International Key Comparison CCQM-K26a and Pilot Study CCQM-P50a (NO)

Final Report

Field - Gas standards

Subject - Comparison of primary standards of nitrogen monoxide (NO) in nitrogen

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Introduction

Accurate measurements of the concentration of nitrogen dioxide (NO_2) in ambient air have become essential to support the regulation of ambient air quality. In general, the primary element of quality assurance for field instruments measuring NO_2 is regular calibration using certified gas mixtures. In the case of NO_2 , there is near universal use of analysers based on the chemiluminescent detection of NO, with NO_2 being measured as the difference between ambient NO and ambient NO_x (this being the sum of NO and NO_2 measured by reducing both species to NO with a catalyst). The response of an analyser is therefore calibrated using an NO mixture in a balance of nitrogen, to minimize oxidation to NO_2. The concentration of NO involved in this comparison has been chosen as that likely to be used for field calibrations mandated by the European Union, which is also typical of values, used around the world.

Another reason for interest in the measurement of NO is to calibrate measurements of ozone by gas-phase titration. This is generally carried out with standards in the range 20 to 90 μmol/mol.

Previous work by the CCQM GAWG has been at higher amount fractions. During 1995/6, CCQM-K1.c demonstrated the equivalence of standards of NO at 100 and 1000 μmol/mol. This was followed in 2002/3 by EUROMET.QM-K1c. at 100 μmol/mol.

Applicability of this Key Comparison to CMC Claims

The following statement for "how far the light shines" from this comparison was agreed by the CCQM GAWG in April 2004:

"The comparison is aimed at typical calibration requirements for ambient NOx analysers, which monitor nitrogen dioxide concentrations using catalytic conversion to nitrogen monoxide and chemiluminescent detection. The techniques used for the comparison should be applicable to concentrations of nitrogen monoxide between around 100 nmol/mol and 10 μmol/mol.

Where primary measurements of nitrogen dioxide are made by conversion to nitrogen monoxide using a well-characterised converter, the results will also be relevant to similar concentrations of nitrogen dioxide."

Overview of the Comparison

The Key comparison CCQM-K26a and the Pilot Study CCQM P50a were conducted in parallel according to the protocol given in Annex A. The key features of this key comparison were:

- An extensive range of gravimetric standards was prepared from three sources of pure NO by the coordinating laboratory.

- Travelling standards were prepared commercially (one for each participant).
- Each travelling standard was measured before despatch to each participating laboratory.
- Travelling standards were measured by participating laboratories and the results submitted to the pilot laboratory.
- Each travelling standard was re-measured by the coordinating laboratory on return.
- Drift of each standard was estimated from measurements carried out by the coordinating laboratory.
- The Key Comparison Reference Value (and its uncertainty) was calculated for each travelling standard.

Work Carried out by the Coordinating Laboratory

Stability of Standards of Nitrogen Monoxide in Nitrogen

The leading NMIs each have more than 20 years experience in the preparation of standards of NO in nitrogen. This experience shows that pure NO is unstable with respect to decomposition to N_2O, NO_2 and nitrogen at high pressures and in the absence of any balance gas. However, when NO is diluted to an amount fraction of 10 mmol/mol, the rate for this reaction is decreased to a negligible rate at room temperature. The other reaction that can limit the stability of NO standards is by oxidation to NO_2. This reaction is eliminated by the use of extremely pure balance nitrogen with levels of oxygen below 50 nmol/mol. Consequently, it is expected that standards of NO in nitrogen at amount fractions in the range 10 mmol/mol to 1 μmol/mol are stable.

The results of previous comparisons involving NO at levels below 1 μmol/mol suggest that it would not be possible to derive an accurate estimate of the Key Comparison Reference Value (KCRV) from the gravimetric preparation of the travelling standards. These studies also gave strong evidence as to the stability of low amount fraction NO mixtures in cylinders prepared by different manufacturers. Consequently, a single batch of 20 cylinders was purchased from Scott Speciality Gases passivated by their proprietary “Megalife” process. They were supplied in 10-litre aluminium cylinders fitted with Ceodeux D200 stainless-steel packed-diaphragm valves with DIN-1 outlet connections. They were filled with a blend tolerance of +/- 5 % to a total pressure of 150 bar.

The batch was analysed on arrival at the coordinating laboratory (by the method described in Annex A), and a sub-set selected for use as travelling standards for the key comparison.

Preparation of Gravimetric Standards by the Coordinating Laboratory

Experience of work with standard mixtures of NO suggests that it is critical that the NO used in their preparation is of the highest possible purity. Pure NO was purchased by the coordinating laboratory from two sources: Takachicho Gas Company (imported by Intergas) and SIAD. In addition, the coordinating laboratory purified the NO from SIAD further using a process designed to remove NO_2 by condensation. This was achieved by passing the pure NO through a 2.5 metre capillary column while cooling the column with methanol mixed with solid carbon dioxide.

The purity of each of these three source gases was measured using a Varian Micro Gas Chromatograph. Separation of N_2O and NO_2 was achieved using a HayeSep A column and N_2 using a 5A molecular sieve column. The results of the analysis are shown in Table 1. The uncertainty in the measured value of each trace impurity is estimated to be +/-5% (*k*=2).

Source	Manufacturer's Specification	Purification	Measured N_2O [μmol/mol]	Measured N_2 [μmol/mol]
Takachicho	99.99%	None	603	86
SIAD	99.90%	None	654	0
SIAD	99.90%	Condensation of NO_2	161	65

Table 1 – Specification and measured impurities for the three sources of pure NO used in the preparation of the hierarchy of gravimetric standards by the coordinating laboratory. The uncertainty in the value of each trace impurity is estimated to be +/-5%.

The hierarchy of standards prepared by the coordinating laboratory to underpin this key comparison is shown in Figure 1. BOC "Spectraseal" cylinders were used for all standards containing NO at amount fractions above 1 μmol/mol. Standards containing 720 nmol/mol NO were prepared in Scott Megalife cylinders. Air Products BIP Grade N_2 was used as the balance gas in all standards.

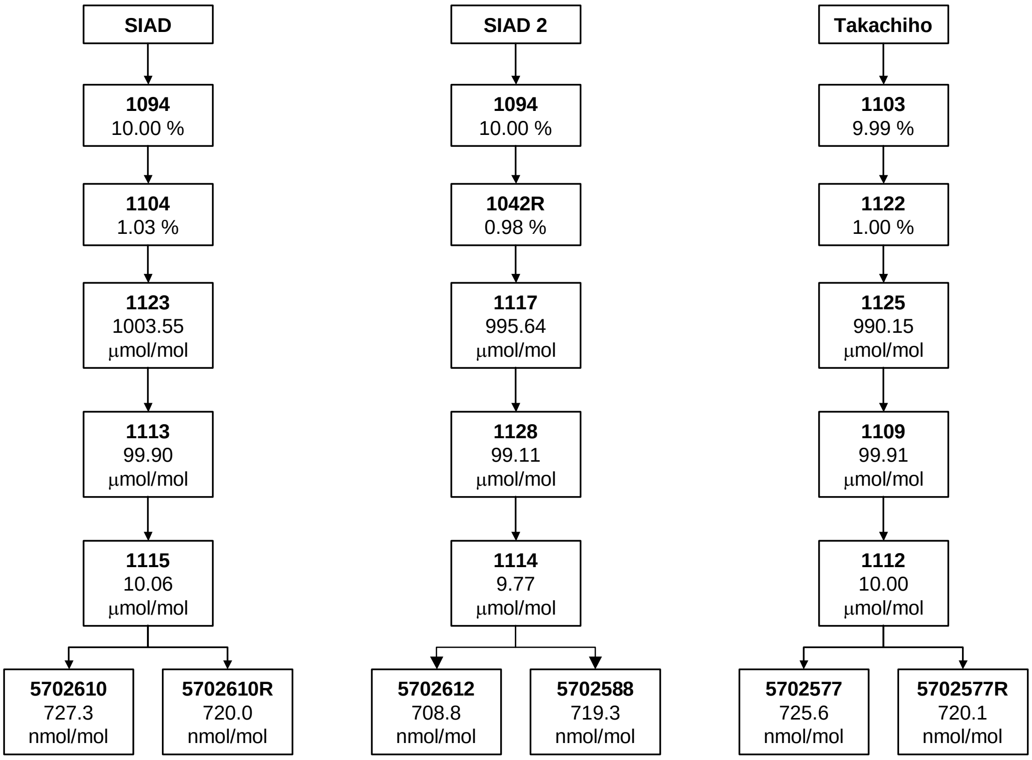


Figure 1 – The hierarchy of the gravimetric standards of NO/N_2 prepared gravimetrically by the coordinating laboratory.

Cylinder number	Preparation date
5702610	10/03/2004
5702610R	31/03/2004
5702612	09/03/2004
5702577	09/03/2004
5702577R	31/03/2004
5702588	09/03/2005

Table 2 - Dates of manufacture of standards by the coordinating laboratory at the 720 nmol/mol (nominal) level.

High Accuracy Comparison Method Developed by the Coordinating Laboratory

This key comparison imposed a requirement on the coordinating laboratory to carry out a large number of comparisons between the gravimetrically prepared NO/N_2 standards and the travelling standards. Since the amount fractions in the travelling standards were distributed over a small range around the nominal amount fraction of 720 nmol/mol, a rapid and accurate comparison method was developed. This involved a rapid series of measurements of the ratio between the travelling standard and the chosen gravimetric standard. The method is described in full in Annex B.

Consistency and Stability of the Standards Prepared by the Coordinating Laboratory

The consistency of the standards in the hierarchy shown in Figure 1 was validated by comparison of the three standards at the nominal amount fraction of 10 µmol/mol. Figure 2 shows the difference ($\Delta_{i,j}$) between the analytical amount fraction (z_{anal}) of and the gravimetric amount fraction (z_{grav}) of cylinders *i* and *j* evaluated using:

$$\Delta_{i,j} = 100 * (1 - \frac{z_{anal,i}}{z_{anal,j}} \frac{z_{grav,j}}{z_{grav,i}})$$

As can be seen, all results were consistent to within 0.15 % and most were consistent to within 0.1 %.

The stability of the hierarchy of standards was confirmed by repeated analysis of a cylinder from the batch of travelling standards with respect to several different standards prepared by dilutions to 720 nmol/mol. These were diluted from different standards at 10 µmol/mol as shown in Figure 1. Since the standards at 10 mmol/mol are known to be stable, the preparation of these dilutions at different times gives an opportunity to estimate their stability. The results are shown in Table 3.

Stability of the Travelling Standards

In order to eliminate any effects of drift due to instability in the amount fraction in the travelling standards, the drift of each travelling standard was determined individually, and the amount fraction in the cylinder was calculated at the time when it was analysed by each participant.

The stability of the travelling standards was determined by analysis carried out by the coordinating laboratory (according to the method described in Annex B). Before each standard was despatched to the participant it was analysed against one of the standards held by the coordinating laboratory at least 3 times. Similarly, each standard was re-analysed a further three times after it was received back from the participant. The results of these analyses were plotted as a function of time and a straight line was fitted through the data using an ordinary-least squares method.

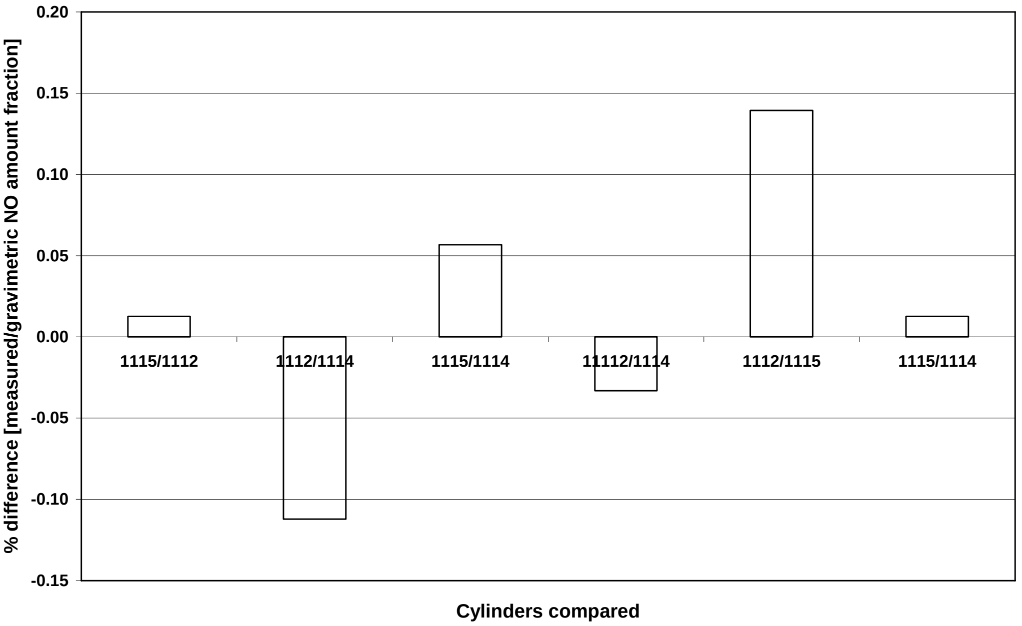


Figure 2 - Fractional difference $\Delta_{i,j}$ between analytical amount fraction and gravimetric amount fraction of the three standards in Figure 1 at 10 µmol/mol NO.

Standard identifier	Measured amount fraction nmol/mol		Change [%]
	Mar-04	**Mar-05**	
5702641	724.17	720.32	-0.53
5702577R	720.10	719.74	-0.05

Table 3 – Results of repeated measurements of the standards shown in Table 2.

An example of one of these plots is given in Figure 3. In all cases it was found the following straight line was a good fit to the data.

$$z = z_{i0} + m_i(t - t_0)$$

where z_{i0} is the value of the standard on 4th March 2004 and m_i is the estimated drift rate (the date 04/03/04 was chosen for convenience and has no influence on the calculation of the degrees of equivalence). The use of a linear fit is further justified because it is consistent with typical chemical decay or absorption processes over a small range of concentrations.

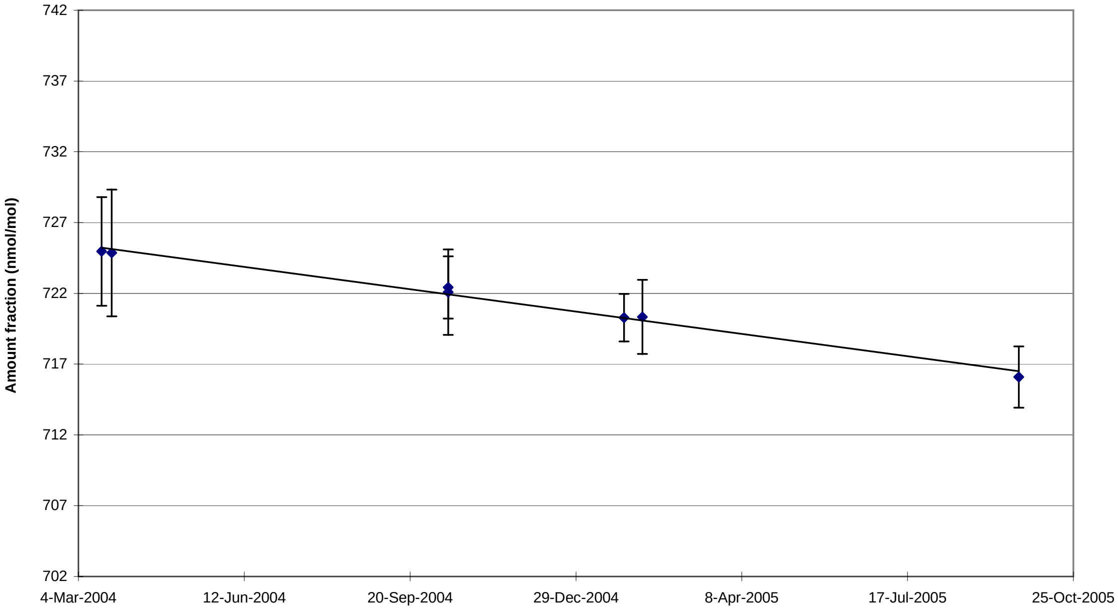


Figure 3 - Example of the estimation of the drift of a travelling standard. The measurements shown were carried out by the coordinating laboratory and span a longer period than those used to evaluate the data given in Table 4. The error bars indicate the standard deviation of the repeat measurements. The regression line has been fitted by ordinary least squares.

The gradient of the straight line fitted through the analytical data from the coordinating laboratory is taken as the “drift” of each travelling standard. The values of the drift for each travelling standard are tabulated in Table 4. The standard error of the drift was estimated using the usual method for calculating the standard error in the gradient (*se*(*m*)) of a line calculated by ordinary least squares:

$$se(m) = \sqrt{\frac{\sum (Y_j - \bar{Y})^2}{\sum (Z_j - \bar{Z})^2}}$$

Standard Identifier	Z_{i0} [nmol/mol]	Estimated drift m [nmol/mol/day]	Standard error of m [nmol/mol/day]	$z_{\bar{T}}$ [nmol/mol]	$u(z_{\bar{T}})$ [nmol/mol]
22414	726.3	-0.03483	0.00357	720.16	0.64
22402	724.6	-0.02754	0.00204	718.81	0.54
22404	722.8	-0.02351	0.00524		
22416	728.6	-0.01718	0.00344	725.32	0.94
22411	712.7	-0.01584	0.00587	710.48	0.63
22496	720.6	-0.01447	0.00204	718.93	0.75
22412	725.3	-0.01412	0.00101	722.74	0.61
22422	726.7	-0.01293	0.00237	725.22	0.6
22418	720.2	-0.01288	0.00495	718.49	0.69
22492	721.1	-0.01197	0.00252	719.40	0.56
22403	716.4	-0.01112	0.00287	713.93	0.72
22396	718.6	-0.01101	0.00212	717.30	0.84
22520	714.1	-0.01018	0.00166	712.60	0.58
22423	713.2	-0.00603	0.00301	712.15	0.69
22417	723.1	-0.00508	0.00379		

Table 4 – Estimated drifts for each travelling standard. z_{i0} is the estimated amount fraction on the 4th March 2004 (which corresponds to the y-axis in Figure 3). The standard errors in the values are calculated according to the equation given in the text. These values are plotted in Figure 4. Values for z_T have not been calculated for two of the standards because results were not submitted by the relevant participants.

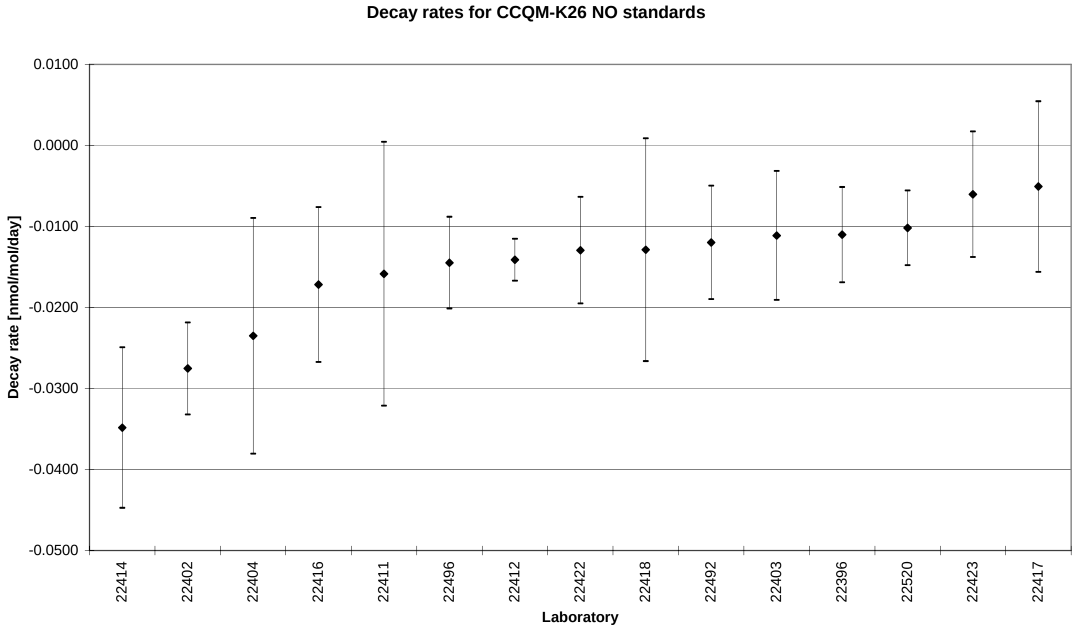


Figure 4 - Estimated drifts for the travelling standards listed in Table 4 displayed in ascending order. The "error bars" indicate the standard errors in the values calculated according to the equation given in the text.

Figure 4 shows the estimated drift of each travelling standard, and its standard error. Inspection of the graph shows that the population has no significant outliers and that the estimated drifts are distributed around a median value of -0.0129 nmol/mol/day. This median drift corresponds to a drift of 0.3% over 6 months in the nominal amount fraction of 720 nmol/mol.

Determination of the Amount Fraction of the Travelling Standards at the Time of Analysis

Having estimated the drift of each travelling standard, it is possible to estimate the amount fraction in each standard at the time (T) when it was analysed by the relevant participating laboratory (z_T) and its uncertainty.

The uncertainty in the estimated value of z_T is straightforward to estimate. If we consider the hypothetical case where the participant carries out the analysis at a time $\overline{T}$ which is the mean of the times (t_j) at which the coordinating laboratory carried out its analyses:

$$\overline{T} = \left(\sum_{j=1}^{N} t_j \right) / N$$

then the estimated value of the amount fraction in the cylinder $z_{\overline{T}}$ is given by the mean of the results of the coordinating laboratory

$$z_{\overline{T}} = \left(\sum_{j=1}^{N} z_j \right) / N$$

The random component in the uncertainty of $z_{\overline{T}}$ is given by

$$u(z_{\overline{T}})_{random} = \left(\sum_{j=1}^{N} \sigma_j \right) / N^{3/2}$$

where σ_j is the standard deviation of the measurements j. Since all of the drift rates have been estimated from 6 measurements by the coordinating laboratory, N=6 in all cases. In addition, a contribution due to the uncertainty in the gravimetric value (u_{grav})of the standards at 720 nmol/mol is added in quadrature.

$$u(z_{\overline{T}}) = \sqrt{u(z_{\overline{T}})_{random}^2 + u_{grav}^2}$$

Inspection of Annex C shows that 0.2 nmol/mol is a reasonable estimate of the expanded uncertainty (k=2) of the gravimetry. The uncertainty in the estimated values of $z_{\overline{T}}$ are listed in Table 4. The uncertainty in z_T was also validated using a GLS fit to the drift curves. The results agreed with the OLS values to better than 0.1%.

Calculation of the Key Comparison Reference Value

The objective of this key comparison is to determine the degree of equivalence (D_i) of each laboratory with respect to the Key Comparison Reference Value (KCRV).

$$D_i = x_i - x_{i,KCRV}$$

During the planning of this key comparison, it was foreseen that some small drift would be observed in the travelling standards. Consequently, it was not expected to be possible to use the values of the amount fraction in the travelling standards derived from their gravimetric preparation as the reference values. The planning of the key comparison also took account of the fact that the KCRV for each travelling standard would be different.

Consequently, the values from the analysis by the coordinating laboratory of each travelling standard ($z_{i,\bar{T}}$) were used to calculate a reference value for each travelling standard, which is used as the KCRV for that standard. This sets

$$x_{i,KCRV} = z_{i,\bar{T}}$$

in the equation above. The validity of this approach was verified by comparison with a consensus value evaluated from all of the submitted results. This is discussed in a subsequent section.

Results Submitted by Participating Laboratories

A full list of the participants, including the contact details, is given in Annex E.

The results submitted by the participants are listed in Table 5.

The methods used by the participants are listed in Annex D. These all involved analysis by chemiluminescence using commercial instrumentation.

The degrees of equivalence calculated as described above are shown in Figure 5 and Table 6. (No degree of equivalence has been calculated for participants in the pilot study).

Laboratory	Cylinder number	Submitted result nmol/mol	Uncertainty nmol/mol *k*=2	Date despatched from NPL	Date of participant measurement	Date received at NPL
Key comparison participants						
CENAM	22402	727	6	04/06/2004	29/09/2004	05/11/2004
CERI/NMIJ	22492	717.7	4.6	04/06/2004	22/07/2004	10/08/2004
CHMI	22418	715.8	7.5	04/06/2004	16/07/2004	06/08/2004
FMI	22416	721.1	11.54	04/06/2004	09/09/2004	27/10/2004
JRC	22496	727.8	2.9	04/06/2004	25/06/2004	03/08/2004
KRISS	22423	713.2	8.7	04/06/2004	27/08/2004	10/09/2004
LNE	22422	725.7	5.8	04/06/2004	30/06/2004	09/08/2004
NIST	22396	715	7	03/06/2004	30/06/2004	24/08/2004
NMi	22414	718.1	8	04/06/2004	26/08/2004	12/11/2004
NPL	22412	722.27	2.6	04/06/2004	31/08/2004	01/10/2004
UBA(D)	22411	713.8	5.82	04/06/2004	22/07/2004	18/08/2004
VNIIM	22403	711.3	9.2	04/06/2004	14/10/2004	17/01/2005
Pilot study participants						
IPQ	22417	No result	No result	04/06/2004	No result	27/01/2005
METAS	22520	714.3	4.4	25/06/2004	28/07/2004	10/08/2004
UBA(A)	22404	No result	No result	04/06/2004	No result	05/11/2004

Table 5 – Results submitted by the participating laboratories

Laboratory	Cylinder number	x_i nmol/mol	u_i nmol/mol	z_T nmol/mol	$\overline{\sigma}$ nmol/mol	u_{grav} nmol/mol	$u(z_T)$ nmol/mol	D_i nmol/mol	$U(D_i)$ nmol/mol
CENAM	22402	727.00	3.00	718.8	1.3	0.1	0.57	8.2	6.1
CERI/NMIJ	22492	717.70	2.30	719.4	1.4	0.1	0.56	-1.7	4.7
CHMI	22418	715.80	3.75	718.5	1.7	0.1	0.69	-2.7	7.6
FMI	22416	721.10	5.77	725.3	2.3	0.1	0.94	-4.2	11.7
JRC	22496	727.80	1.45	718.9	1.8	0.1	0.75	8.9	3.3
KRISS	22423	713.20	4.35	712.1	1.7	0.1	0.69	1.1	8.8
LNE	22422	725.70	2.90	725.2	1.5	0.1	0.60	0.5	5.9
NIST	22396	715.00	3.50	717.3	2.1	0.1	0.84	-2.3	7.2
NMi	22414	718.10	4.00	720.2	1.6	0.1	0.64	-2.1	8.1
NPL	22412	722.27	1.30	722.7	1.5	0.1	0.61	-0.5	2.9
UBA(D)	22411	713.80	2.91	710.5	1.5	0.1	0.63	3.3	6.0
VNIIM	22403	711.30	4.62	713.9	1.8	0.1	0.72	-2.63	9.4
Pilot study									
METAS	22520	714.30	2.20	712.60	1.42	0.2	0.58		

Table 6 – Degrees of equivalence. The combined uncertainties have been expanded with an expansion factor (*k*) of 2 to form the expanded uncertainties ($U(D_i)$).

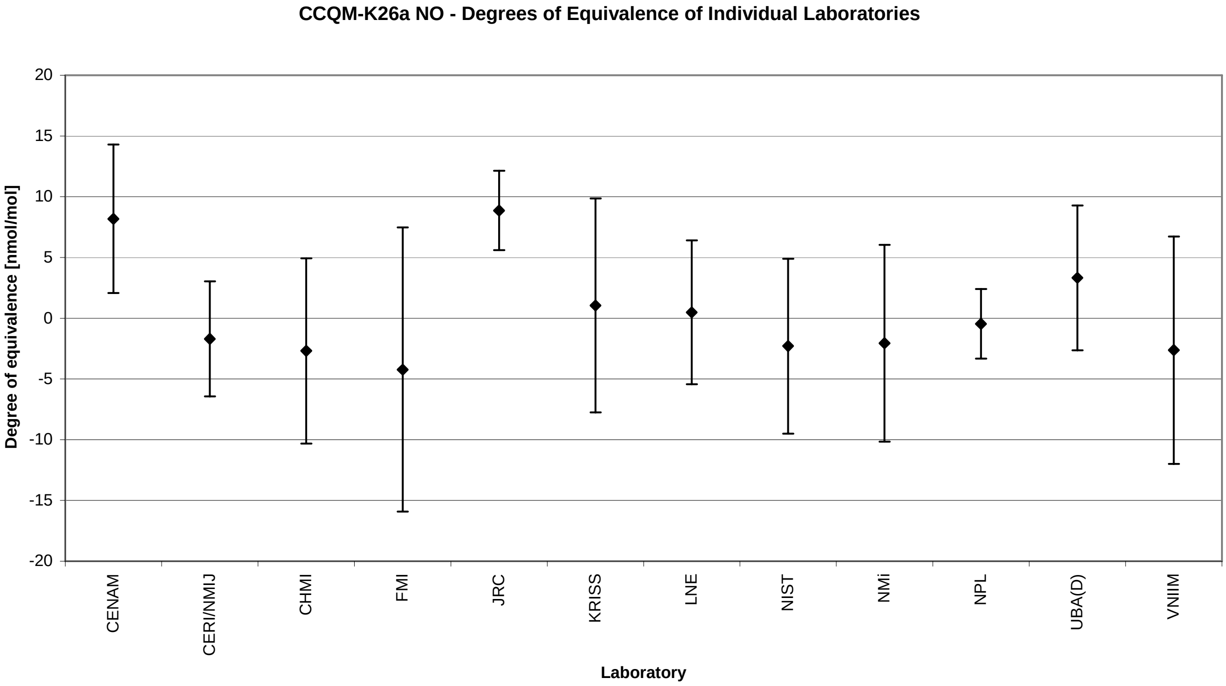


Figure 5 – Degrees of equivalence.

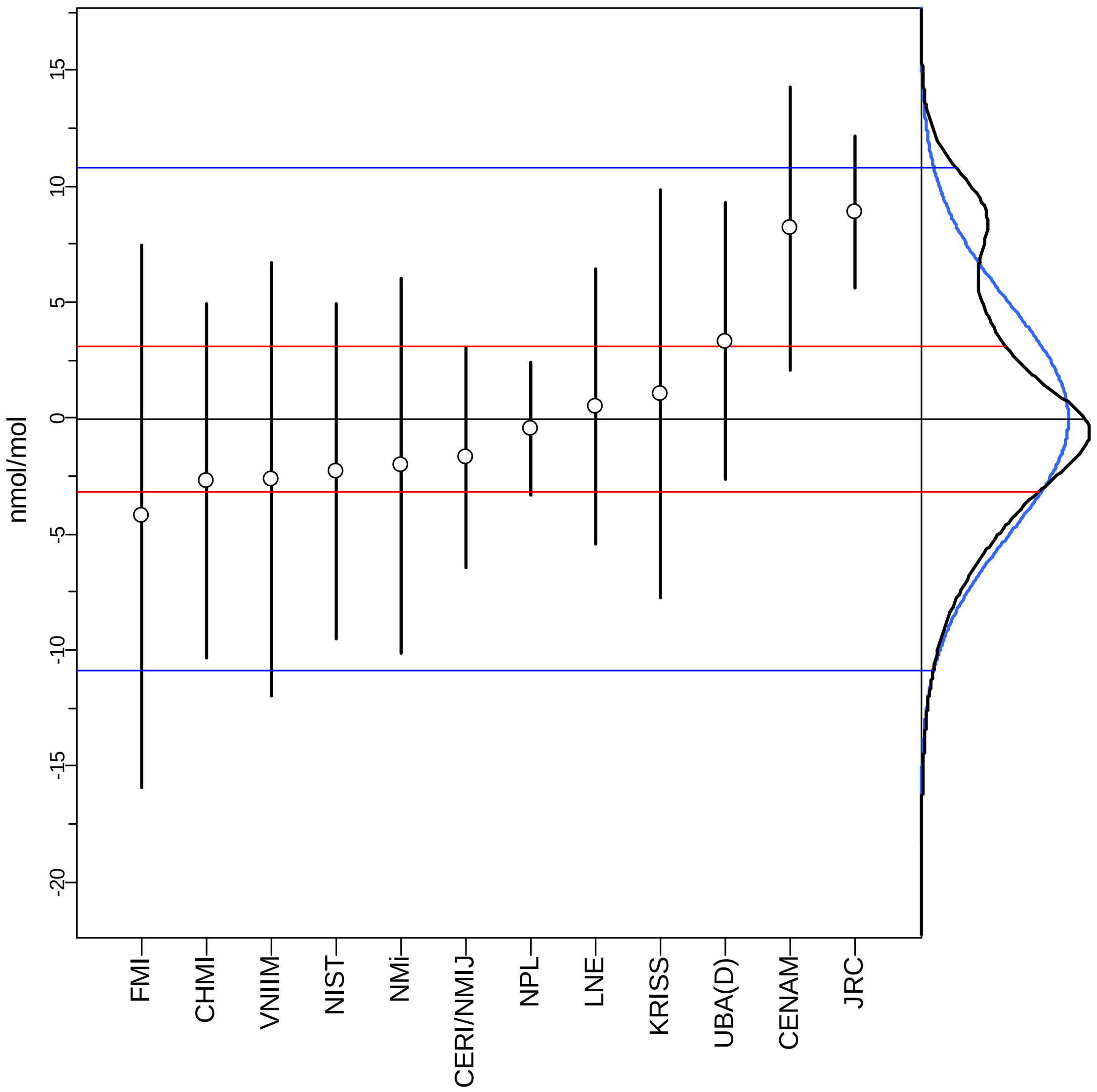
Verification of the Degrees of Equivalence by Reference to a Consensus Value

As described above, the degrees of equivalence were calculated using:

$$D_i = x_i - z_{i,\bar{T}}$$

where x_i is the value submitted by laboratory i, and $z_{i,\bar{T}}$ is the results of the analysis of the travelling standard i by the coordinating laboratory.

Figure 6 shows the distribution of the degrees of equivalence listed in Table 5. The mean of the degrees of equivalence is 0.5 +/- 5.6 nmol/mol. The uncertainty weighted mean of the degrees of equivalence is 2.0 +/- 5.9 nmol/mol and the median is –1.1 +/- 4.3 nmol/mol. Each of these estimates for the centrality of the distribution varies from zero by significantly less than its uncertainty. More importantly, they all vary from zero by significantly less than the typical values for the uncertainty estimated by participants. Hence, we conclude, that within the scope of this exercise, there is no significant bias due to the work of the coordinating laboratory in assigning a KCRV to each travelling standard.



Summary

The results for the 12 participants in CCQM-K26 and the one participant in CCQM-P50a are presented in this report. (Two laboratories registered to participate on CCQM-P50a, but did not report results). Degrees of equivalence have been calculated based on a reference value, corresponding to the KCRV, derived from the analysis of each travelling standard by the coordinating laboratory. This approach was verified by comparing it with the results of calculating the KCRV from a consensus of submitted results.

Annexes

Annex A – Protocol

Key comparison of NO and SO_2 at ambient levels

CCQM K26 a and b - Protocol

Pilot Laboratory:- NPL, UK

Background

Accurate measurements of NO_2 and SO_2 at ambient air concentrations have become essential to support monitoring and legislation concerned with air quality.

In general, the primary element of quality assurance for field instruments is regular calibration using certified gas mixtures. In the case of NO_2 there is near universal use of analysers based on the chemiluminescent detection of NO, with NO_2 being measured as the difference between ambient NO and ambient NOx, this being the sum of NO and NO_2 measured by converting the NO_2 to NO with a catalyst. Analyser response is therefore calibrated using an NO mixture.

NO mixtures have a balance gas of nitrogen, to minimize oxidation to NO_2, while SO_2 mixtures have a balance gas of synthetic air.

The concentrations involved in these comparisons have been chosen as those likely to be used for field calibrations within the appropriate European standards.

The protocol for this Key Comparison was initiated by NPL at the EUROMET Gas Analysis Working Group. Subsequently, laboratories from outside the EUROMET group expressed an interest in participation and the proposal was submitted to the CCQM Gas Working Group as a Key Comparison. This proposal was ratified by the CCQM in April 2002.

Comparison protocol

The mixtures used for the comparison will be acquired from commercial suppliers with a proven track record of preparing stable mixtures of the relevant gases. The analyte amount fractions will lie within the ranges:

Nitrogen monoxide	$600.\ 10^{-9} – 850.\ 10^{-9}$ mol/mol
Sulphur dioxide	$240.\ 10^{-9} – 320.\ 10^{-9}$ mol/mol

NPL will carry out stability checks on the mixtures and will make a determination of their amount fraction using primary facilities at NPL before dispatch to participating laboratories. The stability of the cylinders will be confirmed by a second measurement after they have been returned to the pilot laboratory.

Transport of cylinders to participating laboratories will be organized and paid for by NPL. Participants must arrange and pay for transport of the cylinders back to the pilot laboratory.

Participating laboratories should specify the method and calibration procedure used for the comparison in detail. ***They should also state the route through which the calibration procedure provides traceability to the SI.***

Participating laboratories should make at least three measurements of the amount fraction of the analyte in each cylinder. The results of these measurements should be combined to provide the final result and the expanded uncertainty should be calculated. Detailed information should be provided about how the uncertainty budget was calculated, including an explanation of the sources of uncertainty accounted for and the total number of degrees of freedom in the final result.

NPL will be responsible for collecting and reporting measurement results.

After analysis by participating laboratories, the cylinders must be returned to the pilot laboratory with sufficient pressure for re-analysis. If a participant is not able to return the cylinder to the pilot laboratory with sufficient gas to carry out a further analysis, it may not be possible to allocate an appropriate KCRV to that laboratory.

Blank measurement reports for measurement data and other relevant information are appended.

The final timings of the comparison will be agreed with the CCQM and EUROMET Gas Working Groups and sent out at the time that the cylinders are distributed.

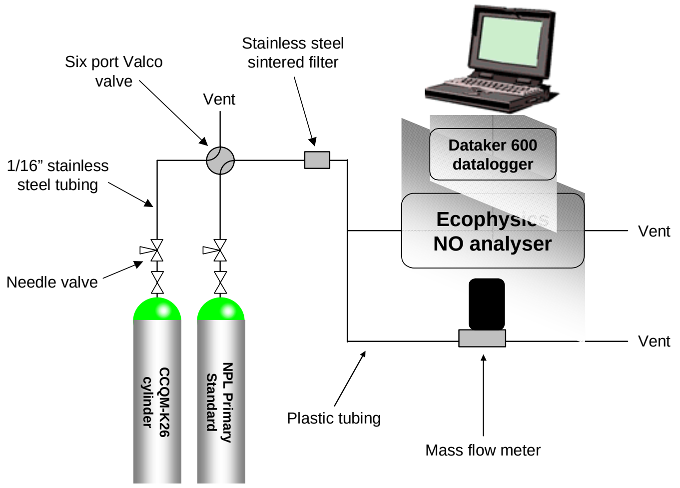
Annex B – Analytical Procedure Used by the Coordinating Laboratory

The following is a description of a single comparison between an NPL Primary Standard and a CCQM-K26 travelling standard.

An NPL NO Primary Standard and a travelling standard are connected to the sample lines as shown in the Figure below. The cylinder connection for each cylinder is purged by the following steps:

1. Ensure the needle valve is closed.
2. Tighten the cylinder connection.
3. Open cylinder valve to pressurise line up to needle valve.
4. Close cylinder valve.
5. Loosen cylinder connection to relieve pressure.
6. Repeat steps 4 and 5 four times.

Both cylinder valves are then opened. Flow from the first standard to be measured [the NPL Primary Standard] is directed through the analyser by setting the six-port valve (Valco) to the appropriate orientation. The flow is adjusted using the needle valve until a flow rate of 11 cc min-1 is achieved [as indicated by the mass flow meter]. Flow from the second standard to be measured [the travelling standard] is directed to the vent from the six-port valve. The system is purged for at least 30 minutes in order to condition the sampling lines and ensure the temperature of the analyser has stabilised. Data are then recorded for the NPL Primary Standard for a period of four minutes during which time the data logger transmits a value for NO and NOx to the computer every ten seconds. After four minutes the six-port valve is adjusted such that the flow from the travelling standard is diverted through the analyser and the flow from the NPL Primary Standard is diverted to the vent. This process is repeated a total of six times such that each standard is measured six times. The NPL Primary Standard is then measured again to complete a single comparison.



Annex C – Uncertainty in the Gravimetric values of Standards Prepared by the Coordinating Laboratory

PARENT:			npl1103		NPL1122	
	Mole fraction	Uncertainty	Mole fraction	Uncertainty	Mole fraction	Uncertainty
NO	0.999734	0.000062	0.099909191	2.38708E-05	0.009990935	3.08359E-06
N2	0.000065	0.000005	0.900048994	2.7136E-05	0.989983158	1.33743E-05
NO2	0.00005	0.00005	4.99679E-06	4.99644E-06	4.9968E-07	4.99642E-07
N2O	0.000161	0.00005	1.60897E-05	4.99573E-06	1.60897E-06	4.99562E-07
Ar			2.25016E-05	1.29879E-05	2.47502E-05	1.30518E-05
CO			2.25016E-08	9.00064E-09	2.47502E-08	9.04489E-09
CxHy			4.50032E-08	2.70019E-08	4.95003E-08	2.71347E-08
CH4			6.75048E-08	8.10058E-09	7.42505E-08	8.1404E-09

BALANCE	BIP N2	
	Mole fraction	Uncertainty
Ar	0.000025	0.00001443
CO	0.000000025	0.00000001
CxHy	0.00000005	0.00000003
N2	0.99997586	0.00001443
CH4	0.000000075	0.000000009

MIXTURE		npl1103		NPL1122		NPL1125	
		Parent mass	Uncertainty	Parent mass	Uncertainty	Parent mass	Uncertainty
	1	125.03	0.03	125.2	0.03	127	0.03
	2	1051.15	0.03	1118.81	0.03	1153.65	0.03
		Mole fraction	Uncertainty	Mole fraction	Uncertainty	Mole fraction	Uncertainty
NO		0.099909191	2.38708E-05	0.009990935	3.08359E-06	0.000990146	3.70754E-07
N2		0.900048994	2.7136E-05	0.989983158	1.33743E-05	0.998985539	1.30575E-05
NO2		4.99679E-06	4.99644E-06	4.9968E-07	4.99642E-07	4.95205E-08	4.95167E-08
N2O		1.60897E-05	4.99573E-06	1.60897E-06	4.99562E-07	1.59456E-07	4.95088E-08
Ar		2.25016E-05	1.29879E-05	2.47502E-05	1.30518E-05	2.49752E-05	1.30641E-05
CO		2.25016E-08	9.00064E-09	2.47502E-08	9.04489E-09	2.49752E-08	9.05344E-09
CxHy		4.50032E-08	2.70019E-08	4.95003E-08	2.71347E-08	4.99505E-08	2.71603E-08
CH4		6.75048E-08	8.10058E-09	7.42505E-08	8.1404E-09	7.49257E-08	8.1481E-09

PARENT:	NPL1125		NPL1109		NPL1112	
	Mole fraction	Uncertainty	Mole fraction	Uncertainty	Mole fraction	Uncertainty
NO	0.000990146	3.70754E-07	9.99131E-05	4.33181E-08	9.99868E-06	4.85194E-09
N2	0.998985539	1.30575E-05	0.999875929	1.30395E-05	0.99996586	1.30512E-05
NO2	4.95205E-08	4.95167E-08	4.99698E-09	4.9966E-09	5.0007E-10	5.0003E-10
N2O	1.59456E-07	4.95088E-08	1.60903E-08	4.9958E-09	1.61022E-09	4.9995E-10
Ar	2.49752E-05	1.30641E-05	2.49975E-05	1.30407E-05	2.49997E-05	1.30513E-05
CO	2.49752E-08	9.05344E-09	2.49975E-08	9.03722E-09	2.49998E-08	9.04459E-09
CxHy	4.99505E-08	2.71603E-08	4.9995E-08	2.71117E-08	4.99995E-08	2.71338E-08
CH4	7.49257E-08	8.1481E-09	7.49925E-08	8.1335E-09	7.49993E-08	8.14013E-09

MIXTURE		NPL1109		NPL1112		5702577	
		Parent mass	Uncertainty	Parent mass	Uncertainty	Parent mass	Uncertainty
	1	125.06	0.03	125.82	0.03	125.82	0.03
	2	1114.22	0.03	1131.47	0.03	1131.47	0.03
		Mole fraction	Uncertainty	Mole fraction	Uncertainty	Mole fraction	Uncertainty
NO		9.99131E-05	4.33181E-08	9.99868E-06	4.85194E-09	7.25553E-07	4.0599E-10
N2		0.999875929	1.30395E-05	0.99996586	1.30512E-05	0.999975134	1.34163E-05
NO2		4.99698E-09	4.9966E-09	5.0007E-10	5.0003E-10	3.629E-11	3.628E-11
N2O		1.60903E-08	4.9958E-09	1.61022E-09	4.9995E-10	1.1685E-10	3.628E-11
Ar		2.49975E-05	1.30407E-05	2.49997E-05	1.30513E-05	2.5E-05	1.34164E-05
CO		2.49975E-08	9.03722E-09	2.49998E-08	9.04459E-09	2.5E-08	9.29754E-09
CxHy		4.9995E-08	2.71117E-08	4.99995E-08	2.71338E-08	5E-08	2.78926E-08
CH4		7.49925E-08	8.1335E-09	7.49993E-08	8.14013E-09	7.5E-08	8.36779E-09

Annex D – Methods used by participating laboratories

Laboratory	Analyser	Method
Key comparison		
CENAM	HORIBA Model APNA-360CE (Chemiluminescence)	The concentration was calculated by interpolation of a calibration curve using three concentration levels of CENAM primary gas mixtures
CERI/NMIJ	Thermo Environmental Instruments Inc. Model 42C Trace Level	High/Low bracketing using two PSMs.
CHMI	Thermo Environmental Instruments Model 42C and 42 (Chemiluminescence)	Diluted PRM by manometric static injection. Direct from manometric static injection system to analysers. Cylinder with reduction valve MG FE62 to analysers.
FMI	TEI Model 42C (Chemiluminescence)	Dynamic dilution method (ISO 6145-6). The measurements of the samples took place according to a sequence of instrument calibration, sample analysis, injection of zero gas into the analyser, and calibration of the analyser (against NPL secondary standard (number QE11/N03/050).
JRC	TEC 42C (Chemiluminescence)	Calibration gases produced by permeation method and static dilution method. A TE 42 C is calibrated with zero gas, span gas 1 and span gas 2. After the calibration the sample is measured.
KRISS	Thermo Environmental Instruments Inc, Model 42 (Chemiluminescence)	Four standard gases were used as reference gases. A-B-A ratio method used
LNE	TEC 42C (Chemiluminescence)	Zero/span calibration using dilution method (Molbloc) to generate span value.
NIST	TEC Model 42C (Chemiluminescence)	Ratio of travelling standard against 8 NIST standards
Nmi	Thermo Environmental Instruments Inc. Model 17C Ammonia Analyzer (Chemiluminescence)	Calibration has been performed using Primary Standard Gas Mixtures (PSMs). A suite of four PSMs ranging in amount-of-substance fraction level from 400 to 1000 nmol/mol NO (nominal) were used.
NPL	Eco-physics Model CLD 700 AL (Chemiluminescence)	Bracketing method using single gravimetrically prepared standards, in an ABABA sequence.
UBA(D)	(Chemiluminescence)	Calibration by a 2 point bracketing procedure. Preparation of the calibration standards by static volumetric injection method according to ISO 6144 and VDI 3490 (p14).
VNIIM	Environment S.A. ModelAC-30M (Chemiluminescence)	The method of absolute calibration (comparison method) was used. Two approx. 700 ppb standards used.
Pilot study		
IPQ		
METAS	(Chemiluminescence)	The calibration standards used were produced by dilution of two METAS NO-standards (with an amount of substance fraction of NO in N_2 of about $60 \cdot 10^{-6}$ mol/mol) with nitrogen of a quality of 99.999 %.
UBA(A)	(Chemiluminescence)	NMi MS 7356, 90,2±0,5 μmol/mol NO

Annex E – Results and reports as submitted by participating laboratories

Key comparison participants:

CENAM

Laboratory : **CENAM - Centro Nacional de Metrología - México**
Cylinder number : **22402**

NOMINAL COMPOSITION
- Nitrogen monoxide : 600 to 850. 10^{-9} mol/mol
- Nitrogen : balance

Measurement No.1	Date	Result (mol/mol)	Standard deviation (% relative)	Number of submeasurements
NO	2004-09-27	726. 10^{-9}	0,23	6

Measurement No.2	Date	Result (mol/mol)	Standard deviation (% relative)	Number of submeasurements
NO	2004-09-28	727. 10^{-9}	0,32	6

Measurement No.3	Date	Result (mol/mol)	Standard deviation (% relative)	Number of submeasurements
NO	2004-09-29	728. 10^{-9}	0,17	6

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	727. 10^{-9}	2	6. 10^{-9}

Reference Method:

To analyze nitric oxide was used one Specific Analyzer brand HORIBA, Model APNA-360CE Serial Number 4152231013 with Chemiluminiscence operation principle. Regulator of low pressure in the outlet of cylinder, with teflon tubing of ¼ inch.

The concentration was calculated by interpolation of a calibration curve using three concentration levels of CENAM primary gas mixtures. The sample and standards were analyzed three times each by duplicate.

Calibration Standards:

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs), this mean prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 4.0 of purity and 6.0 for balance. Their uncertainties were calculated by type B evaluation or/and type A evaluation.
The instrument for weighing was a Mettler balance model PR10003 (10 kg capacity and 1 mg resolution) and sets of weights class E2 (serial number 520779750101, from 1 to 5 kg – 4 pieces) and E2 (serial number 41003979, from 1 mg to 1 kg – 25 pieces) according to the R 111 of OIML, all of them traceable to SI by CENAM´s Standards.

Instrument Calibration:

The calibration procedure was according to ISO 6143 using B_Least program software for multipoint Calibration. It was used 3 concentration levels in the following sequence: Std_1 $SmStd_3SmStd_2$…

The value concentration and associated uncertainty of the primary standard mixtures used to quantify the sample are the following:

Cylinder Number	Component	Result (µmol/mol)	U (µmol/mol)
HH22208	NO	0,5991	0,0010
	Nitrogen	balance	
HH21973	NO	0,7087	0,0012
	Nitrogen	balance	
HH22128	NO	0,8319	0,0014
	Nitrogen	balance	

Sample Handling:

Sample and standards were rolled and left to environmental temperature 24h before analysis.
Between cylinder and Specific Analyzer it was used a configuration system made of Teflon lines of 1/4 inch OD, with a valve and one low pressure regulator to avoid contamination of air in tubing walls and interference between sample and standards.

Uncertainty:

The main sources of uncertainty considered to estimate the combined standard uncertainty are listed in the following tables for each one of the compounds:

Uncertainty source	**Estimate x_i**	**Assumed distribution**	**Standard uncertainty $u(x_i)$**	**Sensitivity coefficient**	**Contribution to standard uncertainty**
Reproducibility and Repeatability	-----------	Normal	$0{,}5.\ 10^{-9}$	1	$0{,}5.\ 10^{-9}$
Mathematical model	-----------	Normal	$1{,}5.\ 10^{-9}$	1	$1{,}5.\ 10^{-9}$
System characteriazation	---------	Rectangular	$2{,}3.\ 10^{-9}$	1	$2{,}3.\ 10^{-9}$

Coverage factor: k=2
Expanded uncertainty: It was obtained by the product of the combined standard uncertainty and a factor of 2 and it was calculated according to the "Guide to the Expression of Uncertainty in Measurement, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1995)"

Model used for evaluating measurement uncertainty:

$$C = \mu + \delta_T + \delta_s + \delta_m$$

The combined uncertainty has three contributions:

a) Reproducibility and Repeatability.
The combined effect (δ_T) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.
b) Mathematical model effect (δ_m). This component corresponds to the estimated uncertainty which come from the B_Least program software for multipoint Calibration.
c) System characterization (δ_S). According to instrument specification and instrument performance

CCQM-K26 – Addendum 1 to the protocol

CENAM Participants List:

Alejandro Pérez Castorena, Víctor Manuel Serrano Caballero, Francisco Rangel Murillo, Carlos Enrique Carbajal Alarcón, Carlos Ramírez Nambo, and Manuel de Jesús Ávila Salas.

CERI

Laboratory : National Metrology Institute of Japan (NMIJ)
(Performed by Chemicals Evaluation and Research Institute, Japan)

Cylinder number : 22492

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	20/07/2004	716.8	0.13	5

Measurement No. 2	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	21/07/2004	717.7	0.08	5

Measurement No. 3	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	22/07/2004	716.4	0.08	5

Results:

Analyte	Result (assigned value) (nmol/mol)	Coverage factor	Assigned expanded uncertainty
NO	717	2	4.6

Reference Method:

Instruments for NO measurement
Principles : Chemiluminescent NO-NO2-Nox Analyzer
Make : Thermo Environmental Instruments Inc.
Type : Model 42C Trace Level
Data collection : output of integrator recording

Calibration Standards:

Preparation : Gravimetric method

Purity analysis ;
NO : certified by NMIJ(National Metrology Institute of Japan)

N2 : The impurities in N2 are determined by analyses and the amount of the major component is conventionally determined by,

$$X_{pure} = 1 - \sum_{i=1}^{N} x_i$$

where:
x_I = mole fraction of impurity i , determined by analysis
N = number of impurities likely in the final mixture
X_{pure} = mole fraction 'purity' of the 'pure' parent gas

Instrument Calibration:

Table 1 concentration of PSMs

Component	Concentration (nmol/mol)	
	R_1	R_2
NO	972.5	482.3

This procedure is for the determination of NO in a sample using CLA.

1) Inject the calibration standard (R_1) into CLA. Record the output.
2) Inject the sample to be tested in same manner as the calibration standard. Record the output.
3) Inject the calibration standard (R_2). Record the output.
4) Calculate the concentration of NO using the formula below.

$$Y = \frac{A(E-D) + B(C-E)}{(C-D)}$$

where Y: Concentration of sample
A: Concentration of standard (R_1)
B: Concentration of standard (R_2)
C: Standard (R_1) output
D: Standard (R_2) output
E: Sample output

Following above procedure, 5 measurements are repeated subsequently in a day and iterated for 3 days.

Sample Handling:

Stabilization : none
Pressure : 100 kPa
Sample flow : 1.5 l/min
Sample line temperature : room temperature 25 degrees
Dilution : none

Uncertainty:

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatability of analysis	716.9	normal	0.9	1	0.9
Reference gas R1 preparation	972.5	normal	1.4	1	1.4
Reference gas R2 preparation	482.3	normal	1.6	1	1.6
total					2.3

Coverage factor: 2
Expanded uncertainty: 4.6 nmol/mol

CHMI

Laboratory: **Czech Hydrometeorological Institute,** Na Sabatce 17, 143 06 Prague 4

Calibration Laboratory of Immission, Gen. Sisky 942, Prague 4

Cylinder number: **22418**

NOMINAL COMPOSITION

- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	15.7.2004	716,1 . 10^{-9}	0,53	1

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	15.7.2004	714,7 . 10^{-9}	0,53	2

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	16.7.2004	716,1 . 10^{-9}	0,52	2

Measurement No.	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	16.7.2004	717,2 . 10^{-9}	0,53	1

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	715,8 . 10^{-9} mol/mol	2	7,5 . 10^{-9} mol/mol

Reference Method: Diluted PRM by manometric static injection

Calibration Standards:

NMi gaseous primary reference material (PRM), cyl. No. MS 7325

concentration nitric oxide (10,05 ± 0,08) x 10^{-6} mol/mol in nitrogen

certificate 318319-01 issue 18.6.2004

Instrument Calibration:

Work etalons: Thermo Environmental Instruments model 42C and 42

Sample Handling:

Direct from manometric static injection system to analyzers

Cylinder with reduction valve MG FE62 to analyzers

Uncertainty:

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)[\%]$
PRM NO in N2	10050µmol/mol	normal	40 µmol/mol	100	0,398
Pressure *p1*	~ 1000 hPa	normal	0,135 hPa	-	-
Pressure *p2*	~ 1100 hPa	normal	0,135 hPa	-	-
Pressure *p3*	~ 1350 hPa	normal	0,275 hPa	-	-
Dilution *f1*	~ 0,073	normal	0,0001445	100	0,198
ΔT	300 K	rectangular	0,173	100	0,058
Work etalon D_{PRM}	734 ppb	rectangular	0,577ppb abs + 0,173% rel	100	0,190
Work etalon D_{CYL}	716 ppb	rectangular	0,577ppb abs + 0,173% rel	100	0,191
NO in N2 cyl.	715,8 µmol/mol				0,523

Coverage factor: k = 2
Expanded uncertainty: 7,5 . 10^{-9} mol/mol

FMI

Laboratory : Finnish Meteorological Institute
Cylinder number : 22416

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	7.9.04	721.0 10^{-9}	0.1	20

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	8.9.04	720.9 10^{-9}	0.1	20

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	9.9.04	721.2 10^{-9}	0.1	20

Measurement No.	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	9.9.04	721.2 10^{-9}	0.1	20

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	721.1 10^{-9} mol/mol	k = 2	1.6 %

Reference Method:

Reference method for the analysis of the CCQM-K26 key comparison Nitrogen monoxide gas cylinder was based on the Chemiluminescence method (ISO 7996:1985). The analyser, TEI 42 C s/n – 366, was calibrated by the dynamic dilution method (ISO 6145-6) in the range of 100 to 500 nmol/mol. The laboratory is accredited by the Centre for Metrology and Accreditation (MIKES/FINAS) as a calibration laboratory according to the standard ISO/IEC 17025. The scope of accreditation is from 5 to 1000 nmol/mol for the calibration and measurement of nitrogen monoxide.

Calibration Standards:

The gas standard used for the calibration of the oxides of nitrogen analyser was a secondary gas standard of the National Physical Laboratory (NPL) in UK. The details of the calibration certificate of the standard are: The certificate number is QE11/N03/050, dated 2, December 2003, and the content of the standard is Nitric oxide in Nitrogen C = 99.2 ± 0.8 µmol/mol where the uncertainty of the results is based on a standard uncertainty multiplied by a coverage factor k = 2, providing a level of confidence of approximately 95 %.

The other reference standards used in the measurements are:
Gas dilutor, Sonimix 6000A1 s/n 1585, calibrated at Laboratoire National de Metrologie, BNM-LNE; certificate C020080/1; March 2002

Pressure meter, Diptron 3 plus with the pressure probe UXD-95942, calibrated at MIKES (certificate no M-04P072) and used to control the dilution pressure of the gas dilutor.

Instrument Calibration:

The analyser TEI 42 C used for the analysis of the CCQM-K26 Nitrogen monoxide cylinder was calibrated according to the standard operation procedure of the laboratory (SOP). The calibration range was 100 to 500 nmol/mol by fixed calibration concentration approximately at 100 nmol/mol intervals i.e. a five-point calibration. Synthetic air was used as the dilution gas. The calibration of the analyser took place before and after the analysis of the sample. The CCQM-K26 cylinders were analysed during three days with the same TEI 42 C analyser. The calibration results were treated according to the SOP of the laboratory: 10 individual values from the stable reading of the analyser were included in the data analysis. The mean value and the standard deviation of the stable reading were calculated and the MS-Excel sum of least squares analysis was used to obtain a linear curve fitting to the data. The response functions of each calibration were compared to each other throughout the measurements. No clear drift was observed.

The dynamic dilution device was used for obtaining the calibration concentration. The dilutor, Sonimix 6000A1 s/n 1585 by LN-Industries Switzerland, is based on the so-called critical orifices which produces multipoint calibration concentration by fixed dilution steps. The linearity of the dilution steps of the dilutor was checked with carbon monoxide using the reference gas standard of the laboratory (carbon monoxide in nitrogen from NPL, UK, C = 0.991 ± 0.008 % certificate no QE11/N02/018/A, 9 July 2002) and the carbon monoxide analyser, APMA-360 s/n 910 007. To complete the correct dilution level of the dilutor the other reference gas standard was injected directly into the carbon monoxide analyser used in the measurements. The other reference gas standard was from the Nederlands Meetinstituut, The Netherlands, certificate no 318230 (carbon monoxide in nitrogen C = 40.01 ± 0.10 µmol/mol, 8 March 2004). During the operation of the dilutor the pressure of the dilution line was controlled by the reference pressure meter of the laboratory. The pressure in the calibration gas line was kept constant by a pressure regulator but not controlled by a pressure meter because of the danger of corrosion of the gauge. The traceability of the pressure meter goes to the national metrological institute (MIKES).

Sample Handling:

The sample was injected into the analyser through the sample port without particulate filter with the excess of gas of 1 l/min. The pressure of the reaction cell of the analyser was recorded during the measurements. The pressure of the reaction cell was within 4 mmHg during the calibration of the analyser and the analysis of the samples. No correction due to the chamber pressure change of the analyseron the results was made.

The tubing, the regulator and the connectors were conditioned during 30 min prior to the measurements.

The measurements of the samples took place according to a sequence of instrument calibration, sample analysis, injection of zero gas into the analyser, and calibration of the analyser. The sample analysis and the injection of zero gas were repeated two to three times in a day. The duration of the sample analysis and the injection of zero gas was at least 20 min in order to reach the stable reading of the analyser.

Uncertainty:

The standard uncertainty of the Sonimix 6000A gas dilutor for one dilution step can be expressed by:

$$u(C(1))^2 = \left(\frac{C_{ST}}{f(bs1)+f(bs2)}\right)^2 u(bs4)^2 + \left(\frac{f(bs4)\cdot C_{ST}}{(f(bs1)+f(bs2))^2}\right)^2 (u(bs1)^2 + u(bs2)^2) +$$

$$\left(\frac{f(bs4)}{f(bs1)+f(bs2)}\right)^2 u(C_{ST})^2 + u(C_{dil})^2$$

Eq(1)

Where
$u(C(I))^2$ is the standard uncertainty of the first dilution step for the calibration concentration
C_{ST} is the concentration of the gas standard (Secondary reference material)
f(bs1) … f(bs4) are the flows of the critical orifices bs1 … bs4
u(bs1)… u(bs4) standard uncertainty of the flows of the critical orifices
$u(C_{ST})$ standard uncertainty of the gas standard (SRM)
$u(C_{dil})$ standard uncertainty of the dilution gas (impurities)

Equation 1 is derived from

$$u_c(y)^2 = \sum_i \left(\frac{\partial f(x_i)}{\partial x_i} \right)^2 u(x_i)^2$$

Eq(2)

Here the equation for the produced calibration gas concentration can be expressed as a function of the contributing variables:

$$\boldsymbol{f} = \boldsymbol{f}(\boldsymbol{C}, \boldsymbol{F}, \boldsymbol{I})$$

Eq(3)

where C is the concentration of the reference gas standard, F is the flow rate of a single critical orifice in each of the dilution steps, and I is the impurities of the zero gas. The pressure on the span and zero line of the dilutor, also affects the results but we have recorded the pressure continuously at the dilution line and checked at frequent intervals that the pressure in the span line is constant. Also the temperature has an effect on the concentration but that is kept constant during the calibration.

We differentiate Eq(2) with respect to all the variables but in doing so we have omitted the cross terms i.e. the covariance terms in the calculations as second order terms. Since the Sonimix operates with fixed dilution steps (10 altogether) we have performed the uncertainty calculation for each of the dilution steps which are similar to Eq(1). The uncertainty components from the Eq(1) are listed in Table 1.

Table 1. The uncertainty components of the sulphur dioxide concentration produced with the gas dilutor.

Parameter	Description of the effect	Standard uncertainty $u()_I$
u_{bs1} … u_{bs7}	The uncertainty of the flow through an individual sonic orifice.	0.3 … 0.5 % of the flow of the sonic orifice
$u(C)_{ST}$	Standard uncertainty of the used gas standard.	0.5 % of the certified concentration.
$u(C)_{dil}$	The impurity of the zero gas as a mean value of the change of zero level by frequent calibration.	0 … 0.5 ppb

The uncertainty of the calibration concentration is an important factor in the uncertainty analysis since it also describes the uncertainty of the traceability chain to the SI-unit as a whole. In our case the gas standards go to gravimetric method conducted by NPL, UK, and to Nmi, The Netherlands. In addition to that the flow measurements were traced to the Laboratoire National de Metrologie, BNM-LNE, France. The pressure and temperature measurements are traced to the Centre for Metrology and Accreditation, MIKES, Finland.

The second part in the uncertainty budget is contributed by the analyser. Since the measurements took place in the laboratory at controlled conditions and the analyser was calibrated prior and after the measurements of the CCQM-K26 samples we have included into the uncertainty budget only those performance characteristics of the analyser that are important in this case. We have therefore included the following performance characteristics that we have tested in the laboratory:

- Linearity of the analyser in the range of 100 to 500 nmol/mol
- Repeatability

Short-term drift is not included, and interferences by other pollutants are also not taken into account here. The impurity of the zero gas is taken into account in the calibration concentration (see Table 1)

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Uncertainty of calibration concentration including dilution and traceability chain to SI	See Eq (1)	rectancular	5.8 nmol/mol	1	0.8 %
Uncertainty due to the analyser - Linearity - Repeatability	0.1 % 0.1 %	rectangular normal	0.8 nmol/mol 0.7 nmol/mol	1 1	0.1 % 0.1 %
					0.8 %

Coverage factor: k=2
Expanded uncertainty: 1.6 %

JRC

Laboratory : Joint Research Centre, IES, ERLAP, Italy
Cylinder number : BOC 172698 SG

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	22.06.04	729.7	0.04	5

Measurement No. 2	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	23.06.04	728.5	0.05	5

Measurement No. 3	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	24.06.04	726.6	0.04	5

Measurement No.	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	25.06.04	726.4	0.09	5

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	727.8	2	2.9

Reference Method:

NO/NOx measurement with Chemiluminescence analyzer TE 42 C
Calibration gases produced by permeation method and static dilution method

Calibration Standards:

Span gas 1 is generated dynamically by means of a permeation oven containing a NO2 permeation tube. The tube is weighed every ~ 4 weeks. The flow measurement is carried out with a Brooks Vol-U-Meter.

The other calibration gas -Span gas 2- is produced by a static dilution system, where pure NO gas is injected by an automatic loop into a vessel of a known volume, which can be pressurized.

Instrument Calibration:

A TE 42 C is calibrated with zero gas, span gas 1 and span gas 2. After the calibration the sample is measured.

Sample Handling:

The pressure reducer has been carefully purged several times. When the concentration stability was given the measurement results were recorded.

Uncertainty:

The standard uncertainty of Span Gas 1 is evaluated by estimating the error sources of the mass, flow and time measurement of the permeation system. The standard uncertainty of Span Gas 2 (static dilution) is evaluated by estimating the error sources of volume (Vessel, loop), pressure and temperature measurement as well as purity of the used gases. The analysis function between analyzer response and analyte content is calculated using ISO 6143 (Determination of composition and checking of calibration gas mixtures – comparison method); out of the comparison method the analyte content and uncertainty of the NPL gas cylinder are evaluated. Analyzer drift has not been taken into account as the measurement is done immediately after calibration.

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
u(xo)			0.12		
u(x1)			1.5		
u(x2)			1.6		

Coverage factor: 2
Expanded uncertainty: 2.9 mol/mol

KRISS

Laboratory : KRISS
Cylinder number : DW1768

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 ×10^{-9} mol/mol
- nitrogen : balance

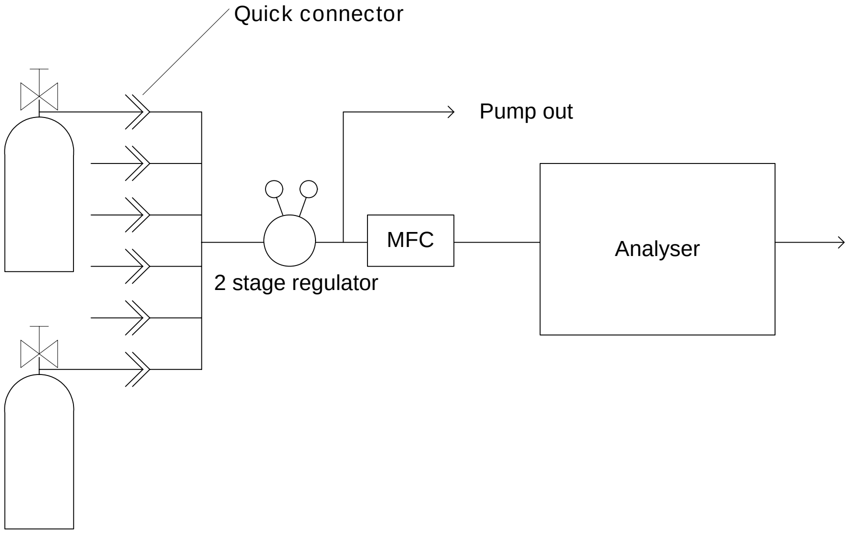
Measurement	Date	Result (10^{-9} mol/mol)	Stand. uncertainty (10^{-9} mol/mol)	Number of sub-measurements
No. 1	04/8/2	713.4	4.1	5
No. 2	04/8/5	710.0	4.1	5
No. 3	04/8/9	712.3	4.2	5
No. 4	04/8/11	711.9	4.1	5
No. 5	04/8/11	718.2	4.3	5
No. 6	04/8/24	710.8	4.7	5
No. 7	04/8/27	715.8	4.4	5

Results:

Analyte	Result (10^{-9} mol/mol)	Coverage factor	Expanded uncertainty (10^{-9} mol/mol)
NO / Nitrogen	713.2	*k*=2	8.7

Reference Method:

We used NOx analyzer (Model 42, TEI) for this measurement.
Configuration of analysis is as follows:



We designed a new gas inlet system using one regulator for this measurement to eliminate adsorption problems on the regulator. Sample and zero gases (pure nitrogen) were introduced into analyzer for 3 min alternatively. We used A-B-A method to correct instrumental drift. Sample and reference gases were determined 5 times, respectively. And gas flow rate was controlled to 700 ml/min by MFC.

Gas inlet sequences for NO measurement:
Nitrogen - STD – Nitrogen – Sample (1st) – Nitrogen – STD –
Nitrogen - STD – Nitrogen – Sample (2nd) – Nitrogen – STD –
Nitrogen - STD – Nitrogen – Sample (3rd) – Nitrogen – STD –
Nitrogen - STD – Nitrogen – Sample (4th) – Nitrogen – STD –
Nitrogen - STD – Nitrogen – Sample (5th) – Nitrogen – STD – Nitrogen

Calibration Standards:

We used Al cylinders (Luxfer, Au) with stainless steel valve pretreated at CERI, Japan.
The calibration standards were prepared by gravimetry method in our institute as follow.
2 %mol/mol (4 cylinders) → 1,000 μmol/mol (4 cylinders)
→ 20 μmol/mol (6 cylinders) → 740 nmol/mol (12 cylinders).

Pretreatment of cylinder:
- Evacuation with heating at 60 °C
- Leave for one week in NO 10 μmol/mol in nitrogen at 20 bar
- Leave for one week in NO 10 μmol/mol in nitrogen at 1 bar
- Evacuation with heating at 60 °C

Purity of NO source gas was determined by impurity analysis. Overall uncertainty of the 740 nmol/mol standards including purity of the source gas, weighing uncertainty, and manufacturing uncertainty was about 0.2 %.

Instrument Calibration:

The twelve standard gases with similar concentration (about 740×10^{-9} mol/mol) were prepared by gravimetry method. Four standard gases were selected and checked by NO analyzer to make sure their accuracy. We used A-B-A method and these standards were used as reference gases.

Sample Handling:

After receiving sample cylinder, cylinder was stood at room temperature with reference cylinders before measurements.

Uncertainty:

Quantity	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution (nmol/mol)	Corr.-coeff.	Index
No. 1	713.41 nmol/mol	4.07 nmol/mol	0.143	0.581	0.13	0.018
No. 2	710.01 nmol/mol	4.12 nmol/mol	0.143	0.589	0.13	0.018
No. 3	712.28 nmol/mol	4.23 nmol/mol	0.143	0.604	0.14	0.019
No. 4	711.92 nmol/mol	4.09 nmol/mol	0.143	0.584	0.13	0.018
No. 5	718.24 nmol/mol	4.29 nmol/mol	0.143	0.613	0.14	0.020
No. 6	710.85 nmol/mol	4.65 nmol/mol	0.143	0.664	0.15	0.023
No. 7	715.76 nmol/mol	4.43 nmol/mol	0.143	0.633	0.15	0.021
Factor related to the manufacturing uncertainty of PRM	1.0	$1.00 \cdot 10^{-3}$	713	0.713	0.16	0.027
Factor related to the linearity of PRM	1.0	0.0	0.0	0.0	0.0	0.0
Factor related to the matrix effect	1.0	0.0	0.0	0.0	0.0	0.0
Factor related to the stability of PRM	1.0	$2.50 \cdot 10^{-3}$	713	1.78	0.41	0.167
Factor related to the uncertainty of measurement reproduceability	1.0	$5.00 \cdot 10^{-3}$	713	3.57	0.82	0.669

Coverage factor: 2.0
Expanded uncertainty: 8.7 nmol/mol

LNE

Laboratory : Laboratoire National d'Essais (LNE)
Cylinder number : 22422

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (10^{-9} mol/mol)	Stand. deviation (% relative)	Number of sub-measurements
NO	25/06/2004	725	0.08	3
		725		
		726		

Measurement No. 1	Date	Result (10^{-9} mol/mol)	Stand. deviation (% relative)	Number of sub-measurements
NO	28/06/2004	726	0.08	3
		726		
		727		

Measurement No. 1	Date	Result (10^{-9} mol/mol)	Stand. deviation (% relative)	Number of sub-measurements
NO	30/06/2004	725	0.08	3
		725		
		726		

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	725.7.10^{-9} mol/mol	2	5.8.10^{-9} mol/mol

Reference Method:

A 42C (TEC) analyser based on the principle of chemiluminescence is used to measure the NO.

Calibration Standards:

A high concentration gas mixture of NO in nitrogen (at about 10.10^{-6} mol/mol) is prepared by a multistage gravimetric method.

Then, a gas mixture of NO in nitrogen at about 740.10^{-9} mol/mol is generated by diluting the gravimetric gas mixture of NO in nitrogen at about 10.10^{-6} mol/mol with synthetic air and by using flowmeters (Molbloc/Molbox).

Instrument Calibration:

Stage 1: Adjustment of the analyser

The analyser is adjusted at 2 points : zero and a full scale point (the concentration of the span gas must be slightly upper to the concentration of the unknown gas to be analysed afterwards).

Stage 2: Determination of the NO concentration of the unknown gas mixture

The unknown gas mixture is injected 3 times into the NO analyser. The NO concentration of the unknown gas mixture is equal to the NO concentration displayed by the analyser (C_{read}).

This procedure (stage 1 + stage 2) is carried out 3 times.

Sample Handling:

Cylinders were maintained inside a laboratory at a nominal temperature of (21±2) °C for all the period.

Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

Uncertainty:

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Zero gas concentration	0	rectangular	$5.774.10^{-10}$	$1.4.10^{-2}$	$8.08.10^{-12}$
Span gas concentration	737	-	$2.74.10^{-9}$	$9.9.10^{-1}$	$2.71.10^{-9}$
Reading for zero gas concentration	0	rectangular	$5.774.10^{-10}$	$1.4.10^{-2}$	$8.08.10^{-12}$
Reading for span gas concentration	737	rectangular	$5.774.10^{-10}$	$9.9.10^{-1}$	$5.72.10^{-10}$
Standard deviation on the mean of the 9 measurements	725.7	-	$0.71.10^{-9}$	1	$0.71.10^{-9}$

Coverage factor: 2
Expanded uncertainty: $U = 5.8.10^{-9}$ mol/mol

NPL

Results of Measurement of Cylinder 22412:

Run Number	nmol/mol
1	722.22
2	721.97
3	720.84
4	723.23
5	722.76
6	722.62
Mean	**722.27**

Dilution Hierarchy of Standards used for Comparison:

	Cylinder Number	Amount Fraction
Pure material	Takachiho	
Dilution 1	1103	9.99 %mol/mol
2	1122	1.00 %mol/mol
3	1125	990.15 µmol/mol
4	1109	99.91 µmol/mol
5	1112	10.00 µmol/mol
6	5702577	725.6 nmol/mol

Comparison Method:

The following is a description of a single comparison between an NPL Primary Standard and the unknown travelling standard. An NPL NO Primary Standard and the unknown standard are connected to the sample lines. The cylinder connection for each cylinder is purged by the following steps:

1. Ensure the needle valve is closed.
2. Tighten the cylinder connection.
3. Open cylinder valve to pressurise line up to needle valve.
4. Close cylinder valve.
5. Loosen cylinder connection to relieve pressure.
6. Repeat steps 4 and 5 four times.

Both cylinder valves are then opened. Flow from the first standard to be measured [the NPL Primary Standard] is directed through the analyser by setting a six-port valve (Valco) to the appropriate orientation. The flow is adjusted using a needle valve until a flow rate of 11 cc min-1 is achieved [as indicated by the mass flow meter]. Flow from the second standard to be measured [the unknown standard] is directed to the vent from the six-port valve. The system is purged for at least 30 minutes in order to condition the sampling lines and ensure the temperature of the analyser has stabilised. Data are then recorded for the NPL Primary Standard for a period of four minutes during which time the data logger transmits a value for NO and NOx to the computer every ten seconds. After four minutes the six-port valve is adjusted such that the flow from the travelling standard is diverted through the analyser and the flow from the NPL Primary Standard is diverted to the vent. This process is repeated a total of six times such that each standard is measured six times. The NPL Primary Standard is then measured again to complete a single comparison.

Ecophysics CLD 700 AL Chemiluminescent NO_x analyser	
Sample flow	0.7 litre/min
Linearity	+/- 1% of FSD
Minimum detectable concentration	1 nmol/mol
Noise at zero point (1s)	0.5 nmol/mol
Catalyst	Molybdenum

Estimation of Uncertainty:

Sources of uncertainty in the values of the reference standards prepared at NPL were identified as:

- Cylinder stability – there is some uncertainty due to drift in the standards prepared at NPL, between the date of preparation ands the date of use. We estimate this to be 0.3 nmol/mol.
- Gravimetry - the uncertainty in the gravimetric preparation of the comparison standards is 0.1 nmol/mol.
- Purity of source materials – the estimated uncertainty in the purity of the source material was up to 0.065% for both N_2O and NO_2. Resulting in a combined purity uncertainty of 0.13% (relative).

All of these uncertainties were of Type B and were combined with the standard deviation of the repeated measurements (0.83 nmol/mol).

Source of uncertainty (*k*=1)	**nmol/mol**
Standard deviation of 6 repeat measurements	0.83
Uncorrected cylinder drift	0.3
Gravimetric preparation	0.1
Purity estimation (of .13% (relative))	0.94
Total (combined in quadrature)	1.29

Result:

Measured value of cylinder 22412 on 31/08/2004 is

722.27 +/- 2.6 (*k*=2) nmol/mol.

NIST

Laboratory : NIST
Cylinder number : DW1740 (22396)

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO				

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO				

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO				

Measurement No.	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO				

Results: As the analysis was conducted over 4 days against different standards each day, the assignment of a concentration was not done each day. Only a final concentration was determined using all the combined data.

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	715 nmol/mol	2	7 nmol/mol

Reference Method:

An ambient NO/NO_2/NO_X Chemiluminescence analyzer (Thermal Environmental Corp. Model 42C NIST# 611034) was used as a comparator to measure NO and NO_X response ratios of each of the eight low NO working standards to the CCQM K26(a) test cylinder, NPL Cylinder# DW1740; over a period of several days. The NO/NO_X instrument was operated in the 0-1000 nmol/mol range with a signal averaging time of 120 seconds. The analyzer is equipped with a hot (634°C ± 5°C) stainless steel thermal converter which efficiently disassociates NO_2 and HNO_3 to NO when operating in the NO_x mode.

An example of the sampling sequence used is: NPL, AAL067379, NPL, AAL067379, NPL, AAL067379, NPL, AAL067379, NPL. This sequence yields four NO and NO_X ratios which were statistically averaged to yield one mean NO ratio and one mean NO_X ratio for each of the eight working standards compared to NPL cylinder DW1740. The average precision of the measured ratios was ± 0.13% rsd.

Calibration Standards:

NIST gravimetrically prepared eight nitric oxide in nitrogen gas mixtures whose nominal NO concentrations are between 500 nmol/mol and 1050 nmol/mol in specially treated 30 L aluminum cylinders (December, 1998). Several analyses have been performed over the past 5.5 years against NIST dynamic NO standards. These dynamic standards are generated by two independant NIST primary methods as follows: NIST Primary Method#1 thermally converts the output of a calibrated nitrogen dioxide permeation tube to NO diluted by a continuous flow of nitrogen from a calibrated mass flow controller to produce a known dynamic NO in N_2 standard. NIST Primary Method#2 uses the Environics Mass Flow dilution system to precisely dilute NIST SRM Lot Standards, certified versus primary standards, to produce a known dynamic NO in N_2 standard.

The stability of NIST"s low NO working standards has been monitored for more than 4 years by periodic analysis against dynamic NO standards produced by Method#1 The low NO working standards have been determined to be stable. Over the past twelve months, each of the low NO standards have been analyzed six times; three times referencing dynamic NO standards generated by Primary Method#1 and three times referencing dynamic NO standards generated by dynamic Method#2. The average of the three measurements referencing Method#1 was observed to be in close agreement with the average result referencing Method#2 for each of the working standards. The final NO concentration value was determined by combining both methods using a NIST SED algorithm called "BOB," which also calculates the combined uncertainty. The final assigned NO (=NO_X) concentration values along with an expanded uncertainty (k=2) for the eight NIST working standards used in this CCQM study are given below:

AAL067379	(489.5 ± 4.9) nmol/mol NO in N_2
AAL067386	(505.1 ± 5.0) nmol/mol NO in N_2
AAL067423	(739.0 ± 7.4) nmol/mol NO in N_2
AAL067426	(750.8 ± 7.5) nmol/mol NO in N_2
AAL067392	(935.1 ± 9.3) nmol/mol NO in N_2

AAL067427 (983.8 ± 9.8) nmol/mol NO in N_2
AAL067424 (1031.4 ± 10.3) nmol/mol NO in N_2
AAL067422 (1056.8 ± 10.6) nmol/mol NO in N_2

Instrument Calibration:

See Above

Sample Handling:

See Above

Uncertainty:

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Calibration Standards		Normal	3.58	1	3.58
GENLINE		Normal	1.28	1	1.28
Least Squares		Normal	0.26	1	0.26

Coverage factor: 2
Expanded uncertainty: GENLINE (and bleast) gave an unreasonably low uncertainty (below the uncertainty of the calibration standards) for the comparison cylinder. Therefore NIST used an algorithm used in determining SRM uncertainties, which gave an expanded uncertainty of 1 % relative, or 7 nmol/mol.

NMI

Laboratory : NMi - Van Swinden Laboratory
Cylinder number : 22414 or DW1759

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2004-07-22	$717{,}4 \cdot 10^{-9}$	0,09	1
	2004-07-22	$717{,}4 \cdot 10^{-9}$	0,11	1
	2004-07-22	$718{,}2 \cdot 10^{-9}$	0,17	1

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2004-07-26	$718{,}9 \cdot 10^{-9}$	0,09	1

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2004-08-06	$718{,}0 \cdot 10^{-9}$	0,12	1
	2004-08-09	$718{,}4 \cdot 10^{-9}$	0,07	1

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2004-08-26	$714{,}7 \cdot 10^{-9}$	0,15	1
	2004-08-26	$719{,}5 \cdot 10^{-9}$	0,08	1

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	$718 \cdot 10^{-9}$	2	$8 \cdot 10^{-9}$

Reference Method:

The measurements have been performed with a Model 17C Chemiluminescent Ammonia Analyzer, from Thermo Environmental Instruments Inc.
This monitor contains four analogue output channels for NO, NO_2, NO_x and NH_3. For the CCQM K26a measurements, only the NO channel has been used.

Calibration Standards:

Calibration has been performed using Primary Standard gas Mixtures (PSMs). All these mixtures have been prepared by the gravimetric method, according to ISO 6142:2001(E) Gas analysis - Preparation of calibration gas mixtures - Gravimetric method.
High purity NO and high purity N_2 are used to prepare high concentration mother mixtures of NO in N_2. Using the same method, these mixtures are diluted to daughters and granddaughters to achieve the appropriate concentrations.

Instrument Calibration:

At NMi Van Swinden Laboratory measurements are performed in ranges of amount-of-substance fractions. For this comparison the measurement range of 100-1000 nmol/mol NO in N_2 is selected. Given the specified nominal amount-of-substance fraction level in this comparison, the range has been limited to mixtures containing 400, 600, 800 and 1000 nmol/mol NO in N_2.

Sample Handling:

A pressure regulator from a dedicated set is connected on each cylinder. These reducers were cleaned at least 8 times by sequential purging. The purging process is spread over a two days period, in order to condition the material of the regulator. All cylinders are connected to an automatic sampler with a 16-port multi-position valve. Alternate samples of an NO mixture and pure nitrogen are taken to correct for baseline drift.
After a flushing time of 5 minutes 90 samples of the response (mV) are collected. The average and standard deviation of these 90 samples are used for calculations.

Uncertainty:

Measurements are performed according to ISO 6143:2001(E) Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures. For this purpose, a suite of four PSMs (Primary Standard gas Mixtures) ranging in amount-of-substance fraction level from 400 to 1000 nmol/mol NO (nominal) has been used. The results of a typical measurement are given in the table below. A straight line was used as calibration model throughout the measurements.

x nmol/mol	u(x) nmol/mol	y mV	u(y) mV
400.1	0.17	3989	10
601.8	0.26	5858	10
800.5	0.22	7736	10
1001.4	0.51	9588	10

The uncertainty given for the amount-of-substance fractions (*x*) is based on the gravimetry and purity verification only. Stability measurements indicated that for the (in)stability of these mixtures at least 1 nmol/mol uncertainty should be accounted for stability and between-cylinder effects. Taking the root–mean–square of these two uncertainty budgets leads to a standard uncertainty of about 1 nmol/mol on the PSMs. It is known that over several years, the standard uncertainty associated with this effect tends to increase up to 2 – 3 nmol/mol.

On the basis of these considerations a TLS–regression with a standard uncertainty of 2 nmol/mol on the amount-of-substance fractions of the PSMs results in a standard uncertainty associated with the amount-of-substance fraction of NO in the comparison cylinder of 3.7 nmol/mol. This estimate is the result of propagating the uncertainties associated with the composition of the PSMs and the responses. Allowing for some run-to-run effects, the over-all standard uncertainty is estimated to be 4 nmol/mol.

Coverage factor: 2
Expanded uncertainty: 8 ppb (95% level of confidence)

UBA(D)

Laboratory : Federal Environmental Agency of Germany (UBA)
Cylinder number : 22 4 11

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to 850 .10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	07-20-04	713,3 E-09	0,02	4

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	07-21-04	715,3 E-09	0,03	4

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	07-21-04	714,3 E-09	0,05	4

Measurement No. 4	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	07-22-04	712,2 E-09	0,03	4

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	713,8 E-09	2	± 5,82 E-09

Reference Method:

For analyzing nitrogen monoxide at the UBA laboratory a chemiluminescence method based monitor HORIBA APNA 360 CE is used.

Calibration Standards:

Calibration standard is prepared by volumetric static injection.

Known volumes of the pure gas compound are added to the complementary gas in a vessel of well-defined volume .
The method is described at ISO 6144 and VDI 3490. p. 14

Equipment:

Cast iron vessel coated with enamel inside	0.014736 m^3 max. pressure 1000 kPa
Pressure gauge	0-1000 kPa Diptron 3 Wallace&Tiernan
Temperature gauge	SPE-Pt 100 Schwille
Vacuum pump	vacuubrand

Operating material:

Digital microliter syringe	100 µl Hamilton series 1710
Nitrogen (balance gas)	5.0 Messer (impurities: O_2, H_2O, Ar < 5ppm)
Nitrogen monoxide	2.5 Messer; certified by NMI Netherlands

After evacuation the vessel is filled with nitrogen at ambient air pressure and temperature. The pure gas is injected by syringe. After that the pressure is increased by introducing additional complementary gas(9-fold ambient air pressure).The mixture have to re-equilibrate to ambient temperature.
The whole procedure is done in accordance with ISO 6144.

Instrument Calibration:

Bracketing -Two-point Calibration
The low and the high standards were prepared by static volumetric injection method .The concentrations were chosen after measuring the unknown gas by our reference analyzer.

Measurement result:	713 nmol/mol
High standard:	726 nmol/mol
Low standard:	711 nmol/mol

The concentrations were prepared by two different final pressures.

High standard: $p_2 = 9{,}3 \cdot p_1$
Low standard: $p_2 = 9{,}5 \cdot p_1$

Sample Handling:

After arriving the cylinder was kept three weeks in the laboratory (stabilization).In order to take samples at ambient air pressure a pressure regulator was used and via T-piece a little overflow was controlled by a valve. For connecting with the monitor sample inlet ¼" Teflon tubes and stainless steel fittings were used.
The gas flow was about 1.3 l/min.
For this intercomparison we took after a running-in period of the pressure regulator (15min.)
4 samples (5 min.) for each measurement result.

Uncertainty:

$$u_c^2 = u_1^2 + s_R^2 + s^2(\bar{q}) \qquad (1)$$

u_c = Combined uncertainty

u_1 = Combined uncertainty given by static injection method at both bracketing points

s_R = Reproducibility of the static injection method in UBA laboratory

$s^2(\bar{q})$ = Estimate of the variance of the mean $\qquad s^2(\bar{q}) = \frac{s^2(q_k)}{4} \qquad (2)$

Calculation of u_1 according to ISO Guide GUM supported by GUM Workbench software.
In this calculation is shown the route of traceability to SI.
The result is valid for both bracketing points.

u_1 = 2,57 nmol/mol

s_R = 1,32 nmol/mol

$s^2(\bar{q})$ = 0,33 nmol/mol (2)

u_c = 2,91 nmol/mol (1)

Coverage factor: 2

Expanded uncertainty: ± 5,82 nmol/mol

Uncertainty calculation of the Static Volumetric Method for the preparation of NO primary standard gas mixtures

The procedure is described in ISO 6144

Model Equation:

$$\mathbf{C = C_p \cdot} \frac{V_s \cdot p_1}{V_d \cdot p_2} \qquad (3)$$

List of Quantities:

Quantity	Unit	Definition
C		Volume fraction in the resulting mixture of NO
C_p		Volume fraction of the pure gas NO
V_s	l	Injected volume by syringe
V_d	l	Volume of the vessel (balance gas)
p_1	kPa	Pressure in the syringe
p_2	kPa	Final pressure in the vessel

C:
Result

C_p:
Type B rectangular distribution
Value: 0.993
Halfwidth of Limits: 0.0035

V_s:
Type B rectangular distribution
Value: $100 \cdot 10^{-6}$ l
Halfwidth of Limits: $0.5 \cdot 10^{-6}$ l

V_d:
Type A
Method of observation: Direct
Number of observation: 5

No.	Observation
1	14.730
2	14.741
3	14.735
4	14.740
5	14.737

Arithmetic Mean: 14.73660 l
Standard Deviation: $4.4 \cdot 10^{-3}$ l

Standard Uncertainty: $1.96\cdot10^{-3}$ l
Degrees of Freedom: 4

p_1:
Type B rectangular distribution
Value: 101.3 kPa
Halfwidth of Limits: 0.04 kPa

p_2:
Type B rectangular distribution
Value: 942.1 kPa
Halfwidth of Limits: 0.38 kPa

Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Index
C_p	0.99300	$2.02\cdot10^{-3}$	∞	rectangular	$730\cdot10^{-9}$	32.9 %
V_s	$100.0\cdot10^{-6}$ l	$289\cdot10^{-9}$ l	∞	rectangular	$7.2\cdot10^{-3}$	66.1 %
V_d	14.73660 l	$1.96\cdot10^{-3}$ l	4	normal	$-49\cdot10^{-9}$	0.1 %
p_1	101.3 kPa	$23.1\cdot10^{-3}$ kPa	∞	rectangular	$7.2\cdot10^{-9}$	0.4 %
p_2	942.1 kPa	0.219 kPa	∞	rectangular	$-770\cdot10^{-12}$	0.4 %
C	$724.54\cdot10^{-9}$	**$2.57\cdot10^{-9}$**	∞			

Result: valid for both bracketing points
Quantity: C
Value: $724.5\cdot10^{-9}$
Uncertainty: **$2.57\cdot10^{-9}$**

<u>VNIIM</u>

Key Comparisons CCQM-K26 a

Nitrogen monoxide at the ambient level

REPORT

Authors: **L.A. Konopelko**
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Reference method

Nitrogen oxide molar fraction in nitrogen was determined by chemiluminescence technique.

The analysis was carried out on gas analyzer “AC-30M” (Environnement S.A., France), which is a part of apparatus of State primary standard of the units of components’ mole fraction and mass concentration in gas media GET 154.

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in table 1.

Table 1 – Description of pure components

Substance	Molar fraction, ppm	Standard uncertainty, ppm	Relative standard uncertainty, %
Nitrogen oxide	**996170**	**512**	**0,05**
Nitrogen	**999988,5**	**0,812**	**0,00008**

Preparation of standard binary gas mixture was carried out in 3 stages

<u>1 stage</u>:

Preparation of binary gas pre-mixture NO/N_2 with nitrogen oxide molar fraction of ≈ 0,5 %.

There were prepared two pre-mixtures with molar fraction 0,4915 % и 0,4993 %.

These pre-mixtures were prepared in stainless overwrapped cylinders. Verification of molar fraction was carried out on IR-Fourier spectrometer ФСМ 1202 (“Monitoring” Russia). Discrepancy between the cylinders was not found out in measurements. Standard deviation for each measurement series was not more than 0,2 %.

<u>2 stage</u>:

Preparation of binary gas pre-mixture NO/N_2 with nitrogen oxide molar fraction of ≈ 50 ppm.

There were prepared also two pre-mixtures (each of its own parent pre-mixture) with molar fraction 48,82 и 49,98 ppm.

These pre-mixtures were also prepared in stainless overwrapped cylinders. Verification of molar fraction in these mixtures was carried out on IR-Fourier spectrometer ФСМ 1202 (“Monitoring” Russia). Discrepancy between the cylinders was not found out in measurements. Standard deviation for each measurement series was not more than 0,2 %.

3 stage:

Preparation of standard binary gas mixture NO/N_2 with nitrogen oxide molar fraction of ≈ 0,7 ppm.

There were prepared also two standard binary gas mixtures (each of its own parent pre-mixture) with molar fraction 0,6526 и 0,7482 ppm.

These mixtures were also prepared in stainless overwrapped cylinders. Verification of molar fraction in these mixtures was carried out on gas analyzer “AC-30M”. Discrepancy between the cylinders was not found out in measurements. Standard deviation for each measurement series was not more than 0,3 %.

In order to check the possible sorption in the cylinder prepared gas mixture was transferred to the other cylinder of the same type. Comparative analysis of these two cylinders was carried out on gas analyzer “AC-30M”. Standard uncertainty of sorption taking into account long-term instability is 0,6 %.

The uncertainty budget of nitrogen oxide molar fraction in the calibration standards is shown in Appendix A.

The characteristics of calibration standards are shown in table 2.

Table 2 – Characteristics of calibration standard

Cylinder №	Substance	Molar fraction, ppm	Relative standard uncertainty, %
6374	Nitrogen oxide	**0,6526**	**0,625**
	Nitrogen	**balance**	
6367	Nitrogen oxide	**0,7482**	**0,624**
	Nitrogen	**balance**	

Instrument calibration

The method of absolute calibration (comparison method) was used.

There were made 5 independent measurements under repeatability conditions with 5 independent calibrations (in 5 days during 10 days). One single measurement consisted of 3 sub-measurements. The measurement sequence was “calibration→measurement”.

Sample handling

Prior to measurements cylinders were stabilized to room temperature.

Results of measurements

Results of measurements of nitrogen oxide molar fraction in cylinder № 22403 are shown in the table 3

Table 3 - Results of measurements of nitrogen oxide molar fraction in cylinder № 22403

№	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
1	05.10.04	712,3	712,0	0,043
		711,7		
		712,1		

№	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
2	08.10.04	712,1	712,2	0,024
		712,4		
		712,0		

№	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
3	11.10.04	714,0	711,1	0,29
		710,0		
		709,4		

№	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
4	12.10.04	711,9	711,9	0,013
		713,0		
		710,7		

№	Date (d/m/y)	Measured value, nmol/mol	Mean value, nmol/mol	Standard deviation (% relative)
5	14.10.04	709,2	709,5	0,041
		709,4		
		709,9		

Evaluation of uncertainty of measurement

Total standard uncertainty of nitrogen oxide molar fraction was calculated on the base of the following components:

- total standard uncertainty of nitrogen oxide molar fraction in standard gas mixture including gravimetry and sorption by cylinder’s walls (look Appendix A);

- standard deviation of the measurement results of nitrogen oxide molar fraction in gas mixture in cylinder № 22403.

Uncertainty budget for nitrogen oxide molar fraction in investigated gas mixture is shown in the table 4.

Table 4 – Estimation of uncertainty of nitrogen oxide molar fraction in gas mixture in cylinder

№ 22403, presented for comparison

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, %	Coefficient of sensitivity	Contribution $U_i(y, \%)$
Preparation of standard gas mixture (gravimetry)	**B**	**0,176**	**1**	**0,176**
Sorption of the component by cylinder's walls and long-term instability of standard gas mixture	**B**	**0,60**	**1**	**0,60**
Standard deviation of the results of measurements of nitrogen oxide molar fraction	**A**	**0,070**	**1**	**0,070**
Total standard uncertainty				**0,63**
Expanded uncertainty (*k*=2)				**1,3**

Final result of measurements

Final result of measurements of nitrogen oxide molar fraction in investigated gas mixture is shown in the table 5.

Table 5– Obtained value of nitrogen oxide molar fraction in gas mixture in cylinder

№ 22403 and expanded uncertainty

Substance	**Result, nmol/mol**	**Expanded uncertainty, %**	**Coverage factor**
Nitrogen oxide	**711,3**	**1,3**	**2,0**
Nitrogen	**остальное**	—	—

Appendix A

Uncertainty budget for nitrogen oxide molar fraction in standard gas mixture

1.1 Uncertainty budget for nitrogen oxide molar fraction in standard gas mixture with molar fraction 0,6526 ppm (gravimetry)

№	Source of uncertainty	Relative standard uncertainty,%
1	Content of the main component in the parent substance	**0,051**
2	Weighing of the 1 pre-mixture	**0,078**
3	Weighing of the 2 pre-mixture	**0,094**
4	Weighing of the standard gas mixture	**0,116**
Total standard uncertainty		**0,176**

1.2 Uncertainty budget for nitrogen oxide molar fraction in standard gas mixture with molar fraction 0,7482 ppm (gravimetry)

№	Source of uncertainty	Relative standard uncertainty,%
1	Content of the main component in the parent substance	**0,051**
2	Weighing of the 1 pre-mixture	**0,082**
3	Weighing of the 2 pre-mixture	**0,087**
4	Weighing of the standard gas mixture	**0,111**
Total standard uncertainty		**0,171**

2.1 Uncertainty budget for nitrogen oxide molar fraction in standard gas mixture with molar fraction 0,6526 ppm (including sorption)

№	Source of uncertainty	Relative standard uncertainty,%
1	Content of the main component in the parent substance	**0,051**
2	Weighing of the 1 pre-mixture	**0,078**
3	Weighing of the 2 pre-mixture	**0,094**
4	Weighing of the standard gas mixture	**0,116**
5	Sorption of the component by cylinder's walls and long-term instability of standard gas mixture	**0,60**
Total standard uncertainty		**0,625**

2.2 Uncertainty budget for nitrogen oxide molar fraction in standard gas mixture with molar fraction 0,7482 ppm (including sorption)

№	Source of uncertainty	Relative standard uncertainty,%
1	Content of the main component in the parent substance	**0,051**
2	Weighing of the 1 pre-mixture	**0,082**
3	Weighing of the 2 pre-mixture	**0,087**
4	Weighing of the standard gas mixture	**0,111**
5	Sorption of the component by cylinder's walls and long-term instability of standard gas mixture	**0,60**
	Total standard uncertainty	**0,624**

Pilot study participants:

METAS

Laboratory : METAS
Cylinder number : **SER NO P2777L / DW 18666**

NOMINAL COMPOSITION
- nitrogen monoxide : 600 to $850 \cdot 10^{-9}$ mol/mol

Measurement No. 1	Date	Result (mol/mol)	number of sub-measurements
NO	13 July 04	$715.1 \cdot 10^{-9}$	74

Measurement No. 2	Date	Result (mol/mol)	number of sub-measurements
NO	14 July 04	$715.2 \cdot 10^{-9}$	43

Measurement No. 3	Date	Result (mol/mol)	number of sub-measurements
NO	14 July 04	$712.8 \cdot 10^{-9}$	51

Measurement No. 4	Date	Result (mol/mol)	number of sub-measurements
NO	14 July 04	$712.6 \cdot 10^{-9}$	67

Measurement No. 5	Date	Result (mol/mol)	number of sub-measurements
NO	15 July 04	$714.5 \cdot 10^{-9}$	81

Measurement No. 6	Date	Result (mol/mol)	number of sub-measurements
NO	26 July 04	$714.3 \cdot 10^{-9}$	75

Measurement No. 7	Date	Result (mol/mol)	number of sub-measurements
NO	26 July 04	$714.9 \cdot 10^{-9}$	44

Measurement No. 8	Date	Result (mol/mol)	number of sub-measurements
NO	27 July 04	$714.1 \cdot 10^{-9}$	109

Measurement No. 9	Date	Result (mol/mol)	number of sub-measurements
NO	28 July 04	$715.2 \cdot 10^{-9}$	146

Results (combined results from measurement No. 1 to 9):

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	$714.3 \cdot 10^{-9}$ mol/mol	2	$4.4 \cdot 10^{-9}$ mol/mol

Reference Method:

Calibration of a Chemiluminescence NO-Analyzer with NO calibration standards in the range
from 600 to $850 \cdot 10^{-9}$ mol/mol NO in N_2 for measurement 1
and
from 700 to $730 \cdot 10^{-9}$ mol/mol NO in N_2 for measurements 2 to 9.

The NPL-test mixture P2777L/DW18666 was measured with the NO-Analyzer and the amount of substance fraction of NO (*X(NO)*) calculated by linear interpolation.

Calibration Standards:

The calibration standards were produced by dilution of two METAS NO-standards (with an amount of substance fraction of NO in N_2 of about $60 \cdot 10^{-6}$ mol/mol) with nitrogen of a quality of 99.999 %.

METAS NO-Standards:	
CB 7935	$(60.18 \pm 0.25) \cdot 10^{-6}$ mol/mol NO in N_2
SL 75139	$(60.65 \pm 0.25) \cdot 10^{-6}$ mol/mol NO in N_2

Flow Standards:
Molbox-molbloc 5000 ml/min, SN 742, 2262
Molbox-molboc 50 ml/min, SN 742, 2344
The Flow Standards were calibrated with the METAS Primary Standard for Low Gas Flows.

Instrument Calibration:

The first instrument calibration (measurement No. 1) was done with a wider measurement range of 600 to $850 \cdot 10^{-9}$ mol/mol NO in N_2 to evaluate the amount of substance fraction of NO in the test mixture. All dilutions were made with the same METAS NO-Standard (CB 7935).
For the following calibrations (measurements No. 2 to 9) dilutions with *X(NO)* ≈ 700 to $730 \cdot 10^{-9}$ mol/mol NO in N_2 were made with both METAS NO-Standards (CB 7935 and SL 75139).

Sample Handling:

Stainless steal pressure regulators with a flushing system were used for the test mixture as well as for the METAS NO-Standards. Several flushing cycles with N_2 and wit the NO gas mixture were carried out.

After stable readings of the NO analyzer, data were sampled for at least ten minutes.

Uncertainty:

Covariances between the calibration standards were taken into account. The Uncertainty budget has been established using the GUM Workbench Pro software. Uncertainty contributions below 1% are not listed.

Example for measurement 6

Uncertainty source	Value	Assumed distribution	Standard uncertainty	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
X_A	60.647 ppm	normal	0.128 ppm	$6.1\cdot10^{-3}$	0.78 ppb
X_B	60.181 ppm	normal	0.124 ppm	$5.7\cdot10^{-3}$	0.70 ppb
X_N	0.7 ppb	triangle	0.2 ppb	0.99	0.20 ppb
q_{A1}	24.653 ml/min	normal	0.062 ml/min	$5.2\cdot10^{-3}$	0.32 ppb
q_{A2}	24.656 ml/min	normal	0.062 ml/min	$5.0\cdot10^{-3}$	0.31 ppb
q_{A3}	24.652 ml/min	normal	0.062 ml/min	$4.7\cdot10^{-3}$	0.29 ppb
q_{B4}	24.856 ml/min	normal	0.062 ml/min	$4.4\cdot10^{-3}$	0.27 ppb
q_{B5}	24.858 ml/min	normal	0.062 ml/min	$4.1\cdot10^{-3}$	0.25 ppb
q_{B6}	24.654 ml/min	normal	0.062 ml/min	$5.1\cdot10^{-3}$	0.32 ppb
q_{N1}	2136.3 ml/min	normal	3.2 ml/min	$-60\cdot10^{-6}$	-0.19 ppb
q_{N2}	2094.9 ml/min	normal	3.1 ml/min	$-59\cdot10^{-6}$	-0.18 ppb
q_{N3}	2051.1 ml/min	normal	3.1 ml/min	$-57\cdot10^{-6}$	-0.18 ppb
q_{N4}	2014.2 ml/min	normal	3.0 ml/min	$-54\cdot10^{-6}$	-0.16 ppb
q_{N5}	1973.1 ml/min	normal	3.0 ml/min	$-51\cdot10^{-6}$	-0.15 ppb
q_{N6}	2110.0 ml/min	normal	3.2 ml/min	$-60\cdot10^{-6}$	-0.19 ppb
Combined standard uncertainty					**2.17 ppb**

Explanation of symbols:
X_A: X(NO) of METAS NO-Standard SL 75139
X_B: X(NO) of METAS NO-Standard CB 7935
X_N: X(NO) in dilution N2 (impurity)

q_{Ai}: Flow of NO-Standard SL 75139 for NO Calibration Standard i
q_{Bi}: Flow of NO-Standard CB 7935 for NO Calibration Standard i
q_{Ni}: Flow of dilution N2 for NO Calibration Standard i

With a coverage factor of 2 the expanded uncertainty is 4.4 ppb.

Annex F – Contact details for participating laboratories

Laboratory	Country	Contact name	Delivery address
Key comparison participants			
CENAM	Mexico	Alejandro Perez	Centro Nacional de Metrología Km. 4.5 Carretera a los Cués Municipio El Marqués 76241 Querétaro México
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CHMI	Czech Republic	Jiri Novak	Czech Hydrometeorological Institute Na Sabatce 17 143 06 Praha 4 Czech Republic
FMI	Finland	Jari Walden	Finnish Meteorological Institute Air Quality Research Sahaajankatu 20 E 00880 HELSINKI FINLAND
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Pilot study participants			
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