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Key Comparison of nitrogen monoxide in nitrogen relevant to ambient levels (EURAMET QM-K26a / Project 1183)

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National
Measurement
System

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Approved on behalf of NPLML by Michael Adeogun, Division Head.

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1 INTRODUCTION

Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are known generally as nitrogen oxides (NO_x) and constitute two of the key species regulated by Directive 2008/50/EC on Ambient Air Quality and Cleaner Air for Europe. Both gases exert a major influence on oxidation processes in the troposphere and a controlling role in free radical chemistry [1] taking part in complex chemical and photochemical reactions with tropospheric ozone, hydroxyl radical and peroxy radicals. Routine measurements of these compounds in air are carried out by the competent authorities of each Member State to fulfil the requirements of Directive 2008/50/EC and also by cooperative programmes such as EMEP (European Monitoring and Evaluation Programme) and WMO GAW (World Meteorological Organisation - Global Atmosphere Watch). Standards gas mixtures of NO in N_2 at parts-per-billion levels are required to disseminate traceability to stations monitoring NO_x in ambient air.

A previous NO/N_2 comparison was carried out in 2004/2005 (CCQM-K26a) [2] and was also coordinated by NPL. The amount fraction level of NO in the primary reference standards was ~720 nmol/mol and 7 out of 12 participants were from EURAMET (European Association of National Metrology Institutes). It is generally considered that the state of the art for measurements of nitrogen monoxide in nitrogen has improved significantly since CCQM-K26a. This was shown on the 200 nmol/mol NO in N_2 bilateral comparison EURAMET 1084 carried out in 2009 by NPL and LNE, where relative uncertainties were lower than 1%. For this reason, another key comparison was proposed, aiming to test the analytical capabilities of National Metrology Institutes (NMIs) to analyse a NO/N_2 mixture at a nominal amount fraction of 450 nmol/mol NO/N_2. Of the 15 participants, 5 in EURAMET already have Calibration and Measurements Capabilities (CMCs) in this area (NPL, VSL, LNE, UBA(D) and FMI). In addition, several other NMIs have CMCs for the analysis of nitrogen monoxide at higher amount fractions.

2 APPLICABILITY OF THIS KEY COMPARISON TO CMC CLAIMS

EURAMET QM-K26a (designated EURAMET Project 1183) was designed to evaluate the level of comparability of the analytical capabilities of laboratories for nitrogen monoxide in nitrogen at 450 nmol/mol.

The following statement for "how far the light shines" was agreed by the CCQM GAWG in April 2004 for K26a and it has therefore been applied to this comparison:

"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."

3 OVERVIEW OF THE COMPARISON

Standards at 450 nmol/mol were prepared commercially and certified at the coordinating laboratory (NPL). These standards were then despatched to each participant for measurement. On return, each travelling standard was re-measured by the coordinating laboratory. The drift of the amount fraction of the travelling standards and the degree of equivalence for each participating laboratory were calculated by the coordinating laboratory.

4 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 at high pressures and in the absence of any balance gas [2]. However, when NO is diluted to an amount fraction of 10 mmol/mol, the rate for this reaction is negligible at room temperature. The other reaction that can limit the stability of NO standards is 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 due to adsorption processes on the cylinder walls. 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 BOC Speciality Gases for the comparison. Pure NO was manufactured by AGA Gases and diluted in pure N_2 (with oxygen content less than 5 nmol/mol) to form a 1 mmol/mol pre-mixture. All of the travelling standards were prepared by dilution of this pre-mixture at BOC Speciality gases in 10 litre aluminium (Luxfer) cylinders pre-treated with Spectraseal (BOC Speciality Gases) and with DIN-1 outlet connections. They were filled with a blend to a total pressure of 200 bar.

The batch was analysed on arrival at the coordinating laboratory by comparison with a reference standard generated by dynamic dilution, and a sub-set was selected for use as travelling standards for the comparison. The selection was based on the proximity of the measured concentration to the target concentration (450 nmol/mol) and also on the lowest decay rates obtained from the measurements.

5 PREPARATION OF GRAVIMETRIC STANDARDS BY THE COORDINATING LABORATORY

The hierarchy of NO/N_2 standards used to underpin this comparison is shown in Figure 1. A 10 μmol/mol NO/N_2 standard (NPL 1366) was diluted by means of a molbloc facility and used to validate the travelling standards. Figure 2 shows comparative measurements of NPL 1366 against three Primary Reference Gas Mixtures (PRGMs). Agreement between the gravimetric value and the certified value was in all cases better than 0.5%. NPL 1366 was also validated before each set of travelling standards measurements to check that the drift in the amount fraction was negligible.

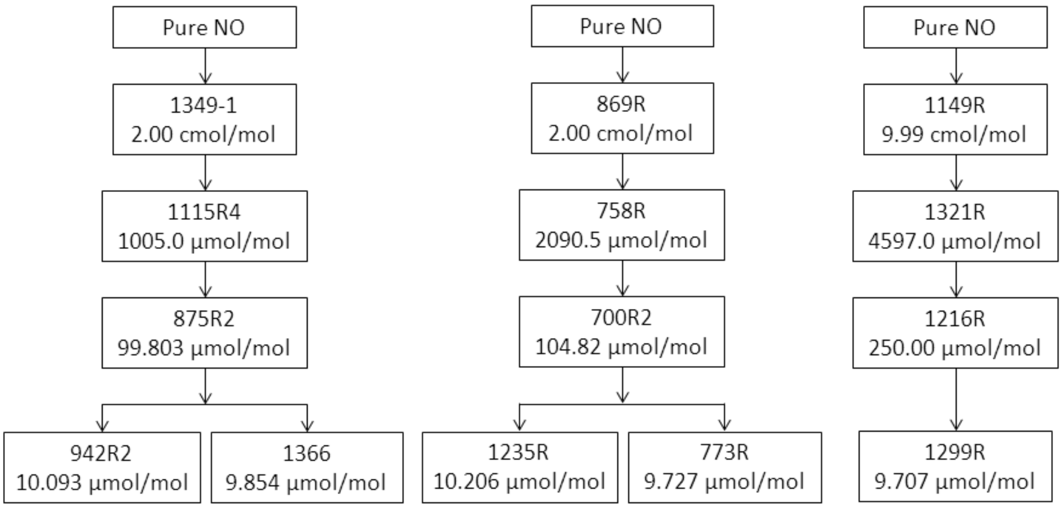

Figure 1 The hierarchy of the gravimetric standards of NO/N_2 prepared gravimetrically by the coordinating laboratory.

Table 1 Dates of manufacture of standards by the coordinating laboratory at 10 µmol/mol (nominal) level.

Cylinder number	Preparation date
1299R	02/10/2009
942R2	23/03/2011
1366	26/04/2011
1235R	15/04/2011
773R	22/03/2011

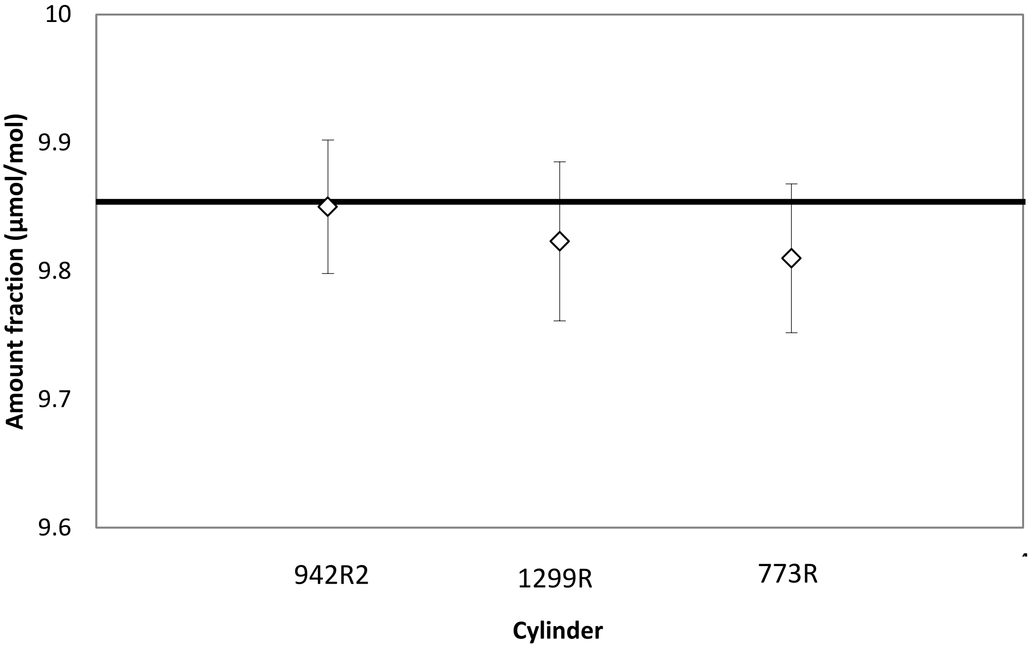

Figure 2 Validation of NPL 1366 against three PRGMs. The solid black line represents the gravimetric amount fraction of NPL 1366. The bars represent 2 standard deviations of each measurement set.

6 HIGH ACCURACY MOLBLOC DILUTION FACILITY

The dynamic gas mixture used for validating the travelling standards is produced by blending a 10 µmol/mol PRGM of nitrogen monoxide with nitrogen (Air products, BIP). The diluent gas is passed through three filters containing silica gel, Purafil and charcoal (Thermo Fisher Scientific) to ensure it is free from the target gas and other impurities such as water. The flows of the diluent and the PRGM are regulated by a 20 mg/s full-scale Viton seal (Brooks SLA5850-SE1AB1B2A1) and a 2 mg/s full scale metal seal (Brooks SLA7950-S1EGG1B2A1) thermal mass flow controllers respectively. The mass flow of each gas is measured accurately with ‘molbloc-L’ laminar mass flow elements (DHI, models 1E3-VCR-V-Q and 1E2-VCR-V-Q for the target and balance gases, respectively), located upstream, and matched to the full scale setting of the mass flow controllers. A schematic of the system is shown in Figure 3.

Each molbloc measures the upstream and downstream pressure using built-in high precision reference pressure transducers (RPTs). An ohmic measurement system reads the resistance of the molbloc platinum resistance thermometers from which the temperature of the molbloc is calculated. The mass flow of the gas through each molbloc is calculated using the measured pressures and temperature. The pressures of the PRGM and diluent gas are controlled by two pressure regulators (LNI Schmidlin SA) that are set to maintain equal input pressures of nominally 3.0 bar absolute to the molblocs (to ensure they are operating at a pressure within the range in which they were calibrated). The RPTs in each molbloc are programmed for the appropriate balance gas, purged with the gas to be used and set equal prior to measurement. A two-way valve is used to either flow the generated reference gas or the travelling standard into an analyser. Two lines venting to atmosphere ensure that the blend and test mixture are flowing continuously, ensuring that an equilibrium is maintained. The excess flow of the blended gas is matched to that of the test mixture to ensure there is no change in upstream pressure to the analyser. Two shut off valves on each input to the blending manifold allow the molblocs to be isolated under pressure for routine leak checks. All manifolds are constructed of stainless steel tubing and the surface area is kept to a minimum to reduce contamination effects from build-up or release of the target gas in the system. The components in the system have been mounted on a dual molbloc mounting system (DHI, model Molstic) to reduce the ambient vibration levels.

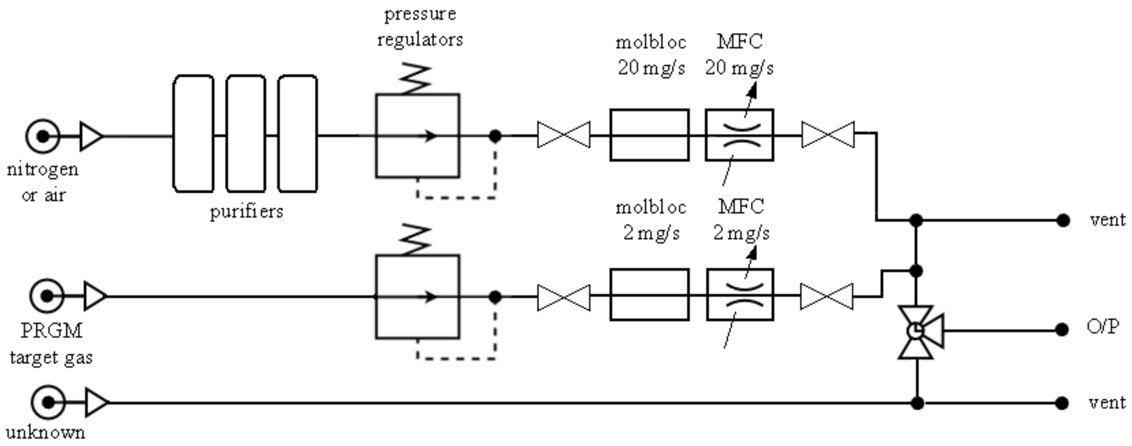

Figure 3 Schematic of the high accuracy dilution system. The output (O/P) is connected to a gas analyser. A two-way valve is used to alternate the flow of the blend and unknown to the analyser.

To check the performance of the dynamic dilution facility, the certification of two NO/N_2 PRGMs (499 and 495 nmol/mol) was carried out. Three different PRGMs of NO/N_2 (with amount fractions of 9.95, 9.90 and 10.14 µmol/mol) were diluted using the dynamic dilution system. In all cases the relative difference between the gravimetric value of the standard and the certified value was better than 0.5% which proves the capability of the dilution system to generate accurate and stable standards (Figure 4).

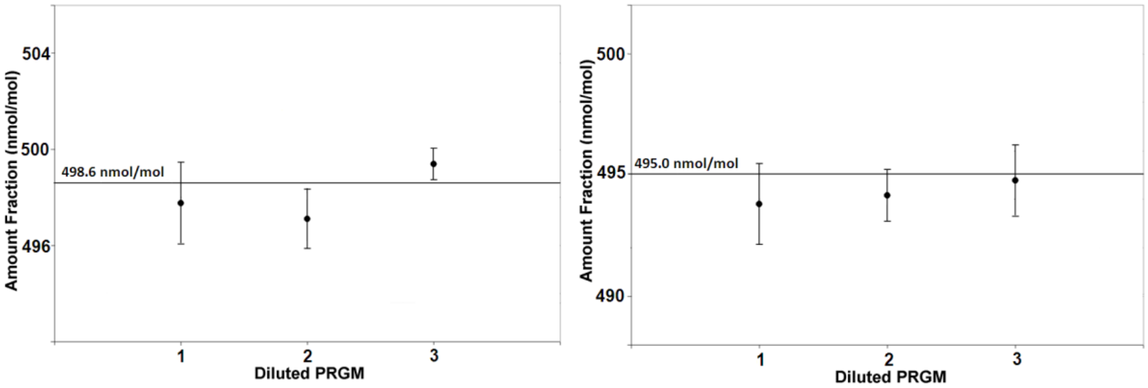

Figure 4 Validation of the dynamic dilution facility by means of the certification of two different 500 nmol/mol standards with three different PRGMs.

7 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 determined at the time when it was analysed by each participant. Before each standard was despatched to the participant, it was analysed three times (monthly) against one of the standards held by the coordinating laboratory (NPL 1366). Similarly, each travelling standard was re-analysed a further three times (monthly) 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 by means of an ordinary-least squares method using the software XLGENLINEv1.1. In Figure 5, an example of the amount fraction drift in one of the cylinders is given. In all cases it was found that a straight line was a good fit to the data. The use of a straight line fit is further justified because it is consistent with typical chemical decay or absorption processes over a small range of amount fractions [2]. Besides, NPL's experience suggests that the linear model is correct over much longer time scales. The straight lines were of the form:

$$Z_{ij} = Z_{i0} + m_i t_j \tag{1}$$

where Z_{ij} is the NO amount fraction (nmol/mol) in the travelling standard i at the time t_j (defined with respect to the measurement time of the participating laboratories at t_j=0 such that Z_{i0} (nmol/mol) is the estimation of the concentration at time t_j=0, when the participant carried out its measurement). Therefore, this value was directly obtained from the y-intercept of each adjustment. The uncertainty of the estimated amount fraction was obtained from the uncertainty associated with the estimation of the y-intercept given by the XLGENLINEv1.1 software. The gradients m_i of the corresponding lines represent the estimated decay rates (nmol.mol^{-1}.day^{-1}) of each travelling mixture. 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 (Eq. 2)

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

The values of the decay rate and the estimated amount fraction at time t_j=0 for each travelling standard are shown in Table 2.

Figure 6 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 -0.0199 nmol.mol^{-1}.day^{-1}. This median drift corresponds to a drift of 0.8% over 6 months calculated at the nominal amount fraction of 450 nmol/mol.

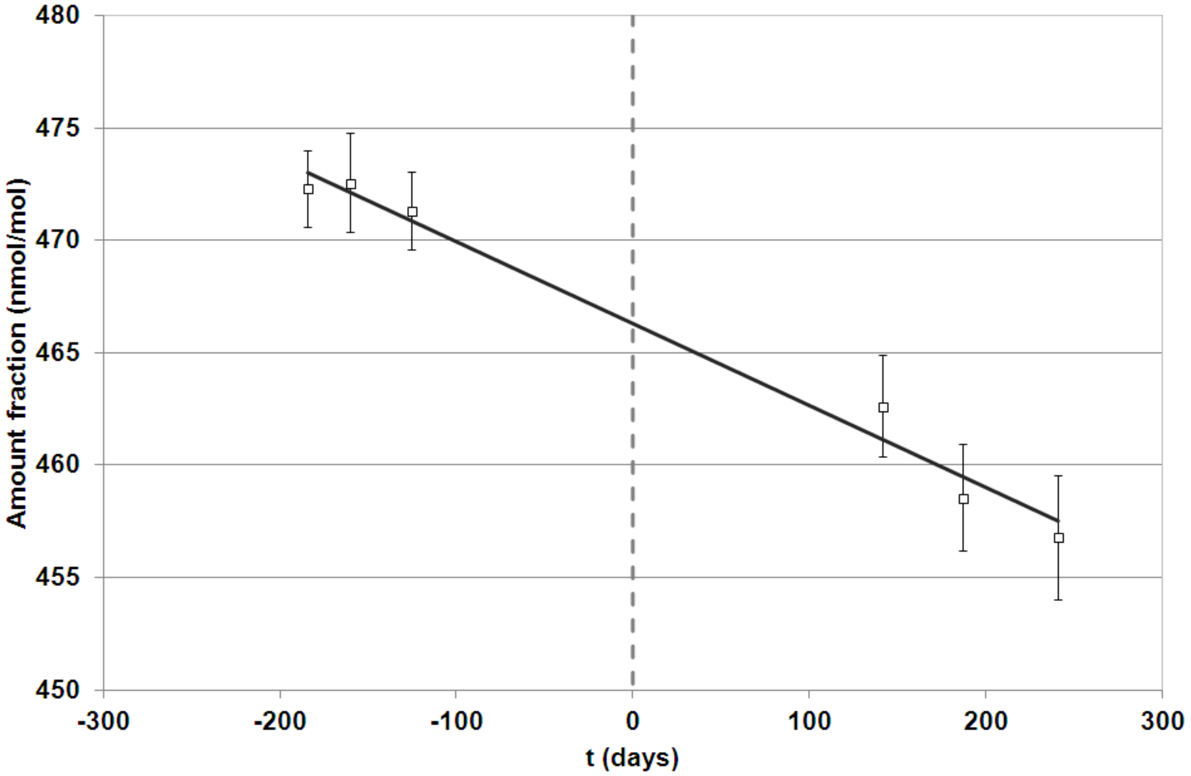

Figure 5 Example of the estimation of the drift in the amount fraction experienced in one of the travelling standards. The regression line has been fitted by ordinary least squares. The *x*-axis represents the time difference between measurements, taking as the reference the date when the participant carried out its measurements (t_j=0). The error bars indicate the standard uncertainty.

Table 2 Estimated drift, m_i, for each travelling standard and estimated amount fraction, Z_{i0}, at time t_j=0 when analysed by the participating laboratory (corresponds to *y*-intercept Figure 5).

Standard Identifier	Estimated Drift m_i [nmol.mol^{-1}.day^{-1}]	Standard Error of m_i [nmol.mol^{-1}.day^{-1}]	Z_{i0} [nmol.mol^{-1}]	$u(Z_{i0})$ [nmol.mol^{-1}]
219509	-0.01705	0.00485	434.38	0.85
219515	-0.01405	0.00412	444.50	0.77
219516	-0.03673	0.00558	442.32	1.11
219517	-0.01468	0.00615	437.23	0.98
219518	-0.04997	0.00473	461.70	0.91
219519	-0.01825	0.00513	438.52	0.85
219520	-0.00551	0.00700	430.36	1.17
219522	-0.04461	0.00525	453.16	0.93
219523	-0.04342	0.00466	455.24	0.83
219524	-0.02936	0.00506	440.60	0.94
219529	-0.01126	0.00507	445.53	0.85
219530	-0.01989	0.00483	438.02	0.82
221863	-0.03646	0.00511	466.31	0.87
221864	-0.01583	0.00456	427.21	0.81
221882	-0.02758	0.00459	457.68	0.87

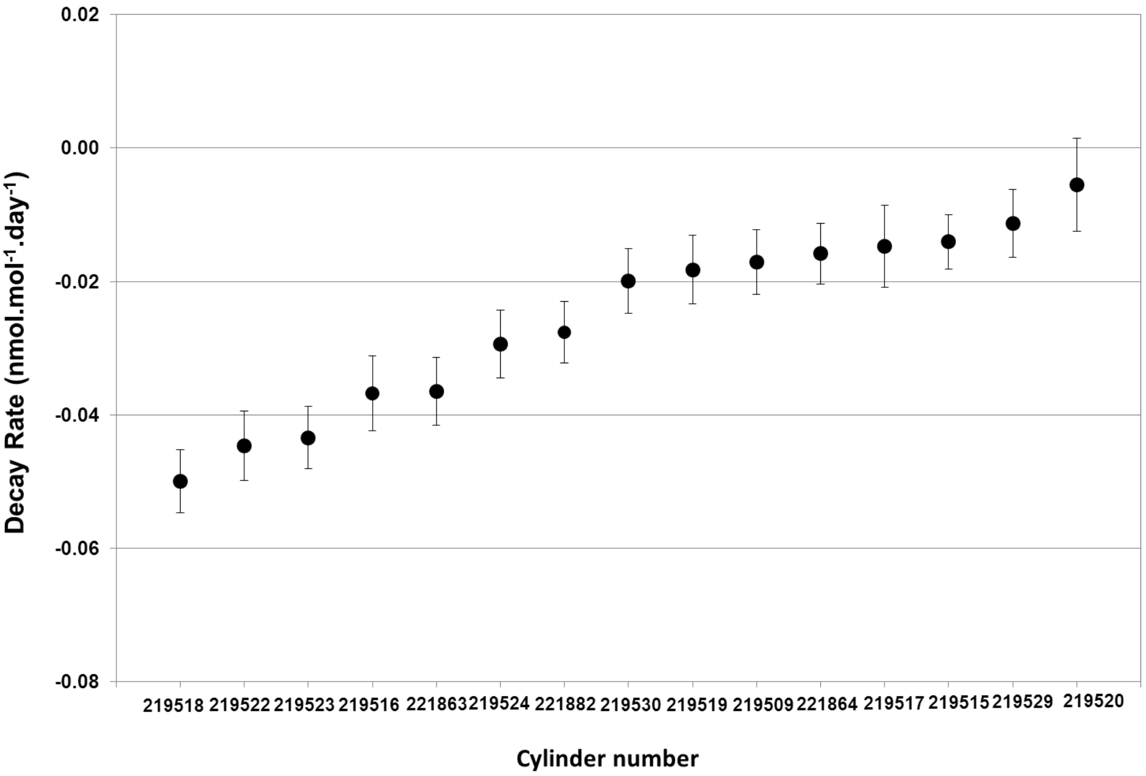

Figure 6 Estimated drifts of the travelling standards listed in Table 2 displayed in ascending order. The error bars indicate the standard errors of the gradients of the respective straight lines.

8 CALCULATION OF THE DEGREE OF EQUIVALENCE

The degree of equivalence (D_i) of the result of each laboratory (x_i) with respect to the Key Comparison Reference Value (KCRV) was calculated using:

$$D_i = x_i - x_{i,KCRV} \tag{3}$$

In this comparison, $x_{i,KCRV}$ is Z_{i0} (the estimated amount fraction of the travelling standard at the time t_j=0). The expanded uncertainty of the degree of equivalence is calculated from the contributions of the measurement uncertainty reported by the participating laboratory (u_i) and the uncertainty of the KCRV, $u_{i,\,KCRV}$, by Eq. 4. The uncertainty of the KCRV was equal to the uncertainty associated to the estimation of the y-intercept, i.e. Z_{i0}, when fitting the decay relationship by the XLGENLINEv1.1 software and which accounts for the measurement uncertainty of the coordinating laboratory and the gravimetric standard uncertainty.

$$U(D_i) = 2\sqrt{u_i^2 + u_{i,KCRV}^2} \tag{4}$$

9 RESULTS SUBMITTED BY PARTICIPATING LABORATORIES

A full list of the participants is given in Annex A. A summary of the results submitted by the participants are listed in Table 3. The methods used by the participants are listed in Annex B. These all involved analysis by chemiluminescence using commercial instrumentation. Annex C provides the full laboratory reports.

The degree of equivalence of each laboratory was plotted against the drift of its assigned cylinder. Figure 7 shows that there is no correlation between the degree of equivalence and the decay rate of the cylinder. Therefore, no participants had any advantage from receiving cylinders that were more stable.

The degrees of equivalence calculated as described above are shown in Figure 8. As can be observed in Figure 8 the submitted results of three of the participating laboratories did not agree with the KCRV within the estimated uncertainty.

Table 3 Results submitted by the participating laboratories.

NMI	Standard Identifier	Date of Participant Measurement	Submitted Result [nmol/mol]	Expanded Uncertainty [nmol/mol]
VSL	219509	26/05/2012	431.6	3.6
NPL	219515	28/06/2012	444.1	4.5
MKEH	219516	21/06/2012	447.3	12.8
JRC	219517	06/04/2012	442.9	5.6
DWD	219518	07/05/2012	468.4	17.0
UBA (D)	219519	25/04/2012	439.1	6.8
GUM	219520	16/04/2012	439.4	8.8
BEV/EAA	219522	14/05/2012	455.3	8.7
METAS	219523	10/04/2012	457.5	2.0
FMI	219524	07/06/2012	450.4	6.8
LNE	219529	07/04/2012	443.2	4.5
BAM	219530	07/06/2012	435.5	13.6
CHMI	221863	15/04/2012	469.6	4.0
SMU	221864	24/04/2012	454.4	11.6
INRIM	221882	13/05/2012	477.7	8.0

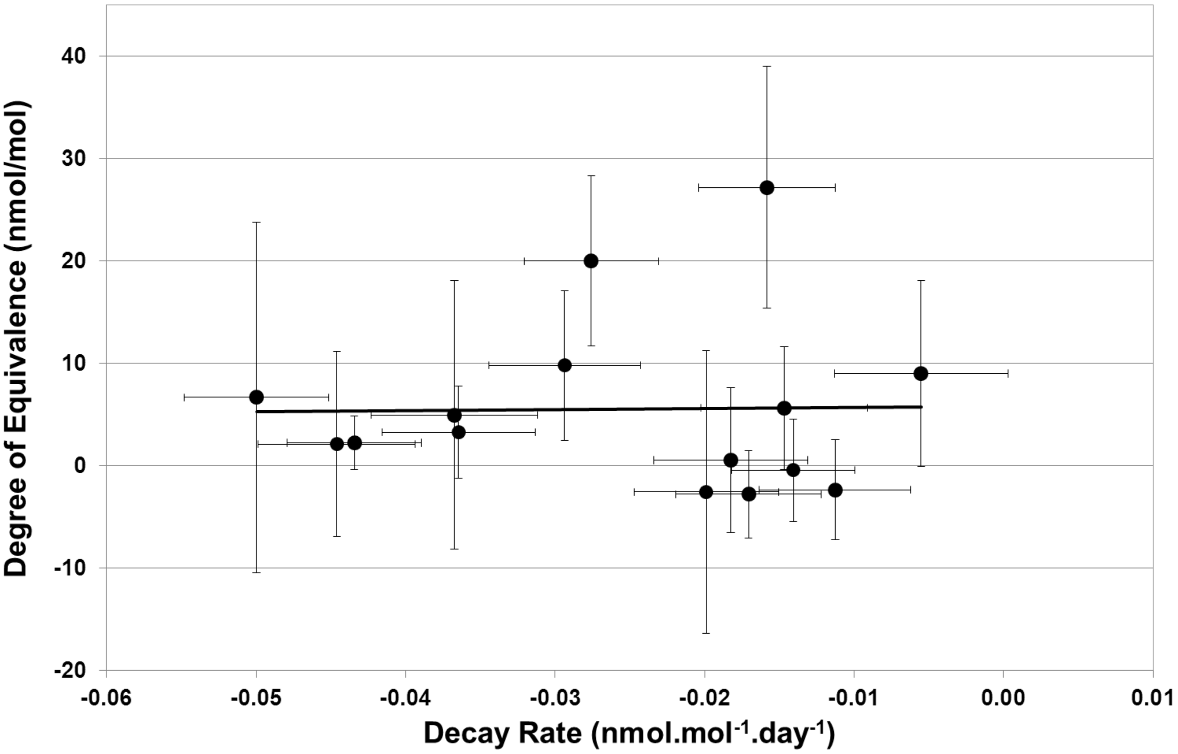

Figure 7 Degree of equivalence vs decay rate. Vertical error bars are the expanded uncertainties of the degree of equivalence. The horizontal ones are the standard errors of the decay rates.

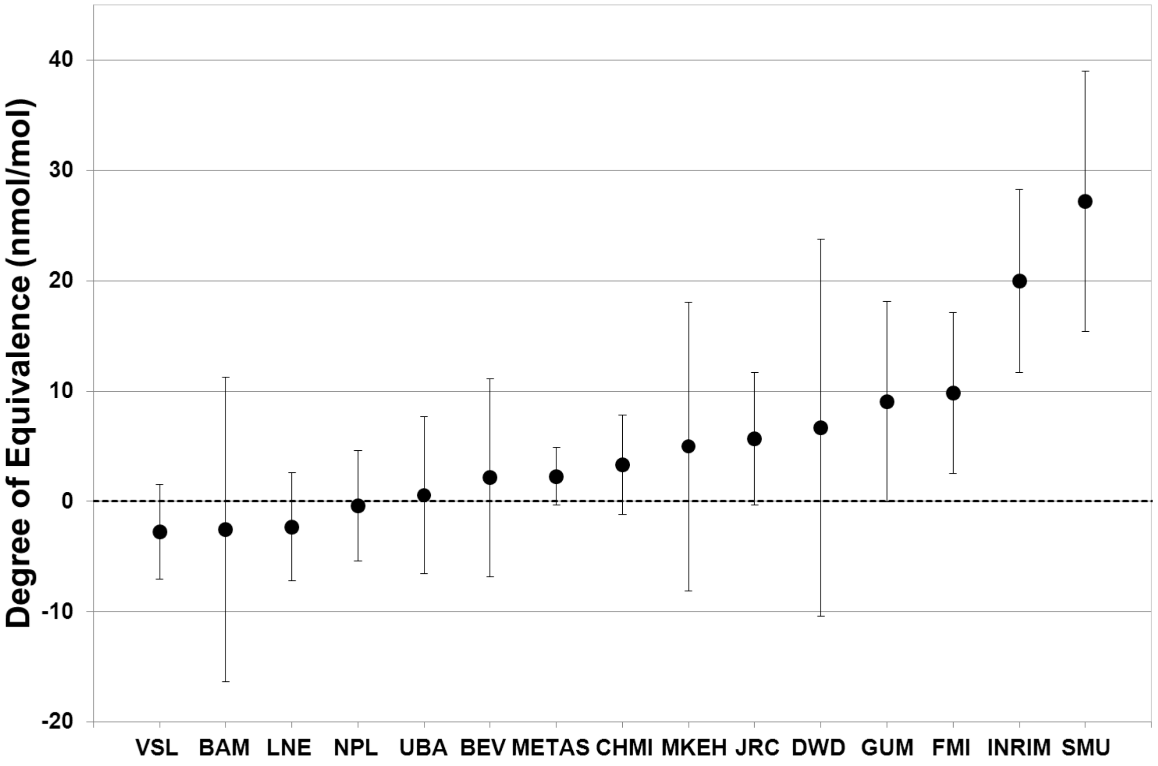

Figure 8 Degrees of equivalence of the participating laboratories. The error bars are the expanded uncertainties of the degrees of equivalence obtained from the uncertainty of the results reported by each participant and the uncertainty in the KCRV.

10 SUMMARY

The results for the 15 participants are presented. Degrees of equivalence have been calculated based on a reference value derived from the analysis of each travelling standard by the coordinating laboratory. 12 of 15 laboratories agree with the reference value to within their estimated uncertainty (*k*=2).

Based on the performance of the comparison, CMCs may be claimed for NO in N_2 between 100 nmol/mol and 10 µmol/mol with an appropriate uncertainty statement. 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.

11 REFERENCES

[1] S. Penkett, S. Gilge, C. Plass-Duelmer and I. Galbally, GAW Report no. 195. http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_195_TD_No_1570_web.pdf.

[2] International Key Comparison CCQM-K26a and Pilot Study CCQM-P50a (NO). Final Report. http://kcdb.bipm.org/appendixB/appbresults/ccqm-k26.a/ccqm-k26.a_final_report.pdf

12 ANNEXES

Annex A – Contact details for participating laboratories

NMI	Country	Contact Name	Address
VSL	Netherlands	Gerard Nieuwenkamp	Thijsseweg 11 2629 JA Delft
NPL	United Kingdom	Paul Brewer	National Physical Laboratory Hampton Road, Teddington, Middlesex TW11 0LW
MKEH	Hungary	Judit Fükö	1124 Budapest Németvölgyi út 37-39, C ép. 101. Szoba
JRC	Italy	Friedrich Lagler	European Comission DG JRC Via Enrico Fermi 2749 TP 442, 21027 Ispra (VA)
DWD	Germany	Stefan Gilge	Deutscher Wetterdienst Meteorologisches Observatorium Hohenpeissenberg Albin-Schweiger-Weg 10, D-82383 Hohenpeiβenberg
UBA (D)	Germany	Volker Stummer	Federal Environment Agency II 4.4 Air Quality Standards and Monitoring Methods EU-Reference Laboratory- Air Quality Paul Ehrlich Str. 29, 63225 Langen
GUM	Poland	Darek Cieciora	Laboratorium Gazowych Materiałow Odniesienia Głowny Urząd Miar, Ul. Elektoralna 2, 00-139 Warszawa
BEV/EAA	Austria	Marina Fröhlich	Umweltbundesamt GmbH Spittelauer Lände 5, 1090 Vienna
METAS	Switzerland	Céline Pascale	Federal Office of Metrology METAS Lindenweg 50, CH-3003 Bern-Wabern
FMI	Finland	Jari Walden	Finnish Meteorological Institute Air Quality Research Erik Palmenin Aukio 1, Fi – 00560 Helsinki
LNE	France	Tatiana Mace	Laboratorire National de Metrologie et d’Essais 25 Avenue Albert Bartholome, 75015 Paris
BAM	Germany	Dirk Tuma	BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin
CHMI	Czech Republic	Jan Beránek	Czech Hydrometeorological Institute Calibration Laboratory of Immission Generala Sisky 942/1, 143 00 Prague 4
SMU	Slovakia	Miroslava Valkova	Slovak Institute of Metrology SMU Karloveská 63, SK- 842 55 Bratislava
INRIM	Italy	Michela Sega	Istituto Nazionale di Ricerca Metrologica Mass building, Strada delle Cacce 73, 10135 Torino

Annex B - Methods used by participating laboratories

NMI	**Standard Identifier**	**Reference standards**	**Technique**
VSL	219509	Gravimetric standards prepared at VSL	Chemiluminescence
NPL	219515	Dilution from 10 ppm NO/N_2 standard molblocs/MFCs	Chemiluminescence
MKEH	219516	Dilution from 100 ppm NO/N_2 PRGM molblocs/MFCs	Chemiluminescence
JRC	219517	Dilution from a 30 ppm NO/N_2 VSL PRGM MFCS/molblocs	Chemiluminescence
DWD	219518	Dilution from 10 ppm NPL PRGM	Chemiluminescence
UBA (D)	219519	Static Volumetric dilution from pure NO, certified by VSL	Chemiluminescence
GUM	219520	Dilution from a 20- 50 ppm NO/N_2 PRGMs prepared at GUM using MFCs	Chemiluminescence
BEV/EAA	219522	Dilution from a 90 ppm NO/N_2 VSL PRGM MFCS/molblocs	Chemiluminescence
METAS	219523	Dilution from a 60 ppm NO/N_2 PRGM MFCs/molblocs	Chemiluminescence
FMI	219524	Dilution from a 50 ppm NO/N_2 NPL PRGM sonimix gas dilutor	Chemiluminescence
LNE	219529	Dilution from a 10 ppm NO/N_2 PRGM MFCS/molblocs	Chemiluminescence
BAM	219530	3 gravimetric standards (nominal 400 ppb)	Chemiluminescence
CHMI	221863	Dilution from a NO/N_2 VSL PRGM manometric injection	Chemiluminescence
SMU	221864	5 gravimetric standards (100-1000 ppb) prepared PRGM at SMU	Chemiluminescence
INRIM	221882	3 gravimetric standards (300, 500, 700 ppb) prepared from 100 ppm NO/N_2 NPL PRGM	Chemiluminescence

Annex C - Results and reports submitted by participants

Measurement report VSL

Laboratory: VSL
Cylinder number: 219509 SG

NOMINAL COMPOSITION
- Nitrogen monoxide: $450 \cdot 10^{-9}$ mol/mol
- Nitrogen: balance

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2012-05-22	431.13	0.01	3
	2012-05-22	429.77	0.07	3

Measurement No. 2	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2012-05-26	431.04	0.22	3
	2012-05-26	431.28	0.14	3

Measurement No. 3	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2012-05-30	433.29	0.24	3
	2012-05-30	433.05	0.12	3

Results:

Analyte	Result (assigned value) (mol/mol)	Coverage factor	Assigned expanded uncertainty
NO	$431.6\ 10^{-9}$	2	$3.6\ 10^{-9}$

Reference Method:
The measurements have been performed with a Thermo Scientific Model 42i Chemiluminescence NO-NO2-NOx Analyzer.

Calibration Standards:
Calibration has been performed in the range from 100 – 1000 nmol/mol NO, using VSL Primary Standard gas Mixtures (PSMs). All these mixtures have been prepared in accordance with ISO 6142:2001(E) Gas analysis - Preparation of calibration gas mixtures - Gravimetric method.
High purity NO and high purity N2 are used to prepare high concentration mother mixtures of NO in N2. Using the same method, these mixtures are diluted to daughters and granddaughters to achieve the appropriate concentrations.

Instrument Calibration:
At VSL measurements are performed in ranges of concentrations. For this comparison the measurement range of 100-1000 nmol/mol NO in N2 is selected. The range contains mixtures of 100, 200, 400, 500, 600, 800 and 1000 nmol/mol NO in N2.

Sample Handling:

A dedicated pressure regulator is connected on the cylinder at least one day before the start of the measurement. This regulator was purged at least 8 times. A constant flow of 500 mL/min is flushed to the monitor, using a Bronkhorst (low Δp, Kalrez seals) mass flow controller.

After a flushing time of 5 minutes, 3 times 90 samples of the response (mV) are collected. The average and standard deviation of these 3 times 90 samples are used for calculations.

Uncertainty:

Measurements are performed in accordance with ISO 6143:2001(E) Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures. The uncertainty is calculated with ISO 6143–compatible regression software based on Generalized Least Squares. For this report a simplified approach of the uncertainty determination is given to compare with the ISO 6143 software results. In this simplified case the data is treated as a single-point calibration using only the 500 ppb standard. In this situation:

$$Xu = (Ru / Rst) \cdot Xst$$

where: X = concentration (mol/mol)
R = respons (mV)
u = unknown sample
st = primary standard gas mixture

Uncertainty source	Estimate *xI*	Assumed distribution	Standard uncertainty *u(xi)*	Sensitivity coefficient c*I*	Contribution to standard uncertainty *uI(y)*
Ru	4015 mV	normal	8 mV	Xst / Rst	0.87 nmol/mol
Rst	4605 mV	normal	9 mV	Ru·Xst/ Rst2	0.85 nmol/mol
Xst	500.3 nmol/mol	normal	1.5 ppb	Ru / Rst	1.31 nmol/mol
Xu	(432 nmol/mol)				1.79 nmol/mol

Coverage factor: 2
Expanded uncertainty: 3.6 nmol/mol

Measurement report NPL

Laboratory : National Physical Laboratory (NPL)
Cylinder number : 219515

Measurements:

Run number	Concentration (nmol/mol)
1	444.0
2	444.1
3	444.5
4	443.9

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (%)
NO	444.1	2	4.5

Information regarding the measurement procedure can be found in Annex 1.

Example of uncertainty budget

Uncertainty in generation of the calibration gas

	Units	**Value**	**un/c**	**Sensitivity**	**Sum of sq**	
Primary standard	ppb	9854	19.7	0.046509	0.839471	
				Contrib from Reference / ppb		1.8325
flow of standard	mg/s	01.018	0.000	429.468660	0.029511	
flow of diluent	mg/s	20.860	0.042	-20.948435	0.763821	
				Contrib from flow measurements / ppb		1.7814
diluent gas contamination	ppb	0	0.300	1.000000	0.090000	
				Contrib from diluent gas contamination / ppb		0.6000
				Total sum of squares	1.722804	
Generated standard	**ppb**	458.299		*Combined Uncertainty*		1.3126
				Expanded(k=2)		2.6251
				Relative to unknown		0.57%

Uncertainty in determining the concentration of the unknown

	Units	Value	un/c	Sensitivity	Sum of sq	
Generated standard	ppb	458.965	1.3143	0.967679	1.617492	
				Contrib from Reference / ppb		1.2718
Zero analytical	V	00.013	0.000	-3.349251	0.000000	
gen stnd analytical	V	04.442	0.013	-100.275299	1.668414	
Unknown analytical	V	04.299	0.013	103.624550	1.785802	
				Contrib from Analysis / ppb		1.8586
				Total sum of squares	5.071708	
Unknown value	**ppb**	444.130		*Combined Uncertainty*		2.2520
				Expanded(k=2)		4.5041
				Relative to unknown		1.01%

Measurement report MKEH

Laboratory: Hungarian Trade Licensing Office (MKEH)
Cylinder number: 219516

NOMINAL COMPOSITION
- Nitrogen monoxide : 450 nmol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	2012.06.21.	447.3	0.00	3
NO_2	2012.06.21.	2.1	4.76	3
NO_x	2012.06.21.	449.4	0.02	3

Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
NO	447.3 (nmol/mol)	2	12.8 (nmol/mol)
NO_2	2.1 (nmol/mol)	2	0.4 (nmol/mol)
NO_x	449.4 (nmol/mol)	2	12.8 (nmol/mol)

Reference Method:
A chemiluminescence nitrogen oxides analyzer was used to analyze NO gas. The measurement method was direct comparison with a primary gas standard.

Calibration Standards:
The primary standard gas was the NO/N_2 100.03 ppm ± 0.40 ppm(mol/mol), cylinder number: 680196.

Instrument Calibration:
The calibration standard gas (100.03 ppm NO) was diluted to 700 ppb concentration by a MFC (Mass Flow Controller).

Sample Handling:
A stainless steel gas regulator for the cylinders was used

Uncertainty:

Uncertainty table: NO

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Standard reference material	100.03 ppm(mol/mol)	Normal	0.002	1	0.002
Dilution	100 %	Normal	0.01	1	0.01
NO analyzer	100 %	Normal	0.01	1	0.01
Standard deviation of the measurement	447.3 (nmol/mol)	Normal	0.0000	1	0.0000
Variance					0.0143

Coverage factor: 2
Expanded uncertainty: 12.8 (nmol/mol)

Uncertainty table: NO_2

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Standard reference material	100.03 ppm(mol/mol)	Normal	0.002	1	0.002
Dilution	100 %	Normal	0.05	1	0.05
NO analyzer	100 %	Normal	0.05	1	0.05
Standard deviation of the measurement	2.1 (nmol/mol)	Normal	0.0476	1	0.0476
Variance					0.0853

Coverage factor: 2
Expanded uncertainty: 0.4 (nmol/mol)

Uncertainty table: NO_x

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
NO result	447.3 (nmol/mol)	Normal	0.014283	0.995327	0.014216
NO_2 result	2.1 (nmol/mol)	Normal	0.085263	0.004673	0.000398
Variance					0.014222

Coverage factor: 2
Expanded uncertainty: 12.8 (nmol/mol)

Measurement report JRC

Laboratory : Joint Research Centre (JRC)
Cylinder number : 219517

Gas mixture	Result (assigned value) (nmol/mol)	Coverage factor	Assigned expanded uncertainty (nmol/mol)
NO	442.9	2	5.6

The result is an average of two analysis done on April 3rd and 10th, 2012.

Each analysis is an average of five 1-min averages measured after stabilization of the signal, usually given after 10 min sampling. The used analyzer is a Thermo Electron 42C, calibrated immediately before, during or right after the analysis of the Euramet cylinder, thus avoiding the influence of analyzer drift.

The calibration standards are PRMs from NMi with 30 *10-6 mol/mol NO in N2, diluted with N2 from Air Liquide, type Alphagas 2 (99.9999) in a dynamic dilution system. Each flow rate is measured with a Molbloc/molbox1 system immediately after the calibration point was sampled. During the experiments we performed 3-point calibrations at 0, 400, 450 and 500 nmol/mol.

Calculation of the result and its uncertainty was done using Gum-workbench and bleast software. We added an additional term to the uncertainty budget (based on uncertainties of PRM and flow measurements plus repeatability) representing the use of N2 as dilution gas instead of air (used usually in our laboratory).

Measurement report DWD

Laboratory : Deutscher Wetterdienst (DWD).
Cylinder number : 219518

Results:

Gas mixture	Result (assigned value) (nmol/mol)	Coverage factor	Assigned expanded uncertainty (nmol/mol)
NO	468.43	2	16.98

Average result from 11 measurements (# of data points: 261).

Measurements refer to NPL Standard #195524 SG from 14th October 2008, 9.94 (+- 0.1) ppm. Additionally we used an "Air :Liquide" standard #9331237001; 9.65 (+- 0.19) ppm. We use three chemiluminescence instruments of the type ECO Physics CLD 770 AL ppt, equipped with blue light converter, photolytic converter and gold converter, respectively. Since October 2012 we have additionally used an "Aerodyne" CAPS monitor for direct NO2 measurements.

Calibration is performed once a week (on Monday, Wednesday and Friday for the three analysers, respectively) using the gas dilution and gas phase titration unit "Environics S100". Zero air is supplied by "ECO Physics PAG4" Zero air generator. Quality of zero air is checked by checking the counting difference between measuring chamber mode and zero chamber mode of NO analyser. Deviations between two calibrations are typically below 1%.

Measurement report UBA(D)

Laboratory : Federal Environment Agency - Germany UBA (D)

Cylinder number : 219519

NOMINAL COMPOSITION
- nitrogen monoxide: 450 x 10^{-9} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	04-24-2012	438,8 E-9	0,05	30

Measurement No. 2	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	04-25-2012	439,2 E-9	0,07	30

Measurement No. 3	Date	Result (mol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	04-26-2012	439,4 E-9	0,05	30

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	439,1	2	6,8

Reference Method:

For analyzing nitrogen monoxide at the UBA laboratory a chemiluminescence method based monitor HORIBA APNA 370 was used.

Calibration Standards:

Calibration standard is prepared by volumetric static injection at UBA.
Known volumes (syringe) of the pure component are added to the complementary gas in a vessel of well-defined volume .
The method is described at EN ISO 6144:2006

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 MD2,MD4
Operating material:	
Microliter syringe	50 µl Hamilton series 1805
Nitrogen (balance gas)	5.0 Air Liquide
Nitrogenmonoxid	3.7 certified by VSL

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. The mixture then has to re-equilibrated to ambient temperature.

The whole procedure is done in accordance with ISO 6144.

Instrument Calibration:

Bracketing -Two-point Calibration
Standards with amount fractions that were lower and higher than the mixture under test, were prepared by static volumetric dilution method .The concentrations were chosen after measuring the unknown gas by the reference analyzer. It was calibrated using a one point calibration at 480 nmol/mol. The reference standard was prepared by static volumetric dilution too.

Measurement result: 438.4 nmol/mol
High standard: 474 nmol/mol
Low standard: 426 nmol/mol

The concentrations were prepared by two different final pressures. For each measurement the high and the low amount fraction standards were prepared respectively.

Sample Handling:

Cylinder was kept under laboratory conditions for four weeks upon arrival for stabilization. Pressure regulator was used for sampling at ambient pressure and a little valve controlled overflow (0,5 Nl/min) was set via T-piece. 6 mm PTFE tubes with stainless steel fittings were used for connection with the monitor.

Measurements

For this comparison three independent measurements were made.

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 dilution method at both bracketing points

s_R = Reproducibility of the static dilution method in the UBA laboratory (0,43%)

$s^2(\bar{q})$ = Estimate of the variance of the mean $s^2(\bar{q}) = \frac{s^2(q_r)}{30}$ (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 and the reference standard.

u_1 = 2,76 nmol/mol

s_R = 1,9 nmol/mol

$s(\bar{q})$ = 0,05 nmol/mol (2)

u_c = 3,4 nmol/mol (1)

Coverage factor: 2

Expanded uncertainty: ± 6,8 nmol/mol

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

The procedure is described in ISO 6144

Model Equation:
$C=C_p*V_s/V_d*p_1/p_2$

List of Quantities:

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

C_p:
Type B rectangular distribution
Value: 0.9997 mol/mol
Halfwidth of Limits: 0.00024 mol/mol

Pure gas cylinder D247836, certified by VSL

V_s:
Type B rectangular distribution

Value: $50 \cdot 10^{-6}$ 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 l
2	14.741 l
3	14.735 l
4	14.740 l
5	14.737 l

Arithmetic Mean: 14.73660 l
Standard Deviation: $4.4 \cdot 10^{-3}$ l
Standard Uncertainty: $1.96 \cdot 10^{-3}$ l
Degrees of Freedom: 4

p_1:
Type B rectangular distribution
Value: 98.22 kPa
Halfwidth of Limits: 0.04 kPa

p_2:
Type B rectangular distribution
Value: 697.9 kPa
Halfwidth of Limits: 0.4 kPa

Uncertainty Budgets:
C: Volume fraction in the resulting mixture of NO

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C_p	0.999700 mol/mol	$139 \cdot 10^{-6}$ mol/mol	rectangular	$480 \cdot 10^{-9}$	$66 \cdot 10^{-12}$ mol/mol	0.0 %
V_s	$50.000 \cdot 10^{-6}$ l	$289 \cdot 10^{-9}$ l	rectangular	$9.5 \cdot 10^{-3}$	$2.8 \cdot 10^{-9}$ mol/mol	99.4 %
V_d	14.73660 l	$1.96 \cdot 10^{-3}$ l	normal	$-32 \cdot 10^{-9}$	$-64 \cdot 10^{-12}$ mol/mol	0.0 %
p_1	98.2200 kPa	0.0231 kPa	rectangular	$4.9 \cdot 10^{-9}$	$110 \cdot 10^{-12}$ mol/mol	0.2 %
p_2	697.900 kPa	0.231 kPa	rectangular	$-680 \cdot 10^{-12}$	$-160 \cdot 10^{-12}$ mol/mol	0.3 %
C	$477.36 \cdot 10^{-9}$ mol/mol	$2.76 \cdot 10^{-9}$ mol/mol				

Results:

Quantity	**Value**	**Expanded Uncertainty**	**Coverage factor**	**Coverage**
C	$477.4 \cdot 10^{-9}$ mol/mol	$5.5 \cdot 10^{-9}$ mol/mol	2.00	manual

Measurement report GUM

Laboratory : Central Office of Measures (GUM)
Cylinder number : 219520

NOMINAL COMPOSITION
- Nitrogen monoxide : $450 \cdot 10^{-9}$ nmol/mol
- Nitrogen : matrix

Measurement No. 1	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	11.04.2012	436,9	0,2	10

Measurement No. 2	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	16.04.2012	438,3	0,2	10

Measurement No. 3	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	17.04.2012	440,7	0,2	10

Measurement No. 4	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	19.04.2012	441,1	0,2	10

Measurement No. 5	Date	Result (nmol/mol)	stand. deviation (% relative)	number of sub-measurements
NO	20.04.2012	440,2	0,2	10

Results:

Gas mixture	Result (assigned value) (nmol/mol)	Coverage factor	Assigned expanded uncertainty (nmol/mol)
NO	439,4	2	8,8

Reference Method:

The measurements were repeated 10 times for the sample and the standards by chemiluminescence analyzer Thermo 42C.

Calibration Standards:

The standards were prepared by dynamic method according to ISO 6144-9 from mixtures which were prepared (by Central Office of Measures) by gravimetric method. The gravimetric mixtures were prepared in aluminum (with coated layers) cylinders and they were (and still are) under metrological control.

Composition of gravimetric mixtures:

No.	Cylinder number	Component	Assigned value (x) [µmol/mol]	Expanded uncertainty (u(x)) [µmol/mol] (*k*=2)
1	D402445	NO	21,12	0,25
2	D752042	NO	39,0	1,0
3	D752051	NO	47,0	1,0
4	D752044	NO	58,0	1,0

The standards were prepared using mass flow controllers (Bronkhorst) and Dry-Cal DC-2M produced by BIOS International Corporation (USA).

Instrument Calibration:

Calibration method according to ISO 6143. The calibration curve was calculated from ratios by the software B_least.exe (linear case) using five standards points. Measurement sequence: standards (for calculation of calibration curve) and sample.

Sample Handling:

The cylinders (gravimetric mixtures and sample) were in the same room for the whole time also during the measurements (temperature stabilization) and the mixtures were mixed up before the measurements. Sample was transferred to the instrument via the reducing valve.

Uncertainty:

The final uncertainty was calculated according to ISO 6143 and consists of the following components:

- the uncertainty of the gravimetric mixtures
- the uncertainty of the Dry-Cal
- the standard deviation of the measurement
- resolution of analyzer

Uncertainty table: NO

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
cylinder no. D402445	$21,12 \cdot 10^{-6}$ mol/mol	normal	$0,125 \cdot 10^{-6}$ mol/mol	1	$0,125 \cdot 10^{-6}$ mol/mol
cylinder no. D752042	$39,0 \cdot 10^{-6}$ mol/mol	normal	$0,5 \cdot 10^{-6}$ mol/mol	1	$0,5 \cdot 10^{-6}$ mol/mol
cylinder no. D752051	$47,0 \cdot 10^{-6}$ mol/mol	normal	$0,5 \cdot 10^{-2}$ mol/mol	1	$0,5 \cdot 10^{-6}$ mol/mol
cylinder no. D752044	$58,0 \cdot 10^{-6}$ mol/mol	normal	$0,5 \cdot 10^{-6}$ mol/mol	1	$0,5 \cdot 10^{-6}$ mol/mol
dry-cal DC-2M	40÷6000 mln/min	normal	0,3 % rel	1	0,3 % rel
reading for standards and sample	$0,4 \cdot 10^{-6}$ mol/mol	normal	$0,0005 \cdot 10^{-6}$ mol/mol	1	$0,0005 \cdot 10^{-6}$ mol/mol
resolution of analyzer	$0,4 \cdot 10^{-6}$ mol/mol	normal	$0,0005 \cdot 10^{-6}$ mol/mol	1	$0,0005 \cdot 10^{-6}$ mol/mol

Coverage factor: 2

Expanded uncertainty: $8,8 \cdot 10^{-6}$ mol/mol

Measurement report BEV/EAA

Amount of NO, NPL 219522
(Average of 6 measurements, performed on May 8th, 9th,11th, 14th, 16th and 25th):
455,3 nmol/mol, U (k=2): 8,67 nmol/mol (1,90%).
The cylinder contained traces of NO2, below 0,9 nmol/mol

Relevant ambient conditions in the laboratory during analysis
Average temperature: 21,8°C Average ambient pressure: 98398 Pa

Traceability of measurement: Primary reference material with dynamic dilution using MFCs
PRM: NO in N_2, VSL # 680194, Zertifikat Nr. 3221621.04
Concentration 90,06 µmol/mol, U (k=2)= 0,36 µmol/mol

Reference instrument: Horiba, APNA 370, S/N TLK 34 DAG

Calibrator for dynamic dilution: Horiba ASGU 364, SerienNr. HA0214

Volume Flow measured by DHInstruments Molbox/Molbloc-System
  Molbloc 1 (1E2-VCR-V-Q molbloc), S/N. 3322;
  Molbloc 2 (5E3-VCR-V-Q molbloc), S/N. 3283;
  Molbox Mass Flow Terminal A350K, S/N 926;

Uncertainty was calculated according the SOP of the accredited calibration laboratory (the calculation for the 6th measurement is shown), with an additional repetability for 6 measurements added (grey area): see the attached Excel-file.

Calculation is carried out using th efollowing paramaters:

Concentration of the diluted PRM: $x_{(Kal)}$
Uncertainty of the diluted PRM, including the repeatabilty of the calibrator: $u_{(XKal)}$
Uncertainty of the calibrated reference instrument (actual standard deviation of the signals and repeatabilty): $u_{RM(xKal)}$
Uncertainty of the gas cylinder, including actual standard deviation of signal and a contribution for short term stabiliy: $u_{Prüfling(x)}$ and $U_{Prüflung(x)}$.
Including repeatability of the 6 measurements (grey): $u_{Prüfling(av\_x)}$ and $U_{Prüflung(av\_x)}$.

Measurement report METAS

METAS: Gas Analysis Laboratory

A chemiluminescence trace level NO-NO_2-NO_x-analyser (“CLD”, Thermo 42i-TL) is calibrated with a certified gravimetrically produced NO gas mixture standard in pressurized cylinder (60 ppm in N_2 Carbagas) by dynamic dilution with nitrogen in the range from 440 to 470 ppb . The dilution gas used is N_2 6.0 (Carbagas, Alphagas II). Mass flow controllers (MFC) from Vögtlin regulate the flows of dilution gas and the standard NO gas. Each mass flow is accurately measured with laminar flow elements, molbloc-molbox system from DHI, which were calibrated with the primary standard of METAS for small gas flows. They are located upstream of the MFCs. To ensure a stable input pressure before the molblocs, both gas flows pass through pressure controllers (PC, Brooks) regulating the pressure downstream at 3.5 bar (the same pressure used for molbloc calibration). Finally, the pressure of the bypass flow (in parallel with the analyser) is set to 1.2 bar upstream of a pressure controller to avoid the influence of ambient pressure fluctuations.

Five measurements of the test mixture were done but only the last one is taken into account for the final result of this report.

First, a calibration of the analyser and straight away 4 independent measurements of the test mixture were done. However, the differences between the results were not satisfactory. The reproducibility of the results was unsatisfactory and an unusually long stabilization time of the NO test mixture concentration was observed. Then, before doing the last analysis with the test mixture, an own bottle of NO in the same concentration range was used to optimize and further validate the method and conditioning process. Indeed, this last analysis was the most accurate one for several reasons which will be explained below.

The first three measurements of the test mixture were done by using Teflon tubing and a simple pressure reducer and manometer after the bottle but w/o flow regulation (the CLD aspirates a flow of ~1.2 l/min) and pressure regulation in the by-pass. The result of each subsequent measurement was lower. Therefore, for the fourth analysis, a mass flow controller was used to avoid flow fluctuations and also a pressure reducer and manometer including a purging and a rinsing system in order to reduce stabilization times. With this system, the result was higher than for the three previous measurements. After these four measurements, we tested several configurations with an own NO gas mixture before doing the last measurement. We tested different materials (Teflon, steel), manometers, with or w/o MFC and PC. Finally, for this last measurement, the Teflon tubing was replaced by electro-polished 1/8’’ diameter inox tubes and the manometer was replaced by a piece of capillary column. Furthermore, considering the fact that the CLD doesn’t properly correct the ambient pressure fluctuations (a fact observed during another project), a pressure controller was added in the bypass flow exit. For the 5th analysis the analyser calibration and the measurement of the test mixture were done again. With all the above measures, the last analysis was the most stable one with minimal external influences and the best material compatibility for NO.

Prior to all measurements (calibration or test mixture), the gas lines were purged and rinsed three times with the corresponding gas and then the whole system closed with gas inside allowing equilibration for ~2h.

Results

Nitrogen oxide amount fraction nmol/mol	Expended uncertainty nmol/mol	Coverage factor
457.5	2.0	2

Uncertainty Budget

Example of the uncertainty calculation for the final analysis. This example is done according to the GUM (Guide for uncertainty of measurement) with the software Gum Workbench Pro Vs 2.4 and the result was checked by the software "BLeast" according to ISO 6143.

Model Equation:

$X_{ppbA1}=(X_A*Q_{A1}+X_N*Q_{NA1})/(Q_{NA1}+Q_{A1});$

$X_{ppbA2}=(X_A*Q_{A2}+X_N*Q_{NA2})/(Q_{NA2}+Q_{A2});$

$X_{ppbA3}=(X_A*Q_{A3}+X_N*Q_{NA3})/(Q_{NA3}+Q_{A3});$

$X_{ppb}meanA=(X_{ppbA1}+X_{ppbA2}+X_{ppbA3})/3;$

$Anz_{meanA}=(Anz_{ppbA1}+Anz_{ppbA2}+Anz_{ppbA3})/3;$

$b=p/q;$
$p=(X_{ppbA1}-X_{ppb}meanA)*(Anz_{ppbA1}-Anz_{meanA})+(X_{ppbA2}-X_{ppb}meanA)*(Anz_{ppbA2}-Anz_{meanA})+(X_{ppbA3}-X_{ppb}meanA)*(Anz_{ppbA3}-Anz_{meanA});$
$q=(X_{ppbA1}-X_{ppb}meanA)^\wedge 2+(X_{ppbA2}-X_{ppb}meanA)^\wedge 2+(X_{ppbA3}-X_{ppb}meanA)^\wedge 2;$

$a=Anz_{meanA}-b*X_{ppb}meanA;$

$XNORes=(AnzRes-X_N-a)/b;$

List of Quantities:

Quantity	**Unit**	**Definition**
X_{ppbA1}	ppb	NO in reference mixture, 1st calibration point
X_A	ppb	NO in reference bottle
Q_{A1}	ml/min	Flow NO, 1st calibration point
X_N	ppb	NO in N2 6.0
Q_{NA1}	ml/min	Flow N2, 1st calibration point
X_{ppbA2}	ppb	NO in reference mixture, 2nd calibration point
Q_{A2}	ml/min	Flow NO, 2nd calibration point
Q_{NA2}	ml/min	Flow N2, 2nd calibration point
X_{ppbA3}	ppb	NO in reference mixture, 3rd calibration point
Q_{A3}	ml/min	Flow NO, 3rd calibration point
Q_{NA3}	ml/min	Flow N2, 3rd calibration point
X_{ppb}meanA	ppb	Average of NO mixtures
Anz_{meanA}	ppb	Average of NO mixtures' display
Anz_{ppbA1}	ppb	Analyser's display, 1st calibration point
Anz_{ppbA2}	ppb	Analyser's display, 2nd calibration point
Anz_{ppbA3}	ppb	Analyser's display, 3rd calibration point

Quantity	Unit	Definition
b	no units	Slope of calibration function for the analyser’s display
p	ppb^2	Numerator of slope
q	ppb^2	Denominator of slope
a	ppb	Y-intercept of calibration function for the analyser's display
XNORes	ppb	NO in test mixture
AnzRes	ppb	Display of test mixture

X_A: Type B normal distribution Value: 60283 ppb Expanded Uncertainty: 0.4 % Coverage Factor: 2	**X_N:** Type B rectangular distribution Value: 0.02 ppb Halfwidth of Limits: 0.02 ppb
Q_{A1}: Type B normal distribution Value: 24.0945 ml/min Expanded Uncertainty: 0.2 % Coverage Factor: 2	**Q_{NA1}:** Type B normal distribution Value: 3276.98 ml/min Expanded Uncertainty: 0.2 % Coverage Factor: 2
Q_{A2}: Type B normal distribution Value: 24.0917 Expanded Uncertainty: 0.2 % Coverage Factor: 2	**Q_{NA2}:** Type B normal distribution Value: 3166.23 ml/min Expanded Uncertainty: 0.2 % Coverage Factor: 2
Q_{A3}: Type B normal distribution Value: 24.1025 mol/min Expanded Uncertainty: 0.2 % Coverage Factor: 2	**Q_{NA3}:** Type B normal distribution Value: 3068.03 ml/min Expanded Uncertainty: 0.2 % Coverage Factor: 2
Anz_{ppbA1}: Type A summarized Mean: 425.85 ppb Experimental Standard Deviation: 0.63 ppb Number of observations: 37	**Anz_{ppbA2}:** Type A summarized Mean: 441.00 ppb Experimental Standard Deviation: 1.10 ppb Number of observations: 37
Anz_{ppbA3}: Type A summarized Mean: 455.02 ppb Experimental Standard Deviation: 0.87 ppb Number of observations: 37	**AnzRes:** Type A summarized Mean: 443.03 ppb Experimental Standard Deviation: 0.63 ppb Number of observations: 33

Uncertainty budget for NO in the test mixture

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
X_A	60283 ppb	121 ppb	50	normal	$7.6\cdot10^{-3}$	0.91 ppb	83.5 %
Q_{A1}	24.0945 ml/min	0.0241 ml/min	50	normal	4.6	0.11 ppb	1.2 %
X_N	0.0200 ppb	0.0115 ppb	∞	rectangular	-0.032	$-370\cdot10^{-6}$ ppb	0.0 %
Q_{NA1}	3276.98 ml/min	3.28 ml/min	50	normal	-0.034	-0.11 ppb	1.2 %
Q_{A2}	24.0917 ml/min	0.0241 ml/min	50	normal	6.2	0.15 ppb	2.3 %
Q_{NA2}	3166.23 ml/min	3.17 ml/min	50	normal	-0.048	-0.15 ppb	2.3 %
Q_{A3}	24.1025 ml/min	0.0241 ml/min	50	normal	8.0	0.19 ppb	3.7 %
Q_{NA3}	3068.03 ml/min	3.07 ml/min	50	normal	-0.063	-0.19 ppb	3.7 %
Anz_{ppbA1}	425.850 ppb	0.104 ppb	36	normal	-0.26	-0.027 ppb	0.0 %
Anz_{ppbA2}	441.000 ppb	0.181 ppb	36	normal	-0.34	-0.062 ppb	0.4 %
Anz_{ppbA3}	455.020 ppb	0.143 ppb	36	normal	-0.42	-0.061 ppb	0.4 %
p	436.0 ppb^2	13.5 ppb^2	220				
q	446.7 ppb^2	27.1 ppb^2	200				
AnzRes	443.030 ppb	0.110 ppb	32	normal	1.0	0.11 ppb	1.3 %
XNORes	457.51 ppb	1.00 ppb	71				

Measurement report FMI

Laboratory : Finnish Meteorological Institute (FMI)
Cylinder number : 219524

NOMINAL COMPOSITION
- nitrogen monoxide: 450 .10^{-9} mol/mol
- nitrogen : balance

Results:

Analyte	Result (assigned value) nmol/mol	Coverage factor	Assigned expanded Uncertainty nmol/mol
NO	450.41	2	6.84

Reference Method:

The Reference method for the analysis of the EURAMET 1183 key comparison Nitrogen monoxide gas cylinder was based on the chemiluminescence method (EN 14211:2005). The analyser, TEI 42 C s/n – 366, was calibrated by the dynamic dilution method (ISO 6145-6) in the range of 400 to 500 nmol/mol.

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, Cylinder NPL no. 1352, certified concentration 49.86 µmol/mol in nitrogen with a relative expanded uncertainty of 0.5 %.

Other reference standards used in the measurements are: Gas dilutor, Sonimix 6000A1 s/n 1585. Calibration of the Sonimix 6000A1 was made against the laboratory system prior to the measurements.

Pressure meter, Diptron 3 plus with the pressure probe UXD-95942, calibrated at MIKES in 2011, and used to control the dilution pressure of the gas dilutor.

Instrument Calibration:

The analyser TEI 42 C used for the analysis of the EURAMET 1183 Nitrogen monoxide cylinder was calibrated according to the standard operation procedure of the laboratory (SOP). The calibration range of the analyser was between 400 to 500 nmol/mol obtained from Sonimix 6000A1 gas dilutor. Purified air from zero air generator by API, model 701 was used as the dilution gas. The calibration of the analyser took place before and after the analysis of the sample.

The gas dilutor, Sonimix 6000A1 s/n 1585 by LN-Industries Switzerland, is based on critical flow 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 and the carbon monoxide analyser, APMA-370 s/n F010A60V. To verify the correct dilution of the Sonimix 6000A1 dilutor, a second reference gas standard of concentration 20 ± 0.10 µmol/mol was used.

During the operation of the dilutor, the pressure of the dilution line was controlled by the reference pressure meter of the laboratory.

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 deviation of the reaction cell of the analyser was within 4 mmHg during the calibration of the analyser and the analysis of the samples.

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) are standard uncertainties 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)

The second part of the uncertainty budget is a contribution from the analyser. Since the measurements took place in the laboratory at controlled conditions and the analyser was calibrated before and after the measurements of EURAMET 1183 samples, only analyser performance characteristics with an influence on the measurement uncertainty were considered. The following performance characteristics have been included into the uncertainty budget of the analyser according to EN 14211:2010:

- Repeatability standard deviation at zero
- Repeatability standard deviation at concentration ct
- Linearity of the analyser in the range of 400 to 500 nmol/mol
- Sensitivity coefficient of sample gas pressure
- Sensitivity coefficient of sample gas temperature
- Sensitivity coefficient of surrounding temperature
- Sensitivity coefficient of electrical voltage
- Interferences at zero and concentration ct
  - H2O concentration
  - CO2 concentration 400 mmol/mol
- Uncertainty of calibration

Uncertainty source	Estimate x_I *nmol/mol*	Assumed distribution	Standard uncertainty % $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$*nmol/mol*
	450				
Analyser				1	
- Repeatibility standard deviation at zero		Rectangular		1	0.03
- Repeatibility standard deviation at concentration 450 nmol/mol		Rectangular		1	0.27
- Linearity of the analyser in the range of 400 to 500 nmol/mol		Rectangular		1	0.74
- Sensitivity coefficient of sample gas pressure		Rectangular		1	0.24
- Sensitivity coefficient of sample gas temperature		Rectangular		1	0.06
- Sensitivity coefficient of surrounding temperature		Rectangular		1	0.34
- Sensitivity coefficient of electrical voltage		Rectangular		1	0.17
- H2O concentration		Rectangular		1	1.28
- CO2 concentration 400 mmol/mol		Rectangular		1	2.74
Calibration	450	Rectangular		1	1.35
Combined std u_c					3,42

Coverage factor: k = 2
Expanded uncertainty: 6.84 nmol/mol

Measurement report LNE

Laboratory	: Laboratoire National de métrologie d'Essais
Cylinder number	: 219529

NOMINAL COMPOSITION

- Nitrogen monoxide	:	450 nmol/mol
- Nitrogen	:	balance

Measurement No. 1	Date	number of sub-measurements	Results (nmol/mol)	Mean result (nmol/mol)	Assigned expanded uncertainty (nmol/mol)
NO	05/04/2012	3	442.0	442.8	4.2
			442.7		
			443.7		

Measurement No. 2	Date	number of sub-measurements	Results (nmol/mol)	Mean result (nmol/mol)	Assigned expanded uncertainty (nmol/mol)
NO	06/04/2012	3	443.9	443.2	4.4
			443.9		
			441.9		

Measurement No. 3	Date	number of sub-measurements	Results (nmol/mol)	Mean result (nmol/mol)	Assigned expanded uncertainty (nmol/mol)
NO	10/04/2012	3	443.8	443.5	3.8
			443.5		
			443.1		

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
NO	**443.2 nmol/mol**	**2**	**4.5 nmol/mol**

Reference Method:

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

Calibration Standards:

A reference gas mixture of NO in nitrogen (at about 450 nmol/mol) is generated by the dynamic dilution of a gravimetric gas mixture at 10 µmol/mol.

Measurements protocol

A reference gas mixture is generated by the dynamic dilution of a gravimetric gas mixture at a concentration (C_1) slightly higher than the concentration of the unknown gas mixture and injected inside the analyser : the response of the analyser is recorded (L_1).
The unknown gas mixture (C_A) is then injected inside the analyser and the response (L_A) is recorded.
The reference gas mixture (C_2) is injected into the analyser : the response of the analyser is recorded (L_2).

The mean reference gas concentration is calculated by

$$C = \frac{(C_1 + C_2)}{2}$$

The concentration of the unknown gas mixture is equal to :

$$C_A = \frac{C \times L_A}{\left(\frac{L_1 + L_2}{2}\right)}$$

This procedure is carried out 3 times per day on 3 different days.

Example of uncertainty calculation on the analysis of the unknown gas (10/04/2012):

1st measurement

Uncertainty source	Estimate x_I *(nmol/mol)*	Assumed distribution	Standard uncertainty $u(x_i)$ *(nmol/mol)*	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$ *(nmol/mol)*
Mean reference gas concentration included contribution of zero gas, gravimetric gas mixture, flow measurements	442.74	-	1.785	1.00248	1.79
1st reading for reference gas concentration	443.67	Standard deviation of the recorded values	0.24	-0.500506	-0.12
Reading for unknown mixture	444.49	Standard deviation of the recorded values	0.26	0.998534	0.26
2nd Reading for reference gas concentration	443.11	Standard deviation of the recorded values	0.42	-0.500506	-0.21

1st measurement result : 443.8 nmol/mol
coverage factor : 2, Expanded uncertainty: U = 3.6 nmol/mol

Measurement Report BAM

Cylinder no.: 219530

Pressure on arrival: 180 bar (2012-04-03)

Methods and Standards

Instrument:

Analyzer HORIBA model “APNA-370” with cross-flow modulation technique

The instrument operates on the principle of chemiluminescence and can be employed for the analysis of nitrous oxide (NO) on trace level in a concentration range up to 1 ppm.

The following consecutive reactions take place:

1. NO + O3 → NO2* + O2

2. NO2* → NO2 + hν (chemiluminescence)

The light intensity is proportional to the concentration of NO.

Calibration standards:

The following calibration standards (gravimetrically prepared according to DIN EN ISO 6142) were employed:

Cylinder BAM 7026-120503

Component	mol-%	Uncertainty (relative) / % (*k* = 2)
NO	0.00003945	0.069
N2	99.999961	0.009

Cylinder BAM 7037-120508

Component	mol-%	Uncertainty (relative) / % (*k* = 2)
NO	0.00004355	0.069
N2	99.999956	0.009

Cylinder BAM 7042-120507

Component	mol-%	Uncertainty (relative) / % (*k* = 2)
NO	0.00004794	0.068
N2	99.999952	0.009

Analysis:

Three measurements were done according to the following corresponding schedule. The result was recorded after letting the instrument (CLD signal) equilibrate. The recorded response is the instrument reading; no calibration function has been implemented. The equilibration curves were assessed by best-fit linear regression.

Analysis no. 1; date of measurement: 2012-05-21 and 2012-05-22; measurement sequence in consecutive order: BAM 7042 — 219530 — BAM 7026 — BAM 7037 — zero gas (= pure nitrogen)

Analysis no. 2; date of measurement: 2012-05-23 and 2012-05-24; sequence: 219530 — BAM 7037 — zero gas — BAM 7026 — BAM 7042

Analysis no. 3; date of measurement: 2012-06-07; sequence: zero gas — 219530 — BAM 7042 — BAM 7026 — BAM 7037

Results and measurement uncertainty

The following NO concentrations (unit: mol-ppb) were evaluated from the three measurements. The uncertainty that is given here refers to the mean standard deviation.

measurement no.	result mol-ppb	*u(result)* mol-ppb
1	436.51	8.69
2	434.86	8.64
3	435.12	8.65

Consolidated value and corresponding expanded measurement uncertainty (*k* = 2): **435.5 ± 13.6 mol-ppb**

The consolidated value is the mean value of the three determinations.

The uncertainty includes the best-fit variance of the signal, the gravimetric uncertainties of the bracketing gases (i.e., calibration gases), and an estimate for the content of NO2. NO2 is the result of a possible side reaction and was estimated from the free-running NO2 signal compared with the NO signal. A value of 0.0105 (relative) was attributed to that contribution.

Measurement report CHMI

EURAMET 1183	Cylinder NO in N2:	NPL No.221863SG
K26a	Reduction valve:	Messer FE62
	Primary material:	
	Dilution method:	Static manometric injection
	Analyzer NO-NO2-NOx:	TE model 42C and 42

Date of measure	**Cylinder pressure** [MPa]	**Measured concentration NO TE42C** [nmol/mol]	**NOx TE42C** [nmol/mol]	**Uncertainty** [nmol/mol]
28/03/2012	14.1	470.5	470.5	4.0
29/03/2012	14.0	470.3	470.3	3.9
30/03/2012	14.0	470.0	470.5	4.0
05/04/2012	10.0	470.2	470.6	4.0
06/04/2012	9.6	468.0	468.4	4.0
16/04/2012	9.2	471.0	471.1	4.0
17/04/2012	8.9	470.1	469.9	4.0
15/05/2012	8.2	468.0	468.0	4.0
23/05/2012	7.6	468.3	468.0	4.0

Measurement report SMU

Laboratory: Slovak Institute of Metrology (SMU)
Cylinder number: 221864

Results

Measuring Month	Nitrogen oxide amount fraction	Expanded uncertainty	Coverage Factor
	x_{NO} [nmol/mol]	$U(x_{NO})$ [nmol/mol]	
28.March	451.07	11.50	2
13.April	454.34	11.15	2
4.May	456.76	11.84	2
23.May	455.44	11.88	2
$\overline{X}$	**454.40**	**11.61**	2

Uncertainty Budget

Combined uncertainty of the NO amount fraction (analysed by luminescence method) was calculated according to the formula:

$$U_C(x) = 2 * \sqrt{u_A(x_{NO})^2 + u_B(x_{NO})^2}$$

Where:
$u_A(x)$: *standard deviation of measurements* (SD)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{X})^2}{(n-1)}}$$

n= 30; number of replicates

$$u_B(x) = \sqrt{(x_{\max} - x_{\min})^2 + d^2 + u_{cal}^2}$$

d= 0.1 nmol/mol; analyser resolution

$$u_{cal} = 11.5 \quad nmol/mol$$

u_{cal} is the standard uncertainty of 4*50 nmol/mol* NO PSM used for the analyzer calibration

it can be checked by equation: $u_{cal}(x) = \sqrt{\frac{\sum \left|(x_{(n+1)} - x_n)\right| + \left|(x_{(n-1)} - x_n\right|}{4}}$

To estimate result uncertainty from 4 independent measurement results we have kept “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method” (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{s_{\bar{x}}{}^2 + s_r \frac{n-1}{n}}$$

$$s_r = \sqrt{\sum_{i=1}^{p} u(\bar{x}_i)^2 \Big/ p}$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}}$$

$$\Delta x = \bar{x}_1 - \bar{x}_2$$

p – Number of measurements
n – Number of replicates

Final result is average from 3 measurement results

$$\overline{X} = \frac{\sum_{i=1}^{p} \bar{x}_i}{p}$$

Max value(sR or sr) was assigned to this result as final standard uncertainty

$$u(\overline{X}) = \max(s_r; s_R)$$

Expanded uncertainty (k=2) of final result

$$U(\overline{X}) = 2 \cdot u(\overline{X})$$

Description of the procedure used during the gas analysis

The concentration of NO was determined by luminescence method in gas laboratory. Thermo Vision 42C analyzer was used for measurements. The SMU`s PSM prepared gravimetrically in according to ISO 6142 was used for the calibration of the analyzer before each measurement. NO content was measured after receiving the cylinder from pilot laboratory and then 4 times after 3 weeks. 5 out of different PSMs in the amount fraction range *(100-1000) nmol/mol* NO were used to make a calibration curve and these curves were used for determination of unknown samples' concentrations. Each measurement was performed under stable conditions:

Pressure: 172.5 mmHg
Flow: 0.725 l per min.
Integration time: 10 sec

Before measuring process the cylinders were homogenized and stabilized for laboratory temperature about 60 minutes.

The laboratory conditions:
Temperature: 20-23°C
Pressure: 98.90 -101.325 KPa,
Rel. humidity: 20%-35%.

Complementary information on the cylinder

The value of the pressure left in the cylinder before shipment to the NPL:
p= 7, 0 MPa

Measurement report INRIM

Laboratory name: Istituto Nazionale di Ricerca Metrologica

Cylinder number: 221882

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard uncertainty (nmol/mol)	number of replicates
NO	07/05/12	475.5	1.2	9

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard uncertainty (nmol/mol)	number of replicates
NO	08/05/12	472.9	1.3	9

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard uncertainty (nmol/mol)	number of replicates
NO	10/05/12	482.0	1.3	9

Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard uncertainty (nmol/mol)	number of replicates
NO	17/05/12	475.5	1.3	9

Measurement #5

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard uncertainty (nmol/mol))	number of replicates
NO	18/05/12	482.2	1.2	9

Measurement #6

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard uncertainty (nmol/mol)	number of replicates
NO	21/05/12	478.3	1.3	9

Results

Component	Result (nmol/mol)	Expanded Uncertainty	Coverage factor
NO	477.7	8.0	2

Method description forms

Reference Method:

The instrument used for NO determination is a chemiluminescence analyser Thermo 42i, having resolution of 1 nmol mol^{-1}. The data are visualized on the instrument display and manually recorded.

Calibration Standards:

The Calibration Standards used are Primary Reference Gas Mixtures of NO in a matrix of nitrogen prepared at INRIM by diluting a gravimetric standard purchased from NPL (concentration: 100,0 µmol/mol, standard uncertainty: 0,2 µmol/mol) with a nitrogen purity of ≥ 99.9999. The composition of the standards were verified, after their gravimetric preparation, by means of chemiluminescence using a set of certified reference gas mixtures having similar composition.
As for purity, the data certified by the producers were used.

Instrument Calibration:

Three standards were used at the following concentrations:

1. NO 301,3·nmol mol^{-1} U = 1,2 nmol mol^{-1} (k=2)
2. NO 499,8 nmol mol^{-1} U = 2,0 nmol mol^{-1} (k=2)
3. NO 698,4 nmol mol^{-1} U = 2,8 nmol mol^{-1} (k=2)

The measurements were carried out at a flow of approximately 37 L h^{-1}. It was previously proved that small flow variations do not affect the measurement value. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.
No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:
Standard n. 1, Sample, Standard n. 2, Sample, Standard n. 3, Sample, Sample, Standard n. 1, Sample, Standard n. 2, Sample, Standard n. 3, Sample, Sample, Standard n. 1, Sample, Standard n. 2, Sample, Standard n. 3, Sample. The first and the last sample measurements were excluded in the computation,

for a total of 9 repetition per day of analysis. A control standard was analysed at the beginning and at the end of the entire sequence.
No correction for ambient temperature was made.
Six different calibration curves were determined, one for each measurement day and they were used to estimate the final result for NO.

3) Determination of calibration curves

The calibration curves, one for each measurement day, were determined by means of the programme *B-Least* which calculated a linear analysis function for each calibration. Covariances between the calibration mixtures were also taken into account assuming a correlation coefficient of 0,9. The software calculated the analysis functions. Their parameter values are reported in the following tables (tab. 1-6):

b		$u_c(b)$
b_0	-41,1	1,4
b_1	1,04	3,4E-3

Tab. 1: calibration curve parameters of 07/05/12 (first set)

b		$u_c(b)$
b_0	-31,4	1,6
b_1	1,01	4,0E-3

Tab. 2: calibration curve parameters of 08/05/12 (second set)

b		$u_c(b)$
b_0	-47,4	1,2
b_1	1,06	2,9E-3

Tab. 3: calibration curve parameters of 10/05/12 (third set)

b		$u_c(b)$
b_0	-40,6	1,1
b_1	1,03	2,5E-3

Tab. 4: calibration curve parameters of 17/05/12 (fourth set)

b		$u_c(b)$
b_0	-46,3	1,2
b_1	1,05	2,7E-3

Tab. 5: calibration curve parameters of 18/05/12 (fifth set)

b		$u_c(b)$
b_0	-47,8	1,1
b_1	1,04	2,3E-3

Tab. 6: calibration curve parameters of 21/05/12 (sixth set)

Sample Handling:

The cylinder was kept indoors and in a horizontal position. Before the measurements campaign, it was rolled for 24 hours to ensure that the mixture was homogenous.
Samples were transferred into the analyser by means of a low volume pressure reducer and a sample line of stainless steel at a flow of 37 L h^{-1}.

Uncertainty:

From each of the six calibration curves a NO concentration value with its combined standard uncertainty was estimated. The main sources of contribution to the estimated uncertainty are:

- the calibration curve which takes into account the uncertainty on the composition of the standards, the covariances between the standards, the repeatability of the instrument readings for each standard
- the repeatability of readings of sample measurements (standard deviation of the readings).

The final result is the arithmetic mean of these six values. The six values had very close uncertainty values, but their scattering was higher than the uncertainties. Hence, for the assignment of the combined standard uncertainty, u_c, to the final result, the largest one among the obtained uncertainties, u_i, and the standard deviation of the six results, u_s, were combined according to the following equation:

$$u_c = \sqrt{(u_i)^2 + (u_s)^2} = \sqrt{(1,3)^2 + (3,8)^2} = 4,0 \text{ nmol/mol}$$