42C reaction chamber was stable at approximately 230 hPa with a typical variation (1 σ) over several hours of 0.04 hPa (0.02% relative). A 30 port auto-sampler was used to allow automatic sampling of gas cylinders.

Measurement Protocol:

All cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours, and then rolled for at least 1 hour to ensure homogeneity of the mixture. The cylinder connector appropriate to the cylinder valve was provided by the BIPM. An appropriate material inert to nitrogen monoxide (typically PCTFE) was used for connectors that required a gasket.. The same model of pressure reducer (Model: Parker Veriflo IR4000 Series Pressure Regulator, model no. IR4002SK2P4B) was connected to each cylinder connector.

Analysis #	Control Mixtures	Sample Mixtures:	Sample Mixtures:	Sample Mixtures:
i		Ascending x _{NO} Order	Descending x _{NO} Order	Random x _{NO} Order
1	N ₂			
2	R ₁			
3	R ₂			
4	R₁			
5	R ₂			
6	R₁			
7	R ₂			
8	2	M1	M25	M18
9		M2	M24	M22
10		M3	M23	M3
11		M4	M22	M16
12		M5	M21	M25
13	R,			
14	R _a			
15	112	M6	M20	M2
16		M7	M19	M23
17	•	M8	M18	M17
18		MQ	M17	M7
19		M10	M16	M13
20	R.	inite		inito
21	R₂			
22		M11	M15	M8
23		M12	M14	M1
24		M13	M13	M11
25		M14	M12	M14
26		M15	M11	M4
27	R1			
28	R ₂			
29		M16	M10	M10
30		M17	M9	M12
31		M18	M8	M20
32		M19	M7	M24
33	1	M20	M6	M15
34	R ₁			
35	R ₂			
36		M21	M5	M9
37		M22	M4	M19
38	1	M23	M3	M5
39	1	M24	M2	M21
40	1	M25	M1	M6
41	R ₁			
42	R ₂			
43	N ₂			
44	N ₂			

Table 2: Order of cylinder analysis for various measurement series

Each cylinder was connected via its pressure reducer to one inlet of a 30-inlet automatic gas sampler. The sampler was connected to the two analysers, a Thermo 42C chemiluminescence NO analyser and an ABB LIMAS UV11 ultraviolet

spectrophotometry NO analyser. The pressure reducer of each cylinder was flushed nine times with the gas mixture of its cylinder. The cylinder valve was then closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at approximately 300 kPa. The cylinders were left standing for at least 24 hours, to allow conditioning of the pressure reducers.

Immediately prior to an analysis, each cylinder valve was opened and the pressure reducer flushed a further three times. The suite of cylinders was analysed sequentially. Three different orders of analysis were employed as outlined in Table 2. They were in ascending order of x_{NO} , descending order of x_{NO} and random order. Normally the ascending x_{NO} order was used. The first analysis provided the zero reading, used for zero correction of each analyser. Analyses 2-5 served to condition the plumbing connections and analysers to the nitrogen monoxide gas mixtures. Each analysis step consisted of two minutes of flushing followed by two minutes of analysis. One pass through the sequence of 44 analyses took approximately 3 hours.

On completion of measurements, the cylinder valves were closed and the pressure reducer and connection to the gas sampler left under pressure.

Analyser responses and measurement uncertainties

The correct interpretation of the measurement results obtained using the above protocol is dependant on a properly characterized measurement system with validated measurement uncertainties within the central measurement facility. In preparation for CCQM-P73, the BIPM carried out a programme of work to characterise:

- the repeatability and reproducibility of its measurements systems;

- any drift in analyser response;

- any biases introduced by the use of pressure regulators and sampling ports.

The results of the studies were used to establish an uncertainty budget for each measurement system used in the comparison, and to validate these using a set of gas standards from National Metrology Institutes that had successfully participated in pervious key comparisons of nitrogen monoxide in nitrogen. The validation studies are summarized in Appendix 1.

The LIMAS UV11 analyser response was corrected for the zero response of the analyser. No further correction of the analyser response was required.

The corrected response of the analyser can be represented by the following equation:

 $y_{LIMASCorrected,i} = y_{Limas,i} - y_{LIMAS,zero} + C$

where,

 $y_{\text{LIMASCorrected},i}$ is the zero corrected *LIMAS UV11* response of the *i*th analysis in the sequence listed in Table 2

 $y_{\text{Limasd},i}$ is the *LIMAS UV11* response of the *i*th analysis in the sequence listed in Table 2

y_{LIMAS,zero} is the LIMAS UV11 response to high purity nitrogen

and *C* is applied to correct for biases introduced by the use of individual pressure regulators and sampling lines/ports for each individual gas standard. The range of responses recorded for the LIMAS analyser varied from 3000 a.u. to 10000 a.u. The calculated uncertainty in the analyser response is summarized in the tables below. Over the three measurement periods of the comparison, the standard deviation of the analyser response was observed to increase. It was assumed that this was due to the ageing of the UV lamp, resulting in reduced intensity and increased signal noise. The standard uncertainties of the LIMAS analyser response and zero value were based on standard deviations of the mean of 120 measurements and validated by calculation of the Allan variance.

Quantity	Value /a.u.	Standard uncertainty /a.u.
YLIMAS, <i>i</i>	3000 to 10000	2.8
YLIMAS,zero	140	2.8
С	0	2
YLIMAS.Corrected,i	3000 to 10000	4.4

Table 3: Uncertainty budget for corrected LIMAS 11UV response (Measurements Series 1)

Quantity	Value /a.u.	Standard uncertainty /a.u.
Ylimas, <i>i</i>	3000 to 10000	3.5
YLIMAS,zero	140	3.5
С	0	2
VLIMAS Corrected i	3000 to 10000	5.4

Table 4: Uncertainty budget for corrected LIMAS 11UV response (Measurements Series 2)

Quantity	Value /a.u.	Standard uncertainty /a.u.
YLIMAS, <i>i</i>	3000 to 10000	5.6
YLIMAS,zero	140	5.6
С	0	2
YLIMAS,Corrected,i	3000 to 10000	8.2

Table 5: Uncertainty budget for corrected LIMAS 11UV response (Measurements Series 3)

The (zero corrected) 42C analyser response, y_{42C} , was corrected for analyser drift by monitoring the analyser response for repeated measurements of control cylinders. Every seventh analysis (every 28 minutes) was of the control mixture R₁. The analyser response to a given CCQM-P73 mixture, y_{42C} , was corrected multiplicatively using the following set of formulae:

$$y_{42C,n=7,i} = \frac{y_{42C,i} \cdot y_{42C,i-2}}{\left(\frac{5}{7} y_{42C,i-2} + \frac{2}{7} y_{42C,i+5}\right)}, \quad \text{for } i = 8, 15, 22, 29, 36$$

$$y_{42C,n=7,i} = \frac{y_{42C,i} \cdot y_{42C,i-2}}{\left(\frac{4}{7} y_{42C,i-3} + \frac{3}{7} y_{42C,i+4}\right)}, \quad \text{for } i = 9, 16, 23, 30, 37$$

$$y_{42C,n=7,i} = \frac{y_{42C,i} \cdot y_{42C,i-4}}{\left(\frac{3}{7} y_{42C,i-4} + \frac{4}{7} y_{42C,i+3}\right)}, \quad \text{for } i = 10, 17, 24, 31, 38$$

$$y_{42C,n=7,i} = \frac{y_{42C,i} \cdot y_{42C,i-4}}{\left(\frac{2}{7} y_{42C,i-5} + \frac{5}{7} y_{42C,i+2}\right)}, \quad \text{for } i = 11, 18, 25, 32, 39$$

$$y_{42C,n=7,i} = \frac{y_{42C,i} \cdot y_{42C,i-6}}{\left(\frac{1}{7} y_{42C,i-6} + \frac{6}{7} y_{42C,i+1}\right)}, \quad \text{for } i = 12, 19, 26, 33, 40$$

where,

 $y_{42C,i}$ is the **42C** response of the *i*th analysis in the sequence listed in Table 2;

 y_0 is the 42C response to high purity nitrogen;

 $y_{42C,i}$ is the zero corrected **42C** response of the *i*th analysis in the sequence listed in Table 2;

 $y_{42C.6}$ refers to the first analysis of the control mixture, R₁, in the sequence;

 $y_{42C,n=7,i}$ refers to the drift corrected $y_{42C,i}$ response

Quantity	Value	Standard	Sensitivity	Uncertainty
		Uncertainty	Coefficient	Contribution
У42С', <i>i</i>	31513 a.u.	5.0 a.u.	1	5.0 a.u.
<i>y</i> 0	38.9 a.u.	20.4 a.u.	-1	-20.4 a.u.
У42С',6	45834.7 a.u.	5.0 a.u.	0.196	0.982 a.u.
<i>Y</i> 42C', <i>i</i> +5	45807.2 a.u.	5.0 a.u.	-0.196	-0.982 a.u.
С	0 a.u.	21.0 a.u.	1	21.0 a.u.
$V_{42C} = 7i$	31479.6 a.u.	29.7 a.u.		

 $y_{42C,n=7,i}$ **S1479.0 a.u.29.7 a.u.**Table 6: Uncertainty budget for corrected 42C analyser response

The uncertainty in the 42C analyser response was calculated from the equation

$$y_{42\mathrm{C},n=7,i} = \frac{\left(y_{42\mathrm{C},i} - y_{0}\right) \cdot \left(y_{42\mathrm{C},6} - y_{0}\right)}{\left(\frac{5}{7}\left(y_{42\mathrm{C},i-2} - y_{0}\right) + \frac{2}{7}\left(y_{42\mathrm{C},i+5} - y_{0}\right)\right)} + C$$

The standard uncertainties of the 42C analyser responses were based on standard deviations of the mean of 120 measurements and validated by calculation of the Allan variance. The zero response of the 42C analyser was observed to increase by 70 a.u. over the course of a whole measurement series. The standard uncertainty of the zero response

was calculated by assuming a rectangular distribution with limits set as the minimum and maximum zero response value, and the mean value used for signal correction.

Comparison Results:

The results for measurements performed on 30/08/06 are shown in Figures 1 and 2, with the corrected analyser responses plotted against the gravimetric mole fractions assigned by NMIs. Regression analysis on all of the other sixteen measurement series did not differ significantly from the measurement series depicted here. Results from selected measurements recorded during Measurement Series 2 and 3 are included in Appendix 2 for comparison. Error bars representing the measurement uncertainties in both axes have not been included in the plots as these are too small to visualise.

				Corrected	Corrected
				LIMAS	42C
				analyser	analyser
	Mixture	X _{NO-grav}	u(x _{NO-grav})	response	response
Laboratory	Label	µmol/mol	µmol/mol	/a.u.	/a.u,
KRISS	M1	31.020	0.007	4160.409	31119.55
CSIR-NML	M2	33.063	0.062	4385.410	32815.37
CERI	M3	34.930	0.020	4684.796	35053.78
VALCRM1	M4	37.170	0.027	4983.457	37311.35
LNE	M5	39.839	0.040	5279.117	39531.76
SMU	M6	40.419	0.031	5350.075	40072.39
CENAM	M7	40.777	0.088	5484.506	41085.3
VNIIM	M8	42.180	0.030	5639.689	42194.59
NIST	M9	43.081	0.032	5790.213	43381.45
NMIA	M10	44.844	0.074	5852.779	43802.96
VALCRM2	M11	46.980	0.028	6295.423	47076.98
IPQ	M12	47.001	0.004	6307.814	47218.59
NMi-VSL	M13	47.011	0.011	6310.080	47241.8
CERI	M14	50.910	0.020	6792.274	50858.76
KRISS	M15	52.984	0.009	7068.559	52913.26
CSIR-NML	M16	55.111	0.104	7273.698	54386.62
VALCRM3	M17	56.950	0.031	7624.182	57059.79
SMU	M18	59.576	0.044	7861.665	58768.38
LNE	M19	60.580	0.065	8078.630	60439.33
CENAM	M20	60.690	0.104	8148.086	60966.93
NMi-VSL	M21	63.012	0.023	8434.911	63103.53
VNIIM	M22	63.320	0.040	8447.391	63157.57
NMIA	M23	64.840	0.110	8428.526	63015.98
NIST	M24	67.085	0.047	8968.432	67111.45
IPQ	M25	69.700	0.007	9318.398	69676.39

Table 7: Corrected LIMAS 11UV and 42C analyser responses for the twenty-five gas standards listed in Table 1, analysed on 30/08/06 (3008a)



ABB LIMAS UV11 analyer results

Figure 1: Corrected LIMAS 11UV responses for the twenty-five gas standards listed in Table 1, analysed on 30/08/06 (3008a)





Figure 2: Corrected 42C Analyser responses for the twenty-five gas standards listed in Table 1, analysed on 30/08/06 (3008a)

The analysis of the data depicted in Figures 1 and 2 required the fitting of a regression line. Previous validation studies performed by the BIPM (Appendix 1) had shown that a linear regression model would be expected. Visual inspection of the data, confirmed by

regression analysis, indicated that data for a number of gas standards were not compatible with the calculated regression line. FTIR analysis of the gas mixtures was performed to confirm that these gas standards could be considered as outliers, before further regression analysis of the remaining data was undertaken.

FTIR analysis of gas standards:

Analysis of all gas standards by FTIR was undertaken to quantify impurities within the gas standards, and to compare these with the impurities and their uncertainties reported by participating laboratories. Significant differences between impurity mole fractions reported by laboratories and the values measured by FTIR at the BIPM would be used as confirmation that the data should be considered as an outlier and not included in the calculation of the regression line. Nitrous oxide (N₂O) and nitrogen dioxide (NO₂) impurity concentrations were of particular importance, as these impurities would be expected in pure nitrogen monoxide gas, and would increase in concentration in the pure gas with time and at elevated pressures.

FTIR system description

AThemoNicolet Nexus FTIR spectrometer, fitted with a MCT-high D* liquid N₂-cooled mid-infrared detector and a 6.4 m pathlength multipass White cell (Gemini Scientific Instruments, USA) was used for all measurements. This ensemble was placed in a plexiglass enclosure which was constantly purged with zero air flowing at 4 L·min⁻¹. The analysed gas sample flowed from the NO facility auto sampler through the White cell, and then to waste. The sample flow rate was controlled immediately downstream of the White cell at 500 mL·min⁻¹. The sample pressure and temperature were measured by means of a calibrated barometer (Series 6000 Digital Pressure Transducer, Mensor, USA) and a calibrated 100 Ω RTD temperature probe attached to the White cell.

Spectra acquisition procedure

The spectra were acquired using Thermo's proprietary OMNIC software. After each change of sample with the autosampler, 6 spectra each consisting of 380 scans at 1 cm⁻¹ resolution averaged over a period of 5 minutes were acquired during 30 minutes. The 6 spectra were then corrected with a reference spectrum (nitrogen 6.0 in cylinder from Messer) collected under similar conditions the same day to finally provide 6 absorbance spectra. After verification that the last 3 to 4 spectra were similar, the last spectrum was retained for quantitative analysis.

Quantitative analysis

Spectra were analysed quantitatively by a non linear least-square fitting of the measured absorption spectra with synthetic spectra using the program NLM4 (Non Linear MALT). NLM4 included the calculation of synthetic spectra from the HITRAN database of infrared absorption line parameters using the core of the program MALT (an acronym for <u>Multiple Atmospheric Layer Transmission</u>), as described in detail by Griffith in 1996¹.

¹ Griffith D.W.T. Appl. Spectrosc. **1996**, 50, 59-70

		NO ₂ mole fraction measurements					
Mixture Label	NMI	NMI	NMI	BIPM	BIPM	⊿ (NO ₂)	U (∆
	Assigned	Assigned	Assigned	FTIR	FTIR	(µmol/mol)	[NO ₂])
	X _{NO} (umol/mol)	X _{NO2} (umol/mol)	U(X _{NO2}) (umol/mol)	X _{NO2-FTIR} (umol/mol)	U(X _{NO2}) (umol/mol)		(µmol/mol) (k=2)
	31.02	0.001	0.0002	0.007	0.010	0.006	0.020
	33.063	0.001	0.0002	0.007	0.010	0.006	0.020
	34.93	0.033215	0.03835	0.278	0.010	0.245	0.135
	27.47			0.007	0.010		
VALCRM1 (M4)	37.17			0.003	0.010		
LNE (M5)	39.839	0.00035	0.000025	0.005	0.010	0.004	0.020
SMU (M6)	40.419	0.086	0.017	0.029	0.010	-0.057	0.039
CENAM (M7)	40.777			0.003	0.010		
VNIIM (M8)	42.18	0.042	0.005	0.033	0.010	-0.009	0.022
NIST (M9)	43.081	0.0341	0.0031	0.031	0.010	-0.003	0.021
NMIA (M10)	44.844	0.045	0.026	0.004	0.010	-0.041	0.056
VALCRM2	46.98						
(M11)				0.005	0.010		
IPQ (M12)	47.001	0.004701	0.00023	0.006	0.010	0.002	0.020
NMi-VSL (M13)	47.011	0.004	0.0008	0.006	0.010	0.002	0.020
CERI (M14)	50.91			0.006	0.010		
KRISS (M15)	52.984	0.002	0.0003	0.007	0.010	0.005	0.020
CSIR-NML	55.111						
(M16)		0.055221	0.06737	0.272	0.054	0.217	0.173
VALCRM3 (M17)	56.95			0 002	0.010		
SMU (M18)	59.576	0 127	0.026	0.002	0.030	0 024	0.080
LNE (M19)	60.58	0.00322	0.0001	0.003	0.010	-0.001	0.020
CENAM (M20)	60.69			0.005	0.010		
NMi-VSL (M21)	63.012	0.0054	0.0011	0.010	0.010	0.005	0.020
VNIIM (M22)	63.32	0.064	0.007	0.032	0.010	-0.032	0.024
NMIA (M23)	64.84	0.065	0.038	0.007	0.010	-0.058	0.079
NIST (M24)	67.085	0.0531	0.0048	0.050	0.010	-0.003	0.022
IPQ (M25)	69.7	0.006975	0.00035	0.006	0.010	-0.001	0.020

Table 8: NMI assigned and BIPM FTIR measurement results for NO₂ mole fractions in gas standards analysed in CCQM-P73

The programme convolved a "stick" spectrum calculated from the line parameters with the temperature, pressure, pathlength, resolution and instrument line shape function specified by the user. Spectra were calculated iteratively from an initial estimate of all input parameters following a modified Levenberg-Marquart algorithm² until a least-square best fit to the measured spectrum was obtained. Gas concentrations in the sample were iteratively adjusted during the fit. The quality of the fit could be improved by choosing a proper spectral window of the measured spectrum. Spectra which had been

² Press W.H. et al, Numerical Recipes, Cambridge University Press, 1992

acquired across a total wavelength range of (1500 to 2500) cm⁻¹, were fitted on two spectral windows according to the impurities of interest: (1400 to 1700) cm⁻¹ for H₂O and NO₂, and (2000 to 2400) cm⁻¹ for CO, CO₂ and N₂O.

Uncertainty budget for FTIR measurements

Previous comparisons between mole fraction determinations by FTIR spectroscopy with fitting to synthetic spectra versus gravimetry³, have indicated that the values determined from FTIR measurements could be biased by up to 5 % relative to gravimetric values, although the precision of the measurements were much better than this. A conservative estimate for the measurement uncertainty of results determined from FTIR analysis was adopted, with 10% of the value taken as the standard uncertainty, with a minimum of 10 nmol.mol⁻¹. The mass fractions NO₂ and N₂O measured at the BIPM are shown in figures 3 and 5 respectively. In the cases where the purity tables provided by participating laboratories gave values of mole fractions of NO₂ and N₂O, the difference between these values and those determined by the BIPM with FTIR analysis (Δ (NO₂) and Δ (N₂O))were calculated and shown in figures 4 and 6.

CENAM reported a value for the sum of both NO_2 and N_2O mole fractions present, and therefore differences for individual components could not be calculated.

LNE and CERI reported N₂O and NO₂ impurities in their pure nitrogen monoxide gas. CERI did not provide information on the N₂O and NO₂ mole fractions in the gas standards submitted for analysis in CCQM-P73, and LNE only provided values for nitrogen dioxide in their gas standards.

³ Esler M.B. et al, Anal. Chem., 2000, 72, 206-215



Figure 3: BIPM FTIR measurement results for NO₂ mole fractions in gas standards analysed in CCQM-P73



Figure 4: Graph of difference between NMI assigned values and BIPM FTIR measurements of NO₂ mole fractions within gas standards analysed in CCQM-P73

		N ₂ O mole fraction measurements					
Mixture Label	NMI	NMI	NMI	BIPM	BIPM	⊿ (N ₂ 0)	$U(\Delta$
	Assigned	Assigned	Assigned	FTIR	FTIR	(µmol/mol)	[N ₂ 0])
	X _{NO}	X _{N2O}	U(X _{N2O})	X _{N2O-FTIR}	<i>u</i> (<i>x</i> _{N2O-}		(µmol/mol) (k=2)
	(µmoi/moi)	(μποι/ποι)	(μποι/ποι)	(µmoi/moi)	FTIR <i>)</i> (µmol/mol)		()
KRISS (M1)	31.02	0.046	0.002	0.089	0.020	0.043	0.040
CSIR-NML (M2)	33.063	0.033	0.0383	0.214	0.043	0.181	0.115
CERI (M3)	34.93			0.035	0.020		
VALCRM1 (M4)	37.17			0.059	0.020		
LNE (M5)	39.839			0.080	0.020		
SMU (M6)	40.419	0.058	0.011	0.272	0.054	0.214	0.111
CENAM (M7)	40.777			0.036	0.020		
VNIIM (M8)	42.18	0.051	0.006	0.057	0.020	0.006	0.042
NIST (M9)	43.081	0.035	0.0035	0.032	0.020	-0.003	0.041
NMIA (M10)	44.844	0.045	0.026	0.483	0.097	0.438	0.200
VALCRM2 (M11)	46.98			0.089	0.020		
IPQ (M12)	47.001	0.001	0.000023	0.020	0.020	0.019	0.040
NMi-VSL (M13)	47.011	0.011	0.0012	0.018	0.020	0.007	0.040
CERI (M14)	50.91			0.092	0.020		
KRISS (M15)	52.984	0.078	0.004	0.145	0.029	0.067	0.059
CSIR-NML (M16)	55.111	0.055	0.06376	0.356	0.071	0.301	0.191
VALCRM3 (M17)	56.95			0.060	0.020		
SMU (M18)	59.576	0.085	0.017	0.398	0.080	0.313	0.163
LNE (M19)	60.58			0.010	0.020		
CENAM (M20)	60.69			0.057	0.020		
NMi-VSL (M21)	63.012	0.015	0.0016	0.020	0.020	0.005	0.040
VNIIM (M22)	63.32	0.076	0.009	0.074	0.020	-0.002	0.044
NMIA (M23)	64.84	0.065	0.038	0.697	0.139	0.632	0.289
NIST (M24)	67.085	0.055	0.0055	0.050	0.020	-0.005	0.041
IPQ (M25)	69.7	0.001	0.000035	0.029	0.020	0.028	0.040

Table 9: NMI assigned and BIPM FTIR measurement results for N_2O mole fractions in gas standards analysed in CCQM-P73



Figure 5: BIPM FTIR measurement results for N_2O mole fractions in gas standards analysed in CCQM-P73



Figure 6: Graph of difference between NMI assigned values and BIPM FTIR measurements of N_2O mole fractions within gas standards analysed in CCQM-P73

The comparison of NMI assigned values and measured values for NO_2 and N_2O mole fractions confirmed that the following standards would be omitted from the calculation of the regression line for the nitrogen monoxide measurement data:

- CSIR-NML standards M2 and M16
- SMU standards M6 and M18
- NMIA standards M10 and M23

Regression analysis:

The procedures outlined in ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) were used for the analysis of the data from the comparison. This required:

- a) the determination of the analysis function x = G(y), which expressed analyte contents in relation to corresponding measured responses;
- b) validation of the analysis function;
- c) and prediction of mole fraction values from measured responses and comparison to NMI assigned values. The difference in these quantities (*D*) could be compared to degrees of equivalence calculated in previous key comparisons for nitrogen monoxide gas standards.

Determination and Validation of Analysis Functions

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

Previous validation studies performed by the BIPM had indicated that a linear response function could be expected for the corrected responses of both analysers. In determining the analysis function to be used, the gas standards M2, M5, M6, M10, M16, M18 and M23 were not included in the regression analysis. It was decided not to include cylinder M5 (LNE gas standard) in the regression analysis as the deviation of the input values for this cylinder relative to those calculated from the regression analysis were as large as those for cylinder M6, which had already been omitted, and its omission validated by the FTIR analysis results for impurities. Additional measurements performed by LNE after the comparison confirmed the results obtained by the BIPM (Appendix 4), however these differed from the results the LNE had obtained in preparation for the comparison. The cylinders VALCRM1,2,3 were not included in the calculations of the analysis function.

Regression analysis of the remaining gas standards was initially performed using the uncertainties of instrument responses reported in tables 3, 4, 5 and 6. However, for all measurement series, the analysis function was not consistent with the calibration data within the relevant uncertainties. Further regression analysis of the data would require modification of the input data, either removal of certain cylinders from the data set for analysis, or an increase in the uncertainty of the analyser responses.

As no additional information was available to the coordinating laboratory to omit further cylinders from the regression analysis data set, it was decided to increase the values for the analyser measurement uncertainties until the analysis function was consistent with the

calibration data. This approach was consistent with the hypothesis that the analytical uncertainties previously validated by the coordinating laboratory had not included systematic effects within the measurement system. In order to arrive at an analysis function that was consistent with the calibration data, the measurement uncertainty values used were increased from 4.4 a.u. to 11.05 a.u. for the LIMAS 11-UV analyser, and from 29.7 a.u. to 89.1 a.u. for the 42C Chemiluminescence analyser.

The alternative approach of maintaining the previously validated values for the analyser measurement uncertainties would have required the omission of several gas standards from the regression analysis data set. This would have been consistent with an approach that considered that the uncertainties of the gravimetrically assigned values had been underestimated for cylinders removed from the regression analysis data set.

Linear analysis functions were calculated for both LIMAS 11-UV and the 42C Chemiluminescence analysers of the form

 $x = b_0 + b_1 y$

where,

x was the mole fraction of nitrogen monoxide, μ mol/mol

y was the corrected instrument response, a.u.

For the measurement results recorded on 30/08/06, the following regression analysis parameters were recorded:

Parameter	LIMAS 11-UV analysis	42C Chemiluminescence
		analysis
b_0	-0.30406	-0.37102
b_1	7.5168 x 10 ⁻³	1.0058 x 10 ⁻³
$u(b_0)$	0.10497	0.11265
$u(b_1)$	1.4964 x 10 ⁻⁵	2.1439 x 10 ⁻⁶
Covariance	-1.5311 x 10 ⁻⁶	-2.3547 x 10 ⁻⁷
Remaining SSD	25.01	26.0
Goodness-of-fit measure	1.844	1.7879

Table 10: Regression analysis parameters for measurement results recorded on 30/08/08 (3008a)



Figure 7: Regression analysis of a sub-set of cylinders from corrected LIMAS 11UV responses recorded on 30/08/06 (3008a), displaying differences between adjusted and assigned mole fraction values for each cylinder in the regression analysis data set.



Figure 8: Regression analysis of a sub-set of cylinders for corrected LIMAS 11UV responses analysed on 30/08/06 (3008a), displaying differences between adjusted and assigned analyser responses for each cylinder in the regression analysis data set.



Figure 9: Regression analysis of a sub-set of cylinders from corrected 42C chemiluminescence analyser responses recorded on 30/08/06 (3008a), displaying differences between adjusted and assigned mole fraction values for each cylinder in the regression analysis data set.



Figure 10: Regression analysis of a sub-set of cylinders for corrected 42C chemiluminescence analyser responses analysed on 30/08/06 (3008a), displaying

differences between adjusted and assigned analyser responses for each cylinder in the regression analysis data set.

The residual sum of weighted squared deviations (SSD) was equal or less than two times the value of the relevant degrees of freedom, indicating that the overall fit of the analysis function to the calibration data was satisfactory. For each experimental data point (x_i, y_i) an adjusted data point (\hat{x}_i, \hat{y}_i) has been calculated as part of the regression analysis. In figures 7,8,9 and 10, the differences between adjusted and experimental points are plotted, $(\hat{x}_i - x_i)$ and $(\hat{y}_i - y_i)$, with uncertainties plotted corresponding to $2u(x_i)$ and $2u(y_i)$ respectively. In all cases it can be seen that the conditions

$$\left|\hat{x}_{i}-x_{i}\right| \leq 2u(x_{i}) \text{ and } \left|\hat{y}_{i}-y_{i}\right| \leq 2u(y_{i})$$

were met, and the analysis function could be considered to be compatible with the entire data set.

Comparison of predicted and assigned mole fraction values

The analysis function and recorded analyser responses and uncertainties were used to predict the nitrogen monoxide mole fractions (x_{pred}) and uncertainties $[u(x_{pred})]$ of the twenty-five gas standards listed in Table 1. The differences (D) between the predicted and gravimetric (x_{grav}) nitrogen monoxide mole fraction values (assigned by NMIs) and the uncertainty of the difference were calculated as:

and

$$D = x_{pred} - x_{grav}$$

$$U(D) = 2\sqrt{u^2(x_{pred}) + u^2(x_{grav})}$$

The differences between predicted and assigned gravimetric values are in Tables 11 and 12 and plotted in figures 11 and 12. By considering the predicted value as the reference value for each gas standard, the calculated values of D can be compared to degrees of equivalence calculated in previous key comparisons for nitrogen monoxide. In order for biases to appear in the same sense, the values of -D from CCQM-K1.c and EUROMET.K1.c are plotted in figure 13 together with the values of D determined in CCQM-P73.

Mixture	<i>x</i> _{NO-grav} umol/mol	<i>u</i> (<i>x</i> _{NO-grav}) umol/mol	У _{LIMAS} /a.u.	<i>u</i> (y _{LIMAS}) /a.u.	<i>x</i> _{NO-pred} umol/mol	u(x _{NO-pred}) umol/mol	D umol/mol	<i>u</i> (D) umol/mol	<i>U(D)</i> umol/mol
KRISS (M1)	31.020	0.007	4160.409	11.050	30.969	0.095	-0.051	0.095	0.191
CSIR-NML (M2)	33.063	0.062	4385.410	11.050	32.660	0.094	-0.403	0.112	0.225
CERI (M3)	34.930	0.020	4684.796	11.050	34.911	0.092	-0.019	0.094	0.189
VALCRM1 (M4)	37.170	0.027	4983.457	11.050	37.156	0.091	-0.014	0.095	0.189
LNE (M5)	39.839	0.040	5279.117	11.050	39.378	0.089	-0.461	0.098	0.196
SMU (M6)	40.419	0.031	5350.075	11.050	39.912	0.089	-0.507	0.094	0.189
CENAM (M7)	40.777	0.088	5484.506	11.050	40.922	0.089	0.145	0.125	0.250
VNIIM (M8)	42.180	0.030	5639.689	11.050	42.088	0.088	-0.092	0.093	0.186
NIST (M9)	43.081	0.032	5790.213	11.050	43.220	0.088	0.139	0.093	0.187
NMIA (M10)	44.844	0.074	5852.779	11.050	43.690	0.088	-1.154	0.115	0.229
VALCRM2 (M11)	46.980	0.028	6295.423	11.050	47.018	0.087	0.038	0.091	0.182
IPQ (M12)	47.001	0.004	6307.814	11.050	47.111	0.087	0.110	0.087	0.174
NMi-VSL (M13)	47.011	0.011	6310.080	11.050	47.128	0.087	0.117	0.087	0.175
CERI (M14)	50.910	0.020	6792.274	11.050	50.752	0.086	-0.158	0.089	0.177
KRISS (M15)	52.984	0.009	7068.559	11.050	52.829	0.086	-0.155	0.087	0.174
CSIR-NML (M16)	55.111	0.104	7273.698	11.050	54.371	0.087	-0.740	0.135	0.271
VALCRM3 (M17)	56.950	0.031	7624.182	11.050	57.006	0.087	0.056	0.092	0.185
SMU (M18)	59.576	0.044	7861.665	11.050	58.791	0.088	-0.785	0.098	0.196
LNE (M19)	60.580	0.065	8078.630	11.050	60.422	0.088	-0.158	0.110	0.219
CENAM (M20)	60.690	0.104	8148.086	11.050	60.944	0.088	0.254	0.137	0.273
NMi-VSL (M21)	63.012	0.023	8434.911	11.050	63.100	0.090	0.088	0.092	0.185
VNIIM (M22)	63.320	0.040	8447.391	11.050	63.193	0.090	-0.127	0.098	0.196
NMIA (M23)	64.840	0.110	8428.526	11.050	63.052	0.090	-1.788	0.142	0.284
NIST (M24)	67.085	0.047	8968.432	11.050	67.110	0.092	0.025	0.103	0.207
IPQ (M25)	69.700	0.007	9318.398	11.050	69.741	0.094	0.041	0.094	0.188

Table 11: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 3008a data set)

Mixture	X _{NO-grav}	<i>u</i> (<i>x</i> _{NO-grav})	У _{42С} /а ц	<i>u</i> (у _{42C}) /а ц	X _{NO-pred}	u(x _{NO-pred})	D umol/mol	u(D)	<i>U(D)</i> umol/mol
KRISS (M1)	31.020	0.007	31119.552	89.100	30.929	0.103	-0.091	0.103	0.206
CSIR-NML (M2)	33.063	0.062	32815.374	89.100	32.634	0.101	-0.429	0.119	0.237
CERI (M3)	34.930	0.020	35053.785	89.100	34.886	0.099	-0.044	0.101	0.203
VALCRM1 (M4)	37.170	0.027	37311.350	89.100	37.156	0.098	-0.014	0.101	0.203
LNE (M5)	39.839	0.040	39531.760	89.100	39.390	0.096	-0.449	0.104	0.209
SMU (M6)	40.419	0.031	40072.395	89.100	39.933	0.096	-0.486	0.101	0.202
CENAM (M7)	40.777	0.088	41085.299	89.100	40.952	0.096	0.175	0.130	0.260
VNIIM (M8)	42.180	0.030	42194.589	89.100	42.068	0.095	-0.112	0.100	0.199
NIST (M9)	43.081	0.032	43381.451	89.100	43.262	0.095	0.181	0.100	0.200
NMIA (M10)	44.844	0.074	43802.957	89.100	43.686	0.094	-1.158	0.120	0.240
VALCRM2 (M11)	46.980	0.028	47076.981	89.100	46.979	0.093	-0.001	0.098	0.195
IPQ (M12)	47.001	0.004	47218.588	89.100	47.121	0.093	0.120	0.094	0.187
NMi-VSL (M13)	47.011	0.011	47241.804	89.100	47.144	0.093	0.133	0.094	0.188
CERI (M14)	50.910	0.020	50858.756	89.100	50.782	0.093	-0.128	0.095	0.190
KRISS (M15)	52.984	0.009	52913.261	89.100	52.849	0.093	-0.135	0.094	0.187
CSIR-NML (M16)	55.111	0.104	54386.625	89.100	54.331	0.093	-0.780	0.140	0.279
VALCRM3 (M17)	56.950	0.031	57059.788	89.100	57.019	0.094	0.069	0.099	0.198
SMU (M18)	59.576	0.044	58768.379	89.100	58.738	0.094	-0.838	0.104	0.208
LNE (M19)	60.580	0.065	60439.333	89.100	60.418	0.095	-0.162	0.115	0.230
CENAM (M20)	60.690	0.104	60966.926	89.100	60.949	0.095	0.259	0.141	0.282
NMi-VSL (M21)	63.012	0.023	63103.526	89.100	63.098	0.096	0.086	0.099	0.198
VNIIM (M22)	63.320	0.040	63157.569	89.100	63.152	0.097	-0.168	0.104	0.209
NMIA (M23)	64.840	0.110	63015.979	89.100	63.010	0.096	-1.830	0.146	0.293
NIST (M24)	67.085	0.047	67111.452	89.100	67.129	0.099	0.044	0.110	0.219
IPQ (M25)	69.700	0.007	69676.385	89.100	69.709	0.101	0.009	0.101	0.203

Table 12: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 3008a data set)



Figure 11: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 3008a data set)



Figure 12: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 3008a data set)

Comparison of results with previous key comparisons

The results of CCQM-P73 can be compared to previous key comparisons for nitrogen monoxide in nitrogen at 100 μ mol/mol, and illustrates the reductions in uncertainties that can be achieved through a comparison with measurements performed at a central facility.



Laboratory (cylinder)

Figure 13: Comparison of results from CCQM-P73 with degrees of equivalence determined in previous key comparisons for nitrogen monoxide in nitrogen at 100 μ mol/mol. The quantity –*D* has been plotted for the results of CCQM-K1.c and EUROMET-K1.c, so that deviations from the reference value in these key comparisons and CCQM-P73 appear in the same sense.

Discussion and Conclusions:

The advantages and complications in organizing a comparison with measurements performed at a central laboratory have been clearly demonstrated, notably:

- analytical measurement uncertainties can be reduced;
- a degree of equivalence parameter and its uncertainty can be calculated;
- regression analysis and therefore reference values for the comparison are highly dependent on the data set chosen for regression analysis and the uncertainty ascribed to analytical measurement system within the central laboratory.

Participating laboratories reported standard uncertainties for gravimetric preparation which ranged from 0.01% to 0.22% relative to the nitrogen monoxide mole fraction value.

Following FTIR analysis, the standards of three laboratories (six gas standards in total) were omitted from the regression analysis data set, as a significant difference between

reported and measured values of impurity contents was observed. An additional standard was removed from the regression analysis set as its deviation from the regression line was of the same order of magnitude as the standards already omitted. A regression line consistent with the remaining calibration data (15 gas standard) could be obtained by increasing estimates of the coordinating laboratory's measurement uncertainty by approximately a factor of three, resulting in analytical standard uncertainties of 0.12% (at 70 μ mol/mol) and 0.27% (at 30 μ mol/mol), and predicted standard uncertainties of the nitrogen monoxide mole fractions of 0.09 μ mol/mol. Reported standard uncertainties related to gravimetric preparation ranged from 0.004 μ mol/mol to 0.11 μ mol/mol with a median of 0.03 μ mol/mol for the twenty-five gas standards listed in Table 1.

An alternative approach, which would result in a regression line based on the coordinating laboratory's initial estimates of its analytical measurement uncertainty and consistent with the calibration data could be obtained by removal of a significant number of data points from the regression analysis data set.

Acknowledgements:

Special acknowledgement is given to Dr Michael Esler who coordinated the comparison prior to his departure from the BIPM in October 2006.

Appendix 1: Summary of validation studies performed by the coordinating laboratory

In preparation for CCQM-P73 the BIPM conducted a number of studies to validate the performance and uncertainty of its analytical systems. Three gravimetrically prepared standards of nitrogen monoxide in nitrogen were purchased from one NMI and a fourth obtained from another. Both NMIs had successfully participated in CCQM-K1.c and EUROMET-K1.c. Details of these standards are contained in Table A1. The gas standards were analysed on 17/05/2005, (results listed in Table A2 and 3) and regression analysis performed as for all standards compared in CCQM-P73. All four cylinders were used for the determination of the analysis function, and the difference (*D*) between predicted and gravimetric values for the nitrogen monoxide mole fraction calculated. Excellent agreement between the analysis function and calibration data was observed. This was consistent with estimates of the standard analytical uncertainty of 0.05% (at 37 μ mol/mol) and 0.08% (at 57 μ mol/mol), and predicted average standard uncertainties of the nitrogen monoxide mole fraction calculated standards analytical uncertainty of 0.05% (at 37 μ mol/mol).

Gas standard	Certification date	X _{NO-grav} µmol/mol	<i>u</i> (x _{NO-grav}) µmol/mol
VALCRM1	05/04/04	37.17	0.0267
NMI-B	Before 08/03/05	40.04	0.0200
VALCRM2	05/04/04	46.98	0.0282
VALCRM3	05/04/04	56.95	0.0305

Table A1: NO gas standards used in validation studies



Figure A1: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas standards in the validation study set. (LIMAS 11-UV analyser)



Figure A2: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas stnadrads in the validation study set. (42C chemiluminescence analyser)

Mixture	x _{NO-grav} µmol/mol	<i>u</i> (<i>x</i> _{NO-grav}) µmol/mol	У _{LIMAS} /a.u.	<i>u</i> (y _{LIMAS}) /a.u.	x _{NO-pred} µmol/mol	u(x _{NO-pred}) µmol/mol	D µmol/mol	<i>u</i> (D) µmol/mol	<i>U(D)</i> µmol/mol
VALCRM1	37.17	0.0267	4839.1595	4.4	37.167	0.046	-0.003	0.053	0.106
NMI-B	40.04	0.0200	5210.694	4.4	40.051	0.043	0.011	0.047	0.094
VALCRM2	46.98	0.0282	6101.227	4.4	46.964	0.041	-0.016	0.050	0.099
VALCRM3	56.95	0.0305	7388.5131	4.4	56.957	0.054	0.007	0.062	0.124

Table A2: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas standards in the validation study set. (LIMAS 11-UV analyser)

Mixture	x _{NO-grav} µmol/mol	<i>u</i> (<i>x</i> _{NO-grav}) µmol/mol	у _{42С} /a.u.	<i>u</i> (y _{42C}) /a.u.	<i>x</i> _{NO-pred} µmol/mol	<i>u</i> (<i>x</i> _{NO-pred}) µmol/mol	D µmol/mol	<i>u</i> (D) µmol/mol	<i>U(D)</i> µmol/mol
VALCRM1	37.17	0.0267	36648.5	29.7	37.167	0.041	-0.003	0.049	0.098
NMI-B	40.04	0.0200	39498.7	29.7	40.050	0.038	0.010	0.043	0.086
VALCRM2	46.98	0.0282	46332.9	29.7	46.963	0.037	-0.017	0.046	0.092
VALCRM3	56.95	0.0305	56212.6	29.7	56.957	0.049	0.007	0.058	0.116

Table A3: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas standards in the validation study set. (42C chemiluminescence analyser)



Appendix 2: Results from measurement series 2 and 3

Figure A4: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 1409a data set)



Figure A5: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 1409a data set)



Figure A6: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 0410c data set)



Figure A7: Difference (D) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 0410c data set)

Appendix 3: Information submitted by participating laboratories (See attachment)

Appendix 4: Additional information provided by the LNE after the comparison

The following information was provided by the LNE on 10 May 2007, after receipt of their cylinders and additional measurements in their laboratory.

<u>Complementary informations on the results of LNE</u> (CCQM-P73)

Different tests have been done on the gas mixture NO in nitrogen at 39.839 μ mol/mol (NO/N2 0040) : the results are presented in the following table.

Date	Action	Results
2006/05/10	Gravimetric preparation	$C_{gravi}(NO) = (39.839 \pm 0.080) \mu mol/mol$ $C_{gravi}(NO_2) = (0.00036 \pm 0.00005) \mu mol/mol$
2006/05/31	Analysis	Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{anal}(NO) = (39.82 \pm 0.40) \mu mol/mol$ Deviation between "Gravimetric concentration" and "Analytical concentration" : - 0.06 %
2006/06/28	$^{\prime\prime}$ 06/28 Analysis Determination of the analytical concentration gas mixture NO/N2 0040 with another gas m NO/N2 0037 by using FTIR $C_{anal}(NO) = (39.74 \pm 0.40) \mu mol/mol$ Deviation between "Gravimetric concentration" - 0.25 %	
2006/07/25	Analysis	Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{anal}(NO) = (39.85 \pm 0.40) \mu mol/mol$ Deviation between "Gravimetric concentration" and "Analytical concentration" : + 0.03 %

2006/07/26	Th	e gas mixture NO/N2 0040 was sent to BIPM
2007/04/18	Analysis	Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{anal}(NO) = (39.25 \pm 0.40) \mu mol/mol$ Deviation between "Gravimetric concentration" and "Analytical concentration" : - 1.48 %

Comments :

• <u>Before delivery in BIPM</u>

The different analyses done on the gas mixture NO/N2 0040 by LNE before delivery to BIPM show a good stability of the NO concentration during the time :

- ✓ During 3 months, the results show no significant bias between analytical and gravimetric concentrations; consequently, the NO concentration of the gas mixture can be considered stable during 3 months (may to july 2006);
- ✓ The analysis done on the gas mixture the day before delivery to BIPM shows a very small deviation of 0.03 % between analytical and gravimetric concentrations : as before, there is no significant bias between analytical and gravimetric concentrations.

• After its return from BIPM

At its return from BIPM, the gas mixture was analysed again by LNE (april 2007). The analysis of the gas mixture shows a decrease of the NO concentration : this result confirms the results obtained by BIPM.

On the other hand, an IR analysis has been done and shows that the N_2O and CO_2 concentrations are higher in april 2007 than in july 2006 :

✓	2006/07/25 :	C _{N2O} = 56 nmol/mol	$C_{CO2} = 52 \text{ nmol/mol}$
✓	2007/04/18 :	C _{N2O} = 140 nmol/mol	C_{CO2} = 119 nmol/mol

The NO_2 concentration measured in april 2007 stays negligible, which confirms the results obtained by BIPM.

Conclusion :

The results obtained by LNE in april 2007 confirm the results of BIPM obtained during the CCQM-P73 comparison, which means that there is a decrease of the NO concentration of the gas mixture NO/N2 0040.

But, no explanation has been found about the decrease of the NO concentration between :

- ✓ the delivery of the gas mixture to BIPM at the end of july 2006 : the NO concentration was stable during 3 months in LNE (may to july 2006),
- ✓ the beginning of the tests done by BIPM in the framework of CCQM-P73 comparison : the NO concentration began to decrease.

Appendix 3: Descriptions of NO/N $_2$ standards prepared by participating laboratories

Forms providing information on NO/N2 standards, submitted by laboratories participating in CCQM-P73, are reproduced in this Appendix. The forms are listed in the following order:

KRISS
CSIR-NML
CERI
LNE
SMU
CENAM
VNIIM
NIST
NMIA
IPQ
NMI-VSL
Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

Institute	KRISS (Korea Research Institute of Standards and Science)
Address	PO box 102, Yuseong, Daejeon, 305-600 KOREA
Contact Person	Sang Hyub Oh
Telephone	82-42-868-5341
Fax	82-42-868-5344
email	shoh@kriss.re.kr

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	2006. 6. 20
Volume (L)	9.5
Total Pressure (bar)	80
Connection type (e.g. DIN1, BS14 etc.)	JIS 8246

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Pure NO gas from Liquid Air Corp.

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO		997,394	96
H ₂	Gas MS	ND	2.89
O ₂	Gas MS	231	25
N ₂	Gas MS	519	25
He	Gas MS	ND	2.89
Ar	Gas MS	ND	2.89
СО	Gas MS	ND	28.9
CH ₄	GC-FID	ND	0.577
CO ₂	Gas MS	ND	28.9
NO ₂	FTIR	32	5
N ₂ O	FTIR	1,470	75
H ₂ O	FTIR	354	25

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂		999,966.6	1.74
H ₂	GC-AED	0.2	0.0289
O ₂	GC-AED	0.0379	0.000577
Ar	GC-AED	31.2	1.73
THC	GC-FID	0.98	0.0577
СО	GC methanizer	0.01	0.00289
CO ₂	GC-AED	0.01	0.00289
H ₂ O	Dew point meter	1.0	0.115

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂	999935.56	1.74
NO	<i>x</i> _{NO,grav} : 31.020	<i>u</i> (<i>x</i> _{NO,grav}) : 0.007
H ₂	0.2	0.0289
O ₂	0.045	0.001
Ar	31.2	1.73
CO	0.01	0.03
CO ₂	0.01	0.003
NO ₂	0.001	0.0002
N ₂ O	0.046	0.002
THC	0.980	0.058
H ₂ O	1.01	0.12
Не	negligible	negligible
CH ₄	negligible	negligible

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction	Expanded Uncertainty
0 th (Parent NO)	99.7394 % mol/mol	0.019 % mol/mol
1st	1.9924 % mol/mol	0.0008 % mol/mol
2 nd	997.57 µmol/mol	0.37 µmol/mol
3 rd	31.020 µmol/mol	0.014 µmol/mol

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Two cylinders of 2% and 1,000 ppm standards were prepared and compared. And three cylinders of 31 ppm standards were tested.

NOx analyzer (Model 42, TEI) and A-B-A methods were used in this test.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 31.020 μmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.12 μmol/mol (about 0.4 %)

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Five cylinders of 20 ppm standards were tested.

One was prepared at 03/8/20, two were prepared at 04/6/30, and two were prepared at 05/11/23.

In this long term stability test, concentration differences of all five standards from measured value and preparation value were less than 0.34 %. Our uncertainty of NO analysis is about 0.4 %

This results means that NO standards more than 20 ppm concentration are stable more than 2 years.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	2006. 6. 20
Volume (L)	9.5
Total Pressure (bar)	80
Connection type (e.g. DIN1, BS14 etc.)	JIS 8246

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Pure NO gas from Liquid Air Corp.

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO		997,394	96
H ₂	Gas MS	ND	2.89
O ₂	Gas MS	231	25
N ₂	Gas MS	519	25
He	Gas MS	ND	2.89
Ar	Gas MS	ND	2.89
СО	Gas MS	ND	28.9
CH ₄	GC-FID	ND	0.577
CO ₂	Gas MS	ND	28.9
NO ₂	FTIR	32	5
N ₂ O	FTIR	1,470	75
H ₂ O	FTIR	354	25

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂		999,966.6	1.74
H ₂	GC-AED	0.2	0.0289
O ₂	GC-AED	0.0379	0.000577
Ar	GC-AED	31.2	1.73
THC	GC-FID	0.98	0.0577
СО	GC methanizer	0.01	0.00289
CO ₂	GC-AED	0.01	0.00289
H ₂ O	Dew point meter	1.0	0.115

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂	999913.61	1.74
NO	<i>x</i> _{NO,grav} : 52.984	<i>u</i> (<i>x</i> _{NO,grav}) : 0.009
H ₂	0.2	0.0289
O ₂	0.050	0.001
Ar	31.2	1.73
СО	0.01	0.03
CO ₂	0.01	0.003
NO ₂	0.002	0.0003
N ₂ O	0.078	0.004
THC	0.980	0.058
H ₂ O	1.02	0.12
Не	negligible	negligible
CH ₄	negligible	negligible

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction	Expanded Uncertainty
0 th (Parent NO)	99.7394 % mol/mol	0.019 % mol/mol
1st	1.9932 % mol/mol	0.0009 % mol/mol
2 nd	1001.3 µmol/mol	0.3 µmol/mol
3 rd	52.984 µmol/mol	0.017 µmol/mol

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Two cylinders of 2% and 1,000 ppm standards were prepared and compared. And three cylinders of 53 ppm standards were tested. NOx analyzer (Model 42, TEI) and A-B-A methods were used in this test.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 52.984 µmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.21 μmol/mol (about 0.4 %)

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Five cylinders of 20 ppm standards were tested.

One was prepared at 03/8/20, two were prepared at 04/6/30, and two were prepared at 05/11/23.

In this long term stability test, concentration differences of all five standards from measured value and preparation value were less than 0.34 %. Our uncertainty of NO analysis is about 0.4 %

This results means that NO standards more than 20 ppm concentration are stable more than 2 years.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING INSTITUTE:

Institute	CSIR National Metrology Laboratory
Address	CSIR, Building 5 P.O. Box 395 Pretoria 0001
Contact Person	Angelique Botha
Telephone	+27 12 841 3800
Fax	+27 12 841 2131
email	abotha@csir.co.za

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	29 June 2006
Volume (L)	5 6
Total Pressure (bar)	120 bar
Connection type (e.g. DIN1, BS14 etc.)	CGA 330
Cylinder number	3775

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

NO 2.5 (99.5%) Air Liquide

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂ O	Specification	1000	1154,700538
NO	Specification	998000	2309,401076
NO ₂	Specification	1000	1154,700538

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂	Specification	999999,375	0,82248650
СО	GC-FID	0,0219999998	0,025
CO ₂	GC-FID	0,0240000002	0,028
H ₂	Specification	0,5	0,57735
H ₂ O	Specification	0,0099999997	0,011547
HC(Hydrocarbons)	Specification	0,050000007	0,057735
O ₂	Specification	0,0049999998	0,005774

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂	999966,15969	32,46133380
NO	X _{NO,grav} :	<i>U</i> (<i>x</i> _{NO,grav}) :k=2
	33,14889796	0,124956560
СО	0,21507658	0,022845823
CO ₂	0,023996811	0,025502571
H ₂	0,499983392	0,531299356
H ₂ O	0,009999667	0,010625987
HC(Hydrocarbons)	0,049998399	0,053129935
N ₂ O	0,033215328	0,038353885
NO ₂	0,033215328	0,038353885
O ₂	0,004999834	0,00531625

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
0 th (Parent NO)	99,5	2309,401076
1st	39916,54862876	149,899614778
2 nd	4000,7181734048	15,0561820537
3 rd	400,27263626564	1,50699076303
4 rd	33,14889796	0,124956560

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

A set of 7 samples of NO/N_2 mixtures (10 - 100 ppm) was compared with a second set of gravimetrically prepared NO/N_2 standards (10 - 100 ppm). The verification was done using chemilumiscence. The verification runs were performed once a week for three weeks in a row.

What NO mole fraction was predicted	X _{NO,anal} :
from your verification analysis?	33,06 x 10 ⁻⁶ mol/mol
What is your estimate of the uncertainty	$U(x_{\rm NO,anal})$:k=2
NO,anal :	0,98 x 10 ⁻ ° mol/mol

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The stability of the mixture was monitored with a verification run once a week for 3 conservative weeks before shipping.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	30 June 2006
Volume (L)	5 e
Total Pressure (bar)	120 bar
Connection type (e.g. DIN1, BS14 etc.)	CGA 330
Cylinder number	3770

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

NO 2.5 (99.5%) Air Liquide

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂ O	Specification	1000	1154,700538
NO	Specification	998000	2309,401076
NO ₂	Specification	1000	1154,700538

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂	Specification	999999,375	0,82248650
CO	GC-FID	0,0219999998	0,025
CO ₂	GC-FID	0,0240000002	0,028
H ₂	Specification	0,5	0,57735
H₂O	Specification	0,0099999997	0,011547
HC(hydrocarbons)	Specification	0,050000007	0,057735
O ₂	Specification	0,0049999998	0,005774

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
N ₂	999944,15378252	27,05014665344
NO	X _{NO,grav} :	<i>U</i> (<i>x</i> _{NO,grav}) :k=2
	55,1108094895	0,2077334323
СО	0,021947386907	0,0227931638
CO ₂	0,023995722945	0,0255276526
H ₂	0,499972389374	0,5264158896
H ₂ O	0,009999447564	0,0105283178
HC(Hydrocarbons)	0,049997239682	0,0526415889
N ₂ O	0,055221251994	0,0637642211
NO ₂	0,055221251994	0,0637642211
02	0,004999723782	0,0052646148

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (x10⁻⁶ mol/mol)	Uncertainty (x10⁻⁶ mol/mol)
0 th (Parent NO)	99,5	2309,401076
1st	53031,67118599	198,878045087
2 nd	5991,396112434	22,5465129825
3 rd	598,8498331181	2,25616669788
4 th	55,11080948958	0,20773343231

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

A set of 7 samples of NO/N₂ mixtures (10 - 100 ppm) was compared with a second set of gravimetrically prepared NO/N₂ standards (10 - 100 ppm). The verification was done using chemilumiscence. The verification runs were performed once a week for three weeks in a row.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 55,01 x 10 ⁻⁶ mol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	(x _{NO,anal}) :k=2 1,52 x 10⁻⁶ mol/mol

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The stability of the mixture was monitored with a verification run once a week for 3 conservative weeks before shipping.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

Institute	Chemicals Evaluation and Research Institute, Japan (CERI)
Address	1600, Shimo-Takano, Sugito-machi, Kitakatsushika-gun, Saitama 345-0043, Japan
Contact Person	Masaaki Maruyama
Telephone	+81-480-37-2601
Fax	+81-480-37-2521
email	maruyama-masaaki@ceri.jp

PARTICIPATING INSTITUTE:

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	28/11/2005
Volume (L)	<u>9.5</u>
Total Pressure (bar)	<u>93</u>
Connection type (e.g. DIN1, BS14 etc.)	JIS

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

The pure NO gas used to prepare is the CRM, which is certificated by NMIJ.

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
NO ₂	FT-IR	79	12
N ₂	GC-PID	144.8	6.6
O ₂	GC-PID	2.3	1.3
N ₂ O	FT-IR	84.85	0.60
CH ₄	GC-FID	9.6	5.6
C ₃ H ₈	GC-FID	1.17	0.67
H ₂ O	Dew point measurement with mirror	24.4	5.5
NO		999654	16

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
H ₂	GC-MS	<0.1	0.029
O ₂	GC-MS	<0.1	0.029
CO	GC-FID	<0.01	0.003
CO ₂	GC-FID	<0.01	0.003
CH4	GC-FID	<0.01	0.003
C ₃ H ₈	GC-FID	<0.01	0.003
NOx(NO+NO ₂)	Chemiluminescent	<0.005	0.001
SO ₂	UV fluorescence	<0.005	0.001
H ₂ O	Dew Point meter	<1	0.289
N ₂		999999.4	0.29

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂	999965.07	71.38
NO	<i>x</i> _{NO,grav} :34.93	<i>u</i> (<i>x</i> _{NO,grav}) :0.02

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
0 th (Parent NO)	999654	16
1st	11921.2	5.3
2 nd	1492.85	0.68
3 rd	34.93	0.02

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Three Primary Standard gases: 51.78 μ mol/mol (R1), 34.99 μ mol/mol (R2), 20.04 μ mol/mol (R3)

Procedure of analysis: $R1 \rightarrow Sample \rightarrow R2 \rightarrow R3$ NO mole fraction is determined by calibration curve (R1,R2,R3)

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 34.91 μmol/mol (01/2006)	
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.13 μmol/mol (0.37%rel)(<i>k</i> =2)	

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The NO mole fraction after preparation is compared with the NO mole fraction before sending to BIPM.

And the stability is evaluated by amount of NO mole fraction of change.

The NO mole fraction after preparation is 34.91 μ mol/mol (01/2006) The NO mole fraction before sending is 34.98 μ mol/mol (07/2006)

The NO mole fraction of change is 0.07 μ mol/mol (6 months)

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	28/11/2005
Volume (L)	<u>9.5</u>
Total Pressure (bar)	100
Connection type (e.g. DIN1, BS14 etc.)	JIS

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

The pure NO gas used to prepare is the CRM, which is certificated by NMIJ. It is the same as L2.

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered: It is the same as L3.

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO ₂	FT-IR	79	12
N ₂	GC-PID	144.8	6.6
O ₂	GC-PID	2.3	1.3
N ₂ O	FT-IR	84.85	0.60
CH ₄	GC-FID	9.6	5.6
C ₃ H ₈	GC-FID	1.17	0.67
H ₂ O	Dew point measurement with mirror	24.4	5.5
NO		999654	16

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
H ₂	GC-MS	<0.1	0.029
O ₂	GC-MS	<0.1	0.029
CO	GC-FID	<0.01	0.003
CO ₂	GC-FID	<0.01	0.003
CH ₄	GC-FID	<0.01	0.003
C ₃ H ₈	GC-FID	<0.01	0.003
NOx(NO+NO ₂)	Chemiluminescent	<0.005	0.001
SO ₂	UV fluorescence	<0.005	0.001
H ₂ O	Dew Point meter	<1	0.289
N ₂		999999.4	0.29

Complete for all components considered: It is the same as L4.

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
N ₂	999949.09	64.64
NO	<i>x</i> _{NO,grav} : 50.91	<i>u</i> (<i>x</i> _{NO,grav}) : 0.02

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
0 th (Parent NO)	999654	16
1st	11921.2	5.3
2 nd	1492.85	0.68
3 rd	50.91	0.02

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Three Primary Standard gases: 51.78 μ mol/mol (R1), 34.99 μ mol/mol (R2), 20.04 μ mol/mol (R3)

Procedure of analysis: $R1 \rightarrow Sample \rightarrow R2 \rightarrow R3$ NO mole fraction is determined by calibration curve (R1,R2,R3)

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 50.81 μmol/mol (01/2006)
What is your estimate of the uncertainty in $x_{NO,anal}$?	u(x _{NO,anal}) : 0.19 μmol/mol (0.37%rel)(<i>k</i> =2)

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The NO mole fraction after preparation is compared with the NO mole fraction before sending to BIPM.

And the stability is evaluated by amount of NO mole fraction of change.

The NO mole fraction after preparation is 50.81 μ mol/mol (01/2006) The NO mole fraction before sending is 50.90 μ mol/mol (07/2006)

The NO mole fraction of change is 0.09 μ mol/mol (6 months)

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING	INSTITUTE:

Institute	Laboratoire national de métrologie et d'essais
Address	1, rue Gaston Boissier 75724 Paris Cedex 15 France
Contact Person	Tatiana Macé / Christophe Sutour
Telephone	33 1 40 43 38 53 / 33 1 40 43 37 49
Fax	33 1 40 43 37 37
email	tatiana.mace@Ine.fr / christophe.sutour@Ine.fr

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	10 May 2006
Volume (L)	10
Total Pressure (bar)	130
Connection type (e.g. DIN1, BS14 etc.)	AFNOR C
Cylinder Number	SMG 1391 (NO/N2 0040)

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Our pure NO gas comes from Air Liquide

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO ₂	FTIR	9.0	0.5
N ₂ O	FTIR	48.0	1.2
N ₂	GC/TCD	149.0	4.0
CO ₂	Air Liquide specifications	25.0	14.5

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
O ₂	Air products specifications	0.0050	0.0029
H ₂ O	Air products specifications	0.0100	0.0058
CO+CO ₂	Air products specifications	0.025	0.014
THC	Air products specifications	0.050	0.029
H ₂	Air products specifications	0.025	0.014

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO	<i>X</i> _{NO,grav} : 39.839	<i>u</i> (<i>x</i> _{NO,grav}) : 0.040
NO ₂	<i>X</i> _{NO2,grav} : 0.000350	<i>u</i> (<i>x</i> _{NO2,grav}) : 0.000025

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
0 th (Parent NO)	Pure NO and Pure N_2	
1 st (SMG 1393 – NO/N2 0039)	30380.09	0.03
2 nd		
3 rd		
4 th		

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The verification preparation consists in :

- $\checkmark\,$ The preparation of several gas mixtures of NO in N_2 at about 40 μ mol/mol by using the gravimetric method,
- ✓ The comparison of the prepared gravimetric gas mixtures by spectrophotometry : the used spectrometer is a BIO-RAD and is equipped with a measurement cell of a 4.8 m optical path.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 39.82 µmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (x _{NO,anal}) : 0.20 μmol/mol

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The prepared gravimetric gas mixtures (L7.) are compared by using spectrophotometry every month.

31 May 2006	39.82 µmol/mol with an uncertainty of 0.20 µmol/mol (u)
28 June 2006	39.74 µmol/mol with an uncertainty of 0.20 µmol/mol (u)
25 July 2006	39.85 $\mu mol/mol$ with an uncertainty of 0.20 $\mu mol/mol$ (u)

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	21 April 2006
Volume (L)	10
Total Pressure (bar)	130
Connection type (e.g. DIN1, BS14 etc.)	AFNOR C
Cylinder Number	AA 7060C (NO/N2 0038)

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Our pure NO gas comes from Air Liquide

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO ₂	FTIR	53.0	1.5
N ₂ O	FTIR	95.0	2.5
N ₂	GC/TCD	97.80	2.45

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
O ₂	Air products specifications	0.0050	0.0029
H ₂ O	Air products specifications	0.0100	0.0058
CO+CO ₂	Air products specifications	0.025	0.014
THC	Air products specifications	0.050	0.029
H ₂	Air products specifications	0.025	0.014

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
NO	<i>x</i> _{NO,grav} : 60.580	<i>u</i> (<i>x</i> _{NO,grav}) : 0.065
NO ₂	<i>x</i> _{NO2,grav} : 0.00322	<i>u</i> (<i>x</i> _{NO2,grav}) : 0.00010

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Uncertainty (µmol/mol)
0 th (Parent NO)	Pure NO and Pure N_2	
1 st (APEO 889 525E – NO/N2 0030)	38298.30	3.55
2 nd		
3 rd		
4 th		

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The verification preparation consists in :

- $\checkmark\,$ The preparation of several gas mixtures of NO in N_2 at about 60 μ mol/mol by using the gravimetric method,
- ✓ The comparison of the prepared gravimetric gas mixtures by spectrophotometry : the used spectrometer is a BIO-RAD and is equipped with a measurement cell of a 4.8 m optical path.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 60.540 μmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.305 μmol/mol

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The prepared gravimetric gas mixtures (H7.) are compared by using spectrophotometry every month.

31 May 2006	60.540 µmol/mol with an uncertainty of 0.305 µmol/mol (u)
28 June 2006	60.690 µmol/mol with an uncertainty of 0.305 µmol/mol (u)
25 July 2006	60.810 µmol/mol with an uncertainty of 0.305 µmol/mol (u)

CCQM-P73_Mixtures: Description of low level NO/N $_2$ mixtures

Institute	Slovak Institute of Metrology
Address	Karloveska 63 84255 Bratislava Slovak Republic
Contact Person	Ing. S. Musil, PhD., RNDr. Viliam Štovčík
Telephone	+421 2 60294 365
Fax	+421 2 60294 561
email	musil@smu.gov.sk, stovcik@smu.gov.sk

PARTICIPATING INSTITUTE:

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	20.IV.2006
Volume (L)	5
Total Pressure (bar)	<u>10</u>
Connection type (e.g. DIN1, BS14 etc.)	DIN1

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

NO 2.5 (Linde) SMU PRM MY9744_1 (c(NO)=40ppm) was prepared from SMU PRM MY9730_1 (c(NO)=0.001 mol/mol). See dilution steps at L6 point.

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Linde NO 2.5

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	rest	0.9965	0.0010
NO ₂	GC-TCD	0.00213	0.00043
CH4	GC-FID	1x10 ⁻⁷	6x10 ⁻⁸
N ₂ O	GC-TCD	0.0014	0.00028

L4. PURITY TABLE FOR NOMINALLY PURE N2

Complete for all components considered:

N₂ BIP PLUS 6.0 (AIR Products)

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	rest	0,999999827	3.5x10 ⁻⁸
CO	GC-FID (methanizer)	1.5x10 ⁻⁸	9x10 ⁻⁹
CO ₂	GC-FID (methanizer)	3.8x10 ⁻⁸	2.2x10 ⁻⁸
H ₂	Air Products decl.	2.5x10 ⁻⁸	1.4x10 ⁻⁸
O ₂	Air Products decl.	5x10 ⁻⁹	3x10⁻ ⁹
H ₂ O	SMU Primary dew point meter	1x10 ⁻⁸	6x10 ⁻⁹
CH ₄	GC-FID	4x10 ⁻⁸	1x10 ⁻⁸
C ₂ H ₆	GC-FID	2x10 ⁻⁸	1.2x10 ⁻⁸
C ₃ H ₈	GC-FID	2x10 ⁻⁸	1.2x10 ⁻⁸

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	0.999959235	6.5x10 ⁻⁸
NO	<i>x</i> _{NO,grav} :0.000040419	<i>u</i> (<i>x</i> _{NO,grav}):3.1x10 ⁻⁸
N ₂ O	5.8x10 ⁻⁸	1.1x10 ⁻⁸
NO ₂	8.6x10 ⁻⁸	1.7x10 ⁻⁸
Ar	1.83x10 ⁻¹⁰	7.5x10 ⁻¹¹
СО	1.50x10 ⁻⁸	8.6x10 ⁻⁹
CO ₂	3.80x10 ⁻⁸	2.1x10 ⁻⁸
H ₂	2.5x10 ⁻⁸	1.3x10 ⁻⁸
O ₂	5.09x10 ⁻⁹	2.9x10 ⁻⁹
H ₂ O	1.05x10 ⁻⁸	5.8x10 ⁻⁹
CH ₄	6.9x10 ⁻⁸	1.9x10 ⁻⁸
C ₂ H ₆	2.0x10 ⁻⁸	1.2x10 ⁻⁸
C ₃ H ₈	2.0x10 ⁻⁸	1.3x10 ⁻⁸

L6. DILUTION SERIES

Dilution Step	x(NO) (mol/mol)	u(x) (mol/mol)
0 th (Parent NO)	0.99645	10x10 ⁻³
1st	0.099636	0.000073
2 nd	0.0099566	0.0000070
3 rd	0.0010097	0.0000073
4 th	0.000040419	0.00000031

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Lumminiscence method, Thermo Vision 43C Calibrated on NMi PRM (49.99 \pm 0.25(k=2)) ppm of NO/N₂ just before measurement NO contents of mixtures were measured after 2 weeks since preparation as well as the same mixture from NMI used for calibration. Integration time 30s.

Preparation data	x _{NO,grav} : 40.419 ppm
(uncertainties from weighings & purity tables)	<i>u</i> (<i>x</i> _{NO,grav}) :0.031 ppm
What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 40.2 ppm
What is your estimate of the uncertainty in <i>x</i> _{NO,anal} ?	$u(x_{NO,anal})$: 0.17 ppm (from repeatability & calibration & display resolution uncertainties) $u_A(x_{NO,anal})$: 0.11 ppm $u_{B,cal}(x_{NO,anal})$: 0.13 ppm $u_{B,drift}(x_{NO,anal})$: 0.00 ppm $u_{B,display resol}(x_{NO,anal})$: 0.03 ppm

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Every three weeks NO content had been measured by luminiscence method on Thermo Vision 43C

The one-point calibration with NMi PRM 50 ppm was performed just before measurement.

	April	May	June	July
MY9744	40.2	40.1	40.2	40.1
Δ	0.1	0.2	0.2	0.2
NMi	50.1	50.0	50.1	50.1
Δ	0.1	0.2	0.2	0.2

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	<u>28.III.2006</u>
Volume (L)	<u>5</u>
Total Pressure (bar)	<u>10</u>
Connection type (e.g. DIN1, BS14 etc.)	DIN1

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

NO (2.5) (Linde, SK) SMU PRM MY9741_1 c(NO)=59ppm) was prepared from SMU PRM MY9730_1 (c(NO)=0.001 mol/mol)

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Linde NO 2.5

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	rest	0.9965	0.0010
NO ₂	GC-TCD	0.00213	0.00043
CH4	GC-FID	1x10 ⁻⁷	6x10 ⁻⁸
N ₂ O	GC-TCD	0.0014	0.00028

H4. PURITY TABLE FOR NOMINALLY PURE N2

Complete for all components considered:

N₂ BIP PLUS 6.0 (AIR Products)

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	rest	0,999999827	3.5x10⁻ ⁸
CO	GC-FID (methanizer)	1.5x10 ⁻⁸	9x10 ⁻⁹
CO ₂	GC-FID (methanizer)	3.8x10 ⁻⁸	2.2x10 ⁻⁸
H ₂	Air Products decl.	2.5x10 ⁻⁸	1.4x10 ⁻⁸
O ₂	Air Products decl.	5x10 ⁻⁹	3x10 ⁻⁹
H ₂ O	SMU Primary dew point meter	1x10 ⁻⁸	6x10 ⁻⁹
CH ₄	GC-FID	4x10 ⁻⁸	1x10 ⁻⁸
C ₂ H ₆	GC-FID	2x10 ⁻⁸	1.2x10 ⁻⁸

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	0.99994002	8.2x10 ⁻⁸
NO	<i>x</i> _{NO,grav} :0.000059576	<i>u</i> (<i>x</i> _{NO,grav}) :0.000000044
N ₂ O	0.00000085	0.00000017
NO ₂	0.000000127	0.00000026
Ar	2.7x10 ⁻¹⁰	1.1x10 ⁻¹⁰
СО	1.50x10 ⁻⁸	6.0x10 ⁻⁹
CO ₂	3.80x10 ⁻⁸	1.5x10 ⁻⁸
H ₂	2.51x10 ⁻⁸	9.4x10 ⁻⁹
O ₂	5.1x10 ⁻⁹	2.0x10 ⁻⁹
H ₂ O	1.07x10 ⁻⁸	4.0x10 ⁻⁹
CH ₄	5.3x10 ⁻⁸	1.0x10 ⁻⁸
C ₂ H ₆	2.0x10 ⁻⁸	8.0x10 ⁻⁹
C ₃ H ₈	2.0x10 ⁻⁸	8.0x10 ⁻⁹

H6. DILUTION SERIES

Dilution Step	x(NO) (mol/mol)	u(x) (mol/mol)
0 th (Parent NO)	0.99645	10x10 ⁻³
1st	0.099636	0.000073
2 nd	0.0099566	0.000070
3 rd	0.0010097	0.0000073
4 th	0.000059576	4.4x10 ⁻⁸

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Lumminiscence method, Thermo Vision 43C Calibrated on NMi PRM (49.99 \pm 0.25(k=2)) ppm of NO/N₂ just before measurement NO contents of mixtures were measured after 2 weeks since preparation as well as the same mixture from NMI used for calibration. Integration time 30s.

Preparation data	<i>x</i> _{NO,grav} : 59.576 ppm
(uncertainties from weighings & purity tables)	<i>u</i> (<i>x</i> _{NO,grav}) :0.044 ppm
What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 59.7 ppm
What is your estimate of the uncertainty in <i>x</i> _{NO,anal} ?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.17 ppm
	(from repeatability & calibration & display resolution uncertainties)
	<i>u_A(x</i> _{NO,anal}) : 0.11 ppm
	<i>u_{B,cal}(x</i> _{NO,anal}) : 0.13 ppm
	<i>u_{B,drift}(x</i> _{NO,anal}): 0.00 ppm
	<i>u_{B,display resol}(x</i> _{NO,anal}) : 0.03 ppm
H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Every three weeks NO content had been measured by luminiscence method on Thermo Vision 43C

The one-point calibration with NMi PRM 50 ppm was performed just before measurement.

		March	April	May	June	July
MY9741	Х	59.9	59.7	59.7	59.9	59.7
	Δ	0.3	0.2	0.2	0.2	0.1
NMi	Х	50.2	50.1	50.0	50.1	50.1
	Δ	0.1	0.2	0.2	0.2	0.1

NOTES:

All uncertainties mentioned are in unextended form.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING	INSTITUTE:

Institute	CENTRO NACIONAL DE METROLOGÍA
Address	KM 4.5 CARRETERA A Los Cués. Municipio El Marques, CP 76241 Querétaro, México.
Contact Person	Alejandro Pérez Castorena
Telephone	(442) 211-05-00 Ext. 3907
Fax	(442) 211-05-69
email	aperezx@cenam.mx

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS (Cylinder number: FF39556)

Date of mixture preparation	2006-01-23
Volume (L)	5,4 L
Total Pressure (bar)	103,4 bar
Connection type (e.g. DIN1, BS14 etc.)	CGA-660

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Manufacture: CENAM

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Component	Method*	Mole Fraction (mol/mol)	Uncertainty** (mol/mol)
NO	specification	3,9697x10 ⁻²	8,9 x10 ⁻⁵
N ₂	specification	9,60159 x10 ⁻¹	1,2 x10 ⁻⁴
O ₂	specification	1,4 x10 ⁻⁷	2,8 x10 ⁻⁸
H ₂ O	specification	1,9 x10 ⁻⁶	3,9 x10 ⁻⁷
THC	specification	8,8 x10 ⁻⁷	1,8 x10 ⁻⁷
CO	specification	2,9 x10 ⁻⁷	8,3 x10 ⁻⁸
CO ₂	specification	7,7 x10 ⁻⁷	2,2 x10 ⁻⁷
$NO_2 + N_2O$	specification	1,39 x10 ⁻⁴	4,0 x10 ⁻⁵

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification". ** κ =1

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty** (mol/mol)
N ₂	1-impurity	9,99975 x10 ⁻¹	7,4 x10 ⁻⁷
O ₂	Electrochemical cell	6,0 x10 ⁻⁸	2,0 x10 ⁻⁸
H ₂ O	Electrochemical cell	8,0 x10 ⁻⁷	2,0 x10 ⁻⁷
СО	FTIR	3,0 x10 ⁻⁷	9,0 x10 ⁻⁸
THC	specification	5,0 x10 ⁻⁷	1,0 x10 ⁻⁷
CO ₂	FTIR	8,0 x10 ⁻⁷	2,0 x10 ⁻⁷

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification". ** κ =1

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty * (mol/mol)	
N ₂	9,99957 x10 ⁻¹	1,4 x10 ⁻⁶	
NO	$X_{\rm NO,grav}$: 4,0777 x10 ⁻⁵	$u(x_{\rm NO,grav})$: 8,8 x10 ⁻⁸	
O ₂	6,0 x10 ⁻⁸	2,0 x10 ⁻⁸	
H ₂ O	8,0 x10 ⁻⁷	2,1 x10 ⁻⁷	
THC	5,0 x10 ⁻⁷	1,3 x10 ⁻⁷	
СО	3,0 x10 ⁻⁷	8,0 x10 ⁻⁸	
CO ₂	8,0 x10 ⁻⁷	2,1 x10 ⁻⁷	
NO ₂ +N ₂ O	1,4 x10 ⁻⁷	4,1 x10 ⁻⁸	

* K=1

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty* (mol/mol)	
0 th (Parent NO)	3,9697 x10 ⁻²	8,9 x10⁻⁵	
1 st	3,9849 x10⁻³	8,6 x10 ⁻⁶	
2 nd	3,9770 x10 ⁻⁴	8,5 x10 ⁻⁷	

*k=1

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Verification procedure:

The verification procedure was according to ISO 6142 clause 6,3 incise a, and ISO 6143 clause 6.2. Were prepared and used for verification processes five calibration gas mixtures covering the range $3,0 - 7,0 \times 10^{-5}$ mol/mol.

Analytical methods:

The nitric oxide was analyzed using a specific analyzer brand ROSEMOUNT ANALYTICAL INC., Model 951A Serial Number 0102177 with Chemiluminiscence operation principle.

What NO mole fraction was predicted from your verification analysis?	X _{NO,anal} :	4,075 x10 ⁻⁵ mol/mol	
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u(x</i> _{NO,anal}):	2,1 x10 ⁻⁷ mol/mol	k=2

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The stability of travelling standards was confirmed by repeated analysis using five standards, in the range of 3,0 to 7,0 $\times 10^{-5}$ mol/mol. Before each travelling standard was despatched to the coordinating laboratory it was analysed at least 5 times in the period between their preparation and their shipping.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS (Cylinder number: FF39527)

Date of mixture preparation	2006-01-23
Volume (L)	5,4 L
Total Pressure (bar)	103,4 bar
Connection type (e.g. DIN1, BS14 etc.)	CGA-660

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Manufacture: CENAM

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Component	Method*	Mole Fraction (mol/mol)	Uncertainty** (mol/mol)
NO	specification	5,96996 x10 ⁻²	1,09 x10 ⁻⁴
N ₂	specification	9,40086 x10 ⁻¹	1,574 x10 ⁻⁴
O ₂	specification	1,8 x10 ⁻⁷	4,0 x10 ⁻⁸
H ₂ O	specification	2,4 x10 ⁻⁶	5,3 x10 ⁻⁷
THC	specification	1,1 x10 ⁻⁶	2,2 x10 ⁻⁷
CO	specification	2,8 x10 ⁻⁷	8,0 x10 ⁻⁸
CO ₂	specification	7,5 x10 ⁻⁷	0,22 x10 ⁻⁷
$NO_2 + N_2O$	specification	2,10 x10 ⁻⁴	6,0 x10 ⁻⁵

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

**K=1

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty* (mol/mol)
N ₂	1-impurity	9,99975 x10⁻¹	7,4 x10 ⁻⁷
O ₂	Electrochemical cell	6,0 x10 ⁻⁸	2,0 x10 ⁻⁸
H ₂ O	Electrochemical cell	8,0 x10 ⁻⁷	2,0 x10 ⁻⁷
CO	FTIR	3,0 x10 ⁻⁷	9,0 x10 ⁻⁸
THC	specification	5,0 x10 ⁻⁷	1,0 x10 ⁻⁷
CO ₂	FTIR	8,0 x10 ⁻⁷	2,0 x10 ⁻⁷

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification". ** κ =1

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	9,999366 x10 ⁻¹	7,0 x10 ⁻⁷
NO	$X_{\rm NO,grav}$: 6,0690 x10 ⁻⁵	$u(x_{\rm NO,grav}): 1,04 \times 10^{-7}$
O ₂	6,0 x10 ⁻⁸	2,0 x10 ⁻⁸
H ₂ O	8,0 x10 ⁻⁷	2,1 x10 ⁻⁷
THC	5,0 x10 ⁻⁷	1,3 x10 ⁻⁷
CO	3,0 x10 ⁻⁷	8,0 x10 ⁻⁸
CO ₂	8,0 x10 ⁻⁷	2,1 x10 ⁻⁷
NO ₂ +N ₂ O	2,1 x10 ⁻⁷	6,0 x10 ⁻⁸

*K=1

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty* (mol/mol)
0 th (Parent NO)	5,96996 x10 ⁻²	1,09 x10 ⁻⁴
1st	5,9784 x10 ⁻³	1,03 x10 ⁻⁵
2 nd	5,964 x10 ⁻⁴	1,0 x10 ⁻⁶

*k=1

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Verification procedure:

The verification procedure was according to ISO 6142 clause 6,3 incise a, and ISO 6143 clause 6.2. Were prepared and used for verification processes five calibration gas mixtures covering the range $3,0 - 7,0 \times 10^{-5}$ mol/mol.

Analytical methods:

The nitric oxide was analyzed using a specific analyzer brand ROSEMOUNT ANALYTICAL INC., Model 951A Serial Number 0102177 with Chemiluminiscence operation principle.

What NO mole fraction was predicted from your verification analysis?	X _{NO,anal} :	6,079 x10 ⁻⁵	mol/mol	
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>U</i> (<i>X</i> _{NO,anal}):	2,6 x10 ⁻⁷	mol/mol	k=2

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

The stability of travelling standards was confirmed by repeated analysis using five standards, in the range of 3,0 to 7,0 $\times 10^{-5}$ mol/mol. Before each travelling standard was despatched to the coordinating laboratory it was analysed at least 5 times in the period between their preparation and their shipping.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

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PARTICIPATING INSTITUTE:

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Institute	VNIIM (D.I. Mendeleyev Institute for Metrology)
Address	19, Moskovsky pr., St. Petersburg, Russia
Contact Person	L.A. Konopelko Y.A. Kustikov
Telephone	(812) 315-11-45
Fax	(812) 327-97-76
email	lkonop@b10.vniim.ru

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	30.05.06
Volume (L)	5
Total Pressure (bar)	<u>73</u>
Connection type (e.g. DIN1, BS14 etc.)	DIN1

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Pure NO was received from "Pure gases, Inc"., Novosibirsk, Russia

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (µmol/mol)	Standard uncertainty (µmol/mol)
NO	-	996800	350
NO ₂	FTIR	1000	120
N ₂ O	FTIR	1200	140
CO ₂	FTIR	500	60
N ₂	suppliers specification	500	290

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

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L4. PURITY TABLE FOR NOMINALLY PURE N2

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Component	Method*	Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
N ₂	-	999990,6	0,7
H ₂ O	Dew-point hygrometry	1,4	0,4
СО	NDIR	1,0	0,20
CO ₂	NDIR	1,0	0,20
O ₂	GC-PDHID	0,45	0,10
Ar	GC-PDHID	5,0	0,5
CH ₄	GC-FID	0,50	0,20

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
N ₂	999948,4	0,7
NO	<i>X</i> _{NO,grav} : 42,18	<i>u</i> (<i>x</i> _{NO,grav}) : 0,03
NO ₂	0,042	0,005
N ₂ O	0,051	0,006
CO ₂	1,02	0,20
H ₂ O	1,4	0,4
O ₂	0,45	0,10
Ar	5,0	0,5
CO	1,0	0,20
CH ₄	0,50	0,20

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
0 th (Parent NO)	996800	350
1st	24636	11
2 nd	1817,7	0,9
3 rd	42,18	0,03

L7. VERIFICATION

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Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The measurements were carried out by chemiluminescence technique with the help of Gas analyzer "AC-30M" (Environnement S.A., France). Verification was performed by checking consistency between 4 freshly prepared nominally similar PSMs.

What NO mole fraction was predicted from your verification analysis?	X _{NO,anal} : 42,18
What is your estimate of the uncertainty (standard) in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0,05

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Stability testing was performed by direct comparison with the other traceable PSM (previously prepared).

Stability study was carried out during a period of 1,5 month.

There were made three measurement series - 05.06.06; 30.06.06; 20.07.06.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	<u>31.05.06</u>
Volume (L)	5
Total Pressure (bar)	<u>79</u>
Connection type (e.g. DIN1, BS14 etc.)	DIN1

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Pure NO was received from "Pure gases, Inc"., Novosibirsk, Russia

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Standard uncertainty (μmol/mol)
NO	-	996800	350
NO ₂	FTIR	1000	120
N ₂ O	FTIR	1200	140
CO ₂	FTIR	500	60
N ₂	suppliers specification	500	290

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H4. PURITY TABLE FOR NOMINALLY PURE N2

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Component	Method*	Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
N ₂	-	999990,6	0,7
H ₂ O	Dew-point hygrometry	1,4	0,4
СО	NDIR	1,0	0,20
CO ₂	NDIR	1,0	0,20
O ₂	GC-PDHID	0,45	0,10
Ar	GC-PDHID	5,0	0,5
CH ₄	GC-FID	0,50	0,20

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Standard uncertainty (μmol/mol)
N ₂	999927,2	0,7
NO	X _{NO,grav} : 63,32	<i>u</i> (<i>x</i> _{NO,grav}) : 0,04
NO ₂	0,064	0,007
N ₂ O	0,076	0,009
CO ₂	1,03	0,20
H ₂ O	1,4	0,4
O ₂	0,45	0,10
Ar	5,0	0,5
CO	1,0	0,20
CH ₄	0,50	0,20

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (µmol/mol)	Standard uncertainty (μmol/mol)
0 th (Parent NO)	996800	350
1st	24756	11
2 nd	1823,6	1,0
3 rd	63,32	0,04

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The measurements were carried out by chemiluminescence technique with the help of Gas analyzer "AC-30M" (Environnement S.A., France). Verification was performed by checking consistency between 4 freshly prepared nominally similar PSMs.

What NO mole fraction was predicted from your verification analysis?	X _{NO,anal} : 63,32
What is your estimate of the uncertainty (standard) in $x_{NO,anal}$?	<i>u</i> (x _{NO,anal}) : 0,08

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Stability testing was performed by direct comparison with the other traceable PSM (previously prepared).

Stability study was carried out during a period of 1,5 month.

There were made three measurement series - 06.06.06; 03.07.06; 21.07.06.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING INSTITUTE:

Institute	National Institute of Standards and Technology
Address	100 Bureau Drive Gaithersburg MD 20899-8393
Contact Person	Bill Thorn/Franklin Guenther
Telephone	301-975-3939
Fax	301-977-8392
email	fguenther@nist.gov

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	July 17, 2006
Volume (L)	6 L water volume
Total Pressure (bar)	<u>120 bar</u>
Connection type (e.g. DIN1, BS14 etc.)	

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source? Takachiho Trading Company, Tokyo Japan

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	FTIR	0.99827	0.00030
NO ₂	FTIR	0.00079	0.00007
N ₂ O	FTIR	0.00082	0.00008
N ₂	GC/TCD	0.00012	0.00001

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂		0.999965	0.000005
O ₂	Delta –F NT	<2 nmol/mol	1 nmol/mol
H ₂ O	Spec	<20 nmol/mol	10 nmol/mol
THC	Spec	<100 nmol/mol	60 nmol/mol
Argon	GC/TCD	35 µmol/mol	5 µmol/mol

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂		
NO	x _{NO,grav} : 43.081 μmol/mol	<i>u</i> (<i>x</i> _{NO,grav}) : 0.062 µmol/mol
NO ₂	0.0341 µmol/mol	0.0031 µmol/mol
N ₂ O	0.0353 µmol/mol	0.0035 µmol/mol

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty (mol/mol)
		(Expanded k=2)
0 th (Parent NO)	0.9983	0.0003
1st	0.012468	0.000018
2 nd	0.0017582	0.0000022
3 rd	383.26 µmol/mol	0.50 µmol/mol
4 th	43.081 µmol/mol	0.063 µmol/mol

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The mixture was compared to another NIST PSM containing (42.572 ± 0.046) μ mol/mol NO using Chemi. Agreement was to within 0.2 % relative.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 43.030 μmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	u(x _{NO,anal}): 0.065 μmol/mol

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Primary standards are monitored over many years by comparing to freshly made PSMs. This mixture was monitored for one month, too short to obtain any meaningful stability data, except to say that it agrees with the gravimetric value.

High range (50-70) µmol/mol mixture (SEE ABOVE FOR INFORMATION ALL THE SAME EXCEPT WHERE NOTED BELOW IN TABLES)

H1. CYLINDER DETAILS

Date of mixture preparation	July 17, 2006
Volume (L)	
Total Pressure (bar)	
Connection type (e.g. DIN1, BS14 etc.)	

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO			

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H4. PURITY TABLE FOR NOMINALLY PURE N2

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂			

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂		
NO	x _{NO,grav} : 67.082 μmol/mol	<i>u</i> (x _{NO,grav}) : 0.087 μmol/mol
NO ₂	0.0531 µmol/mol	0.0048 µmol/mol
N ₂ O	0.0550 µmol/mol	0.0055 µmol/mol

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty (mol/mol)
		(Expanded k=2)
0 th (Parent NO)	0.9983	0.0003
1st	0.015468	0.000024
2 nd	0.0025603	0.000030
3 rd	679.29 µmol/mol	0.82 µmol/mol
4 th	67.085 µmol/mol	0.094 µmol/mol

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

The mixture was compared to another NIST PSM containing (65.653 ± 0.051) μ mol/mol NO using Chemi. Agreement was to within 0.1 % relative.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 67.13 μmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.15 μmol/mol

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

See above

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING INSTITUTE:

Institute	National Measurement Institute Australia
Address	Bradfield Rd West Lindfield NSW 2070 Australia (PO Box 264, Lindfield NSW 2070)
Contact Person	Damian Smeulders
Telephone	+61 2 8467 3534
Fax	+ 61 2 8467 3752
email	damian.smeulders@measurement.gov.au

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS [MK0787]

Date of mixture preparation	26/06/2006
Volume (L)	<u>5.4L</u>
Total Pressure (bar)	<u>50 Bar</u>
Connection type (e.g. DIN1, BS14 etc.)	<u>BS14</u>

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Nominally pure NO – manufactured by Air Liquide Deutschland GMBH Specialty Gases

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
NO	Specification	998.0	0.8
N ₂ O	Specification	1.0	0.6
NO ₂	Specification	1.0	0.6

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L4. PURITY TABLE FOR NOMINALLY PURE N2

Complete for all components considered:

Component	Method*	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
N ₂		999.99825	0.00008
O ₂	Systech/Illinios Model 276 Oxygen analyser (Hersch cell)	0.00015	0.00008
H ₂ O	Systech/Illinios Model 510 Moisture analyser (P ₂ O ₅)	0.0016	0.0008

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N₂ MIXTURE Complete for all components considered:

Component	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
N ₂	999.95332	0.00010
NO	<i>x</i> _{NO,grav} : 0.044844	$u(x_{\rm NO,grav}): 0.000074$
NO ₂	4.5 x 10 ⁻⁵	2.6 x 10 ⁻⁵
N ₂ O	4.5 x 10 ⁻⁵	2.6 x 10 ⁻⁵

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
0th (Parent NO)	998.0	0.8
1st	39.959	0.065
	(MK0783)	
2nd	1.5759	0.0026
	(MK0784)	
3rd	0.044844	0.000074
	(MK0787)	

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Mixtures were verified using chemiluminescence. A Thermo 42i NOx analyser was used to check mixtures after manufacture.

The concentration of the mixture was tested with respect to other NO/N_2 gravimetric mixtures manufactured at NMIA. An additional 10 mixtures near the target concentrations were used in the verification process.

What NO mole fraction was predicted from your verification analysis?	<i>x</i> _{NO,anal} : 0.04485 mmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.00021 mmol/mol

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

• No stability testing was performed due to the short period of time between manufacture and shipping.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS [MK0781]

Date of mixture preparation	26/06/2006
Volume (L)	<u>5.4L</u>
Total Pressure (bar)	<u>50 Bar</u>
Connection type (e.g. DIN1, BS14 etc.)	<u>BS14</u>

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

Nominally pure NO – manufactured by Air Liquide Deutschland GMBH Specialty Gases

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
NO	Specification	998.0	0.8
N ₂ O	Specification	1.0	0.6
NO ₂	Specification	1.0	0.6

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H4. PURITY TABLE FOR NOMINALLY PURE N2

Complete for all components considered:

Component	Method*	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
N ₂		999.99825	0.00008
O ₂	Systech/Illinios Model 276 Oxygen analyser (Hersch cell)	0.00015	0.00008
H ₂ O	Systech/Illinios Model 510 Moisture analyser (P ₂ O ₅)	0.0016	0.0008

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N₂ MIXTURE Complete for all components considered:

Component	Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
N ₂	999.93328	0.00012
NO	<i>x</i> _{NO,grav} : 0.06484	<i>u</i> (<i>x</i> _{NO,grav}) : 0.00011
NO ₂	6.5 x10⁻⁵	3.8 x10⁻⁵
N ₂ O	6.5 x10 ⁻⁵	3.8 x10 ⁻⁵

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mmol/mol)	Uncertainty (mmol/mol)
0 th (Parent NO)	998.0	0.8
1st	39.811	0.065
	(MK0776)	
2nd	1.5898	0.0026
	(MK0778)	
3rd	0.06484	0.00011
	(MK0781)	

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

Mixtures were verified using chemiluminescence. A Thermo 42i NOx analyser was used to check mixtures after manufacture.

The concentration of the mixture was tested with respect to other NO/N_2 gravimetric mixtures manufactured at NMIA. An additional 10 mixtures near the target concentrations were used in the verification process.

What NO mole fraction was predicted from your verification analysis?	<i>x</i> _{NO,anal} : 0.06497 mmol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0.00020 mmol/mol

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

• No stability testing was performed due to the short period of time between manufacture and shipping.

Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

Institute	Instituto Português da Qualidade
Address	R. António Gião, 2, 2829-513 Caparica, Portugal
Contact Person	Florbela Dias
Telephone	00351 212 948 175
Fax	00351 212 948 188
email	florbelad@mail.ipq.pt

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS – PSM 103453

Date of mixture preparation	<u>17-11-2005</u>
Volume (L)	5
Total Pressure (bar)	100
Connection type (e.g. DIN1, BS14 etc.)	DIN1

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

The source of our nominally pure NO is Air Liquide.

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	specification	> 99,9 x10 ⁻²	
H ₂ O	specification	< 20 x10 ⁻⁶	
NO ₂	specification	< 100 x10 ⁻⁶	
CO ₂	specification	< 100 x10 ⁻⁶	
N ₂ O	specification	< 200 x10 ⁻⁶	
N ₂	specification	< 500 x10 ⁻⁶	

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	specification	> 99,9999 x10 ⁻²	
H ₂ O	specification	< 0,5 x10 ⁻⁶	
O ₂	specification	< 0,1 x10 ⁻⁶	
C _n H _m	specification	< 0,1 x10 ⁻⁶	
СО	specification	< 0,1 x10 ⁻⁶	
CO ₂	specification	< 0,1 x10 ⁻⁶	
H ₂	specification	< 0,1 x10 ⁻⁶	

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	99,995203 x10 ⁻²	0,000091 x10 ⁻²
NO	<i>x</i> _{NO,grav} : 47,0014 x10 ⁻⁶	<i>u</i> (<i>x</i> _{NO,grav}) : 0,0044 x10 ⁻⁶
CO	1,00 x10 ⁻⁷	0,45 x10 ⁻⁷
CO ₂	5,5 x10 ⁻⁸	2,3 x10 ⁻⁸
NO ₂	4,704 x10 ⁻⁹	0,023 x10 ⁻⁹
N ₂ O	6,58 x10 ⁻¹⁰	0,23 x10 ⁻¹⁰
H ₂ O	6,0 x10 ⁻⁷	2,7 x10 ⁻⁷
H ₂	1,00 x10 ⁻⁷	0,45 x10 ⁻⁷
O ₂	1,00 x10 ⁻⁷	0,45 x10 ⁻⁷
C _n H _m	1,00 x10 ⁻⁸	0,45 x10 ⁻⁸

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction Uncertainty (mol/mol) (mol/mol)	
0 th (Parent NO)	99,9 x10 ⁻²	
1st	4,98934 x10 ⁻²	0,00035 x10 ⁻²
2 nd	5,00018 x10 ⁻³	0,00042 x10 ⁻³
3 rd	499,315 x10 ⁻⁶	0,044 x10 ⁻⁶
4 th	47,0014 x10 ⁻⁶	0,0044 x10 ⁻⁶

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

We did the verification procedure according to the international standard ISO 6143. The verification was done by comparison with other traceable NO/N_2 standards. We used five NMi standards. The analytical method used was Chemiluminescence.

What NO mole fraction was predicted from your verification analysis?	x _{NO,anal} : 47,04 x10 ⁻⁶ mol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>U</i> (<i>x</i> _{NO,anal}) : 0,71 x10 ⁻⁶ mol/mol

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Cylinder	X _{NO,grav} /	Date	X NO,anal /	U(x _{NO,anal}) /	En
	mol/mol		mol/mol	mol/mol	
PSM103453	47,00 x 10 ⁻⁶	18-11-2005	47,04 x10 ⁻⁶	0,71 x10 ⁻⁶	0,1
		17-01-2006	46,74 x10 ⁻⁶	0,75 x10 ⁻⁶	-0,4
		14-03-2006	47,17 x10 ⁻⁶	0,85 x10 ⁻⁶	0,2
		25-05-2006	47,17 x10 ⁻⁶	0,83 x10 ⁻⁶	0,2
				•	

High range (50-70) µmol/mol mixture PSM 103406

H1. CYLINDER DETAILS

Date of mixture preparation	<u>16-11-2005</u>
Volume (L)	<u>5</u>
Total Pressure (bar)	100
Connection type (e.g. DIN1, BS14 etc.)	DIN1

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

The source of our nominally pure NO is Air Liquide.

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	specification	> 99,9 x10 ⁻²	
H ₂ O	specification	< 20 x10 ⁻⁶	
NO ₂	specification	< 100 x10 ⁻⁶	
CO ₂	specification	< 100 x10 ⁻⁶	
N ₂ O	specification	< 200 x10 ⁻⁶	
N ₂	specification	< 500 x10 ⁻⁶	

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	specification	> 99,9999 x10 ⁻²	
H ₂ O	specification	< 0,5 x10 ⁻⁶	
O ₂	specification	< 0,1 x10 ⁻⁶	
C _n H _m	specification	< 0,1 x10 ⁻⁶	
CO	specification	< 0,1 x10 ⁻⁶	
CO ₂	specification	< 0,1 x10 ⁻⁶	
H ₂	specification	< 0,1 x10 ⁻⁶	

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	99,992932 x10 ⁻²	0,000087 x10 ⁻²
NO	<i>x</i> _{NO,grav} : 69,7000 x10 ⁻⁶	<i>u</i> (<i>x</i> _{NO,grav}) : 0,0065 x10 ⁻⁶
СО	1,00 x10 ⁻⁷	0,43 x10 ⁻⁷
CO ₂	5,7 x10 ⁻⁸	2,2 x10 ⁻⁸
NO ₂	6,975 x10 ⁻⁹	0,035 x10 ⁻⁹
N ₂ O	9,76 x10 ⁻¹⁰	0,35 x10 ⁻¹⁰
H ₂ O	6,0 x10 ⁻⁷	2,6 x10 ⁻⁷
H ₂	1,00 x10 ⁻⁷	0,43 x10 ⁻⁷
O ₂	1,00 x10 ⁻⁷	0,43 x10 ⁻⁷
C _n H _m	1,00 x10 ⁻⁸	0,43 x10 ⁻⁸

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction Uncertainty (mol/mol) (mol/mol)	
0 th (Parent NO)	99,9 x10 ⁻²	
1st	4,98934 x10 ⁻²	0,00035 x10 ⁻²
2 nd	5,00018 x10 ⁻³	0,00042 x10 ⁻³
3 rd	499,315 x10 ⁻⁶	0,044 x10 ⁻⁶
4 th	69,7000 x10 ⁻⁶	0,0065 x10 ⁻⁶

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

We did the verification procedure according to the international standard ISO 6143. The verification was done by comparison with other traceable NO/N_2 standards. We used five NMi standards. The analytical method used was Chemiluminescence.

What NO mole fraction was predicted from your verification analysis?	<i>x</i> _{NO,anal} : 69,84 x10 ⁻⁶ mol/mol
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>U</i> (<i>x</i> _{NO,anal}) : 0,63 x10 ⁻⁶ mol/mol

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

Cylinder	X _{NO,grav} /	Date	X NO,anal /	U(x _{NO,anal}) /	En
	mol/mol		mol/mol	mol/mol	
PSM103406	69,70 x 10⁻ ⁶	18-11-2005	69,84 x10 ⁻⁶	0,63 x10 ⁻⁶	0,2
		17-01-2006	69,68 x10 ⁻⁶	0,62 x10 ⁻⁶	0,0
		14-03-2006	69,86 x10⁻ ⁶	0,68 x10 ⁻⁶	0,2
		25-05-2006	69,46 x10 ⁻⁶	0,76 x10 ⁻⁶	-0,3
	•	•	•	•	•
Form CCQM-P73_Mixtures: Description of NO/N $_2$ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING INSTITUTE:

Institute	Nederlands Meetinstituut (NMi) Van Swinden Laboratorium (VSL)
Address	Thijsseweg 11 2629 JA Delft The Netherlands
Contact Person	Gerard Nieuwenkamp / Rob Wessel
Telephone	+31 15 2691682 / +31 15 2691677
Fax	+31 15 2612971
email	gnieuwenkamp@nmi.nl rwessel@nmi.nl

Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

Date of mixture preparation	2006-06-23
Volume (L)	5 liter
Total Pressure (bar)	100 bar
Connection type (e.g. DIN1, BS14 etc.)	DIN1

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

- Started with pure NO, obtained from Air Liquide via Scott Specialty Gases

L3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	1 - impurities	0.999402	0.000043
N ₂	GC-TCD	165 · 10 ⁻⁶	10 · 10 ⁻⁶
N ₂ O	average GC/FTIR *	232 · 10 ⁻⁶	25 · 10 ⁻⁶
NO ₂	FTIR	86 · 10 ⁻⁶	17 · 10 ⁻⁶
HNO ₂	FTIR	40 · 10 ⁻⁶	15 · 10⁻ ⁶
HNO ₃	FTIR	75 · 10 ⁻⁶	25 · 10 ⁻⁶
* N ₂ O	GC-TCD	238 · 10 ⁻⁶	30 · 10⁻ ⁶
* N ₂ O	FTIR	226 · 10 ⁻⁶	30 · 10 ⁻⁶

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	1 - impurities	0.999996912	0.0000011
Ar	GC (random check)	3 ⋅ 10 ⁻⁶	1 ⋅ 10 ⁻⁶
CH ₄	FTIR (random check)	8 · 10 ⁻⁹	5 · 10 ⁻⁹
CO	FTIR (random check)	15 · 10 ⁻⁹	9 ⋅ 10 ⁻⁹
CO ₂	FTIR (random check)	10 · 10 ⁻⁹	6 ⋅ 10 ⁻⁹
H ₂	specification	25 · 10 ⁻⁹	14 · 10 ⁻⁹
H ₂ O	CRDS (random check)	20 · 10 ⁻⁹	10 · 10 ⁻⁹
O ₂	specification	10 · 10 ⁻⁹	10 · 10 ⁻⁹

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

L5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	0.99994986	0.00000105
NO	<i>x</i> _{NO,grav} : 47.0105 · 10 ⁻⁶	$u(x_{\rm NO,grav}): 0.0112 \cdot 10^{-6}$
Ar	3.00 · 10 ⁻⁶	0.95 · 10 ⁻⁶
CH ₄	8.0 · 10 ⁻⁹	4.8 · 10 ⁻⁹
CO	15.0 · 10 ⁻⁹	8.6 · 10 ⁻⁹
CO ₂	10.0 · 10 ⁻⁹	5.7 · 10 ⁻⁹
HNO ₂	1.9 · 10 ⁻⁹	0.7 · 10 ⁻⁹
HNO ₃	3.5 · 10 ⁻⁹	1.2 · 10 ⁻⁹
H ₂	25.0 · 10 ⁻⁹	13.4 · 10 ⁻⁹
H ₂ O	31.0 · 10 ⁻⁹	11.2 · 10 ⁻⁹
NO ₂	4.0 · 10 ⁻⁹	0.8 · 10 ⁻⁹
N ₂ O	10.9 · 10 ⁻⁹	1.2 · 10 ⁻⁹
O ₂	18.8 · 10 ⁻⁹	10.8 · 10 ⁻⁹

L6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty (mol/mol)
0 th (Parent NO)	0.999402	0.000043
1st	0.059907	0.0000079
2 nd	0.010005	0.0000013
3 rd	997.77 · 10 ⁻⁶	0.15 · 10 ⁻⁶
4 th	47.011 · 10 ⁻⁶	0.011 · 10 ⁻⁶

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

- Verification to 11 primary standard gasmixtures (PSMs) in a concentration range of $10 \cdot 10^{-6} 100 \cdot 10^{-6}$.
- Analysis with ND-UV
- Quadratic curve fitting, according to ISO-6143

What NO mole fraction was predicted from your verification analysis?	<i>x</i> _{NO,anal} : 46,97 · 10 ⁻⁶	(mol/mol)
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0,08 · 10 ⁻⁶	(mol/mol)

L8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

- The mixture has been analysed twice in a three weeks period.
- Similar mixtures prepared in similar treated cylinders have shown no instability in a period of two years.

High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

Date of mixture preparation	2006-06-22
Volume (L)	<u>5 Liter</u>
Total Pressure (bar)	<u>100 bar</u>
Connection type (e.g. DIN1, BS14 etc.)	DIN1

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N_2 , what is its source?

- Started with pure NO, obtained from Air Liquide via Scott Specialty Gases

H3. PURITY TABLE FOR NOMINALLY PURE NO (OR NO PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
NO	1 - impurities	0.999402	0.000043
N ₂	GC-TCD	165 · 10 ⁻⁶	10 · 10 ⁻⁶
N ₂ O	average GC/FTIR *	232 · 10 ⁻⁶	25 · 10 ⁻⁶
NO ₂	FTIR	86 · 10 ⁻⁶	17 · 10 ⁻⁶
HNO ₂	FTIR	40 · 10 ⁻⁶	15 · 10 ⁻⁶
HNO ₃	FTIR	75 · 10 ⁻⁶	25 · 10 ⁻⁶
* N ₂ O	GC-TCD	238 · 10 ⁻⁶	30 · 10⁻ ⁶
* N ₂ O	FTIR	226 · 10 ⁻⁶	30 · 10 ⁻⁶

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H4. PURITY TABLE FOR NOMINALLY PURE N2

Component	Method*	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	1 - impurities	0.999996912	0.0000011
Ar	GC (random check)	3 ⋅ 10 ⁻⁶	1 ⋅ 10 ⁻⁶
CH ₄	FTIR (random check)	8 · 10 ⁻⁹	5 · 10 ⁻⁹
СО	FTIR (random check)	15 · 10 ⁻⁹	9 · 10 ⁻⁹
CO ₂	FTIR (random check)	10 · 10 ⁻⁹	6 ⋅ 10 ⁻⁹
H ₂	specification	25 · 10 ⁻⁹	14 · 10 ⁻⁹
H ₂ O	CRDS (random check)	20 · 10 ⁻⁹	10 · 10 ⁻⁹
O ₂	specification	10 · 10 ⁻⁹	10 · 10 ⁻⁹

Complete for all components considered:

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL NO/N2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N ₂	0.99993387	0.00000107
NO	<i>x</i> _{NO,grav} : 63.0119 · 10 ⁻⁶	$u(x_{\rm NO,grav}): 0.0226 \cdot 10^{-6}$
Ar	3.00 · 10 ⁻⁶	0.97 · 10 ⁻⁶
CH ₄	8.5 · 10 ⁻⁹	4.9 · 10 ⁻⁹
CO	15.0 · 10 ⁻⁹	8.7 · 10 ⁻⁹
CO ₂	10.0 · 10 ⁻⁹	5.8 · 10 ⁻⁹
HNO ₂	2.5 · 10 ⁻⁹	0.9 · 10 ⁻⁹
HNO ₃	4.7 · 10 ⁻⁹	1.6 · 10 ⁻⁹
H ₂	25.0 · 10 ⁻⁹	13.6 · 10 ⁻⁹
H ₂ O	20.0 · 10 ⁻⁹	9.7 · 10 ⁻⁹
NO ₂	5.4 · 10 ⁻⁹	1.1 · 10 ⁻⁹
N ₂ O	14.6 · 10 ⁻⁹	1.6 · 10 ⁻⁹
O ₂	10.0 · 10 ⁻⁹	9.7 · 10 ⁻⁹

H6. DILUTION SERIES

Dilution Step	NO Mole Fraction (mol/mol)	Uncertainty (mol/mol)
0 th (Parent NO)	0.999402	0.000043
1st	0.040022	0.0000073
2 nd	0.0019973	0.00000046
3 rd	63.012 · 10 ⁻⁶	0.023 · 10 ⁻⁶

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N_2 standards; how many such standards; which analytical methods were used?

- Verification to 11 primary standard gasmixtures (PSMs) in a concentration range of $10 \cdot 10^{-6} 100 \cdot 10^{-6}$.
- Analysis with ND-UV
- Quadratic curve fitting, according to ISO-6143

What NO mole fraction was predicted from your verification analysis?	<i>x</i> _{NO,anal} : 63,11 · 10 ⁻⁶	(mol/mol)
What is your estimate of the uncertainty in $x_{NO,anal}$?	<i>u</i> (<i>x</i> _{NO,anal}) : 0,11 · 10 ⁻⁶	(mol/mol)

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the BIPM.

- The mixture has been analysed twice in a three weeks period.
- Similar mixtures prepared in similar treated cylinders have shown no instability in a period of two years.