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

Final Report


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Field: Amount of Substance, Gas Standards
Subject: Comparison of primary standards of nitrogen monoxide (NO) in nitrogen.
Participants:

<table>
<thead>
<tr>
<th>Institute</th>
<th>Acronym</th>
<th>Country</th>
</tr>
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<td>KRISS</td>
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<td>CSIR National Metrology Laboratory*</td>
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* The CSIR National Metrology Laboratory (CSIR NML) became The National Metrology Institute of South Africa (NMISA) on 1 May 2007.

Coordinating laboratory

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Organizing Body: CCQM

Rationale for Comparison:
The aim of the pilot study was to evaluate the level of comparability of laboratories’ preparative capabilities for gravimetric nitrogen monoxide/nitrogen primary reference mixtures in the range (30-70) µmol/mol. Such primary gas reference mixtures are prepared and maintained by a number of NMIs in order to provide NOx calibration services in the areas of environmental and emissions analysis at the national level. The comparison was designed so that measurements would be performed at a central laboratory (the BIPM) and measurement results compared to values assigned by each National Metrology Institute (NMI) based on gravimetry. It had already been demonstrated that measurement uncertainties achievable for stable gas mixture standards
using such a comparison protocol could be considerably smaller than reported for comparison in which gas standards were distributed from one laboratory for measurement by all participating laboratories. CCQM-P73 would be the first comparison organized within the CCQM in which reactive gas standards would be compared against each other at a central measurement facility, with the additional complication that the stability of gas concentration within cylinders could be a limiting factor to the level of comparability achievable.

**Measurement Standards:**

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

Each participating laboratory was asked to provide:

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

Together with the following information:

- a purity table with uncertainties for the nominally pure NO parent gas; or
- in the case that the highest level parent gas was not nominally pure NO, a purity table with uncertainties for the highest level parent NO/N$_2$ mixture;
- a purity table with uncertainties for the nominally pure N$_2$ parent gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they were prepared and the time they were shipped to the BIPM.

Information submitted by participating laboratories is listed in Appendix 3.

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

- the twenty-two gravimetric mixtures provided by the eleven participating laboratories;
- three gravimetric mixtures (referred to as VALCRM1,2,3) provided by an NMI that did not participate in the CCQM-P73, but had participated successfully in CCQM-K1.c and EUROMET-K1.c. These gas standards had been used in the validation studies performed at the BIPM in preparation for the coordination of CCQM-P73. These gas mixture were contained in aluminium cylinders passivated with the BOC Spectraseal process. They were not pre-treated with nitrogen monoxide.
- two gas standards from a speciality gas company used as control mixtures for instrument drift monitoring and correction;
- and N₂ (6.0 grade, Messer) used as the zero gas.

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

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<tr>
<th>Mixture Label</th>
<th>Source</th>
<th>Cylinder #</th>
<th>Range (µmol/mol)</th>
<th>NMI Assigned ( x_{NO} ) (µmol/mol)</th>
<th>NMI Assigned ( u(x_{NO}) ) (µmol/mol)</th>
<th>Autosampler Port #</th>
<th>Pressure Reducer #</th>
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<td>CPB29491</td>
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Table 1: Gas standards and mixtures analysed as part of CCQM-P73

**Schedule:**
Measurements on gas standards received by the BIPM were carried out on the following dates:
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<th>Measurement Series</th>
<th>Date of measurement</th>
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**Description of measurement systems used at the BIPM:**

Two analysers, the ABB Advance Optima LIMAS 11-UV analyser and the Thermo Environmental Instruments Model 42C Chemiluminescence NO-NO₂-NOₓ analyser, were used for the comparison of nitrogen monoxide gas standards. The two analysers were connected in series, with the **42C** downstream of the **LIMAS**. A sample flow of 500 ml/min was sufficient to supply both analysers when connected in series.

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

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

<table>
<thead>
<tr>
<th>Analysis #</th>
<th>Control Mixtures</th>
<th>Sample Mixtures: Ascending $x_{\text{NO}}$ Order</th>
<th>Sample Mixtures: Descending $x_{\text{NO}}$ Order</th>
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<td>M22</td>
<td>M4</td>
<td>M19</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>M23</td>
<td>M3</td>
<td>M5</td>
</tr>
<tr>
<td>39</td>
<td></td>
<td>M24</td>
<td>M2</td>
<td>M21</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>M25</td>
<td>M1</td>
<td>M8</td>
</tr>
<tr>
<td>41</td>
<td>$R_1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>$R_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Order of cylinder analysis for various measurement series

Each cylinder was connected via its pressure reducer to one inlet of a 30-inlet automatic gas sampler. The sampler was connected to the two analysers, a Thermo 42C chemiluminescence NO analyser and an ABB LIMAS UV11 ultraviolet
spectrophotometry NO analyser. The pressure reducer of each cylinder was flushed nine times with the gas mixture of its cylinder. The cylinder valve was then closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at approximately 300 kPa. The cylinders were left standing for at least 24 hours, to allow conditioning of the pressure reducers.

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

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

**Analyser responses and measurement uncertainties**

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

- the repeatability and reproducibility of its measurements systems;
- any drift in analyser response;
- any biases introduced by the use of pressure regulators and sampling ports.

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

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

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

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

where,

- $y_{LIMASCorrected,i}$ is the zero corrected LIMAS UV11 response of the $i^{th}$ analysis in the sequence listed in Table 2.
- $y_{Limas,i}$ is the LIMAS UV11 response of the $i^{th}$ analysis in the sequence listed in Table 2.
- $y_{LIMAS,zero}$ is the LIMAS UV11 response to high purity nitrogen.
and $C$ is applied to correct for biases introduced by the use of individual pressure regulators and sampling lines/ports for each individual gas standard. The range of responses recorded for the LIMAS analyser varied from 3000 a.u. to 10000 a.u. The calculated uncertainty in the analyser response is summarized in the tables below. Over the three measurement periods of the comparison, the standard deviation of the analyser response was observed to increase. It was assumed that this was due to the ageing of the UV lamp, resulting in reduced intensity and increased signal noise. The standard uncertainties of the LIMAS analyser response and zero value were based on standard deviations of the mean of 120 measurements and validated by calculation of the Allan variance.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value /a.u.</th>
<th>Standard uncertainty /a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_{\text{LIMAS}}$</td>
<td>3000 to 10000</td>
<td>2.8</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, zero}}$</td>
<td>140</td>
<td>2.8</td>
</tr>
<tr>
<td>$C$</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, Corrected}}$</td>
<td>3000 to 10000</td>
<td>4.4</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value /a.u.</th>
<th>Standard uncertainty /a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_{\text{LIMAS}}$</td>
<td>3000 to 10000</td>
<td>3.5</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, zero}}$</td>
<td>140</td>
<td>3.5</td>
</tr>
<tr>
<td>$C$</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, Corrected}}$</td>
<td>3000 to 10000</td>
<td>5.4</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value /a.u.</th>
<th>Standard uncertainty /a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_{\text{LIMAS}}$</td>
<td>3000 to 10000</td>
<td>5.6</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, zero}}$</td>
<td>140</td>
<td>5.6</td>
</tr>
<tr>
<td>$C$</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>$y_{\text{LIMAS, Corrected}}$</td>
<td>3000 to 10000</td>
<td>8.2</td>
</tr>
</tbody>
</table>

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

The (zero corrected) 42C analyser response, $y_{42C}$, was corrected for analyser drift by monitoring the analyser response for repeated measurements of control cylinders. Every seventh analysis (every 28 minutes) was of the control mixture R1. The analyser response to a given CCQM-P73 mixture, $y_{42C}$, was corrected multiplicatively using the following set of formulae:
\[ y_{42C,\text{i}=7,j} = \frac{y_{42C,j} \cdot y_{42C,6}}{(\frac{1}{2} y_{42C,j-2} + \frac{1}{2} y_{42C,j+5})}, \quad \text{for } i = 8, 15, 22, 29, 36 \]

\[ y_{42C,\text{i}=7,j} = \frac{y_{42C,j} \cdot y_{42C,6}}{(\frac{1}{2} y_{42C,j-3} + \frac{1}{2} y_{42C,j+4})}, \quad \text{for } i = 9, 16, 23, 30, 37 \]

\[ y_{42C,\text{i}=7,j} = \frac{y_{42C,j} \cdot y_{42C,6}}{(\frac{1}{2} y_{42C,j-4} + \frac{1}{2} y_{42C,j+3})}, \quad \text{for } i = 10, 17, 24, 31, 38 \]

\[ y_{42C,\text{i}=7,j} = \frac{y_{42C,j} \cdot y_{42C,6}}{(\frac{1}{2} y_{42C,j-5} + \frac{1}{2} y_{42C,j+2})}, \quad \text{for } i = 11, 18, 25, 32, 39 \]

\[ y_{42C,\text{i}=7,j} = \frac{y_{42C,j} \cdot y_{42C,6}}{(\frac{1}{2} y_{42C,j-6} + \frac{1}{2} y_{42C,j+1})}, \quad \text{for } i = 12, 19, 26, 33, 40 \]

where,

\( y_{42C,j} \) is the 42C response of the \( i \)th analysis in the sequence listed in Table 2;

\( y_0 \) is the 42C response to high purity nitrogen;

\( y_{42C,\text{i}=j} \) is the zero corrected 42C response of the \( i \)th analysis in the sequence listed in Table 2;

\( y_{42C,6} \) refers to the first analysis of the control mixture, R1, in the sequence;

\( y_{42C,\text{i}=7,j} \) refers to the drift corrected \( y_{42C,j} \) response

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Standard Uncertainty</th>
<th>Sensitivity Coefficient</th>
<th>Uncertainty Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_{42C,\text{i}=j} )</td>
<td>31513 a.u.</td>
<td>5.0 a.u.</td>
<td>1</td>
<td>5.0 a.u.</td>
</tr>
<tr>
<td>( y_0 )</td>
<td>38.9 a.u.</td>
<td>20.4 a.u.</td>
<td>-1</td>
<td>-20.4 a.u.</td>
</tr>
<tr>
<td>( y_{42C,6} )</td>
<td>45834.7 a.u.</td>
<td>5.0 a.u.</td>
<td>0.196</td>
<td>0.982 a.u.</td>
</tr>
<tr>
<td>( y_{42C,\text{i}=5} )</td>
<td>45807.2 a.u.</td>
<td>5.0 a.u.</td>
<td>-0.196</td>
<td>-0.982 a.u.</td>
</tr>
<tr>
<td>( C )</td>
<td>0 a.u.</td>
<td>21.0 a.u.</td>
<td>1</td>
<td>21.0 a.u.</td>
</tr>
<tr>
<td>( y_{42C,\text{i}=7,j} )</td>
<td>31479.6 a.u.</td>
<td>29.7 a.u.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Uncertainty budget for corrected 42C analyser response

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

\[ y_{42C,\text{i}=7,j} = \left( \frac{y_{42C,j} - y_0}{\frac{1}{2} y_{42C,j-2} - y_0} \right) \left( y_{42C,6} - y_0 \right) \left( \frac{1}{2} y_{42C,j-5} - y_0 \right) + C \]

The standard uncertainties of the 42C analyser responses were based on standard deviations of the mean of 120 measurements and validated by calculation of the Allan variance. The zero response of the 42C analyser was observed to increase by 70 a.u. over the course of a whole measurement series. The standard uncertainty of the zero response
was calculated by assuming a rectangular distribution with limits set as the minimum and maximum zero response value, and the mean value used for signal correction.

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

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

Table 7: Corrected LIMAS 11UV and 42C analyser responses for the twenty-five gas standards listed in Table 1, analysed on 30/08/06 (3008a)
ABB LIMAS UV11 analyser results

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

Thermo 42C Chemiluminescence analyser results

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

The analysis of the data depicted in Figures 1 and 2 required the fitting of a regression line. Previous validation studies performed by the BIPM (Appendix 1) had shown that a linear regression model would be expected. Visual inspection of the data, confirmed by
regression analysis, indicated that data for a number of gas standards were not compatible with the calculated regression line. FTIR analysis of the gas mixtures was performed to confirm that these gas standards could be considered as outliers, before further regression analysis of the remaining data was undertaken.

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

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

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

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

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

<table>
<thead>
<tr>
<th>Mixture Label</th>
<th>NMI Assigned NO2 (µmol/mol)</th>
<th>NMI Assigned NO2 (µmol/mol)</th>
<th>NMI Assigned NO2-FTIR (µmol/mol)</th>
<th>BIPM FTIR u(NO2-FTIR) (µmol/mol)</th>
<th>BIPM FTIR u(NO2) (µmol/mol)</th>
<th>( \Delta (\text{NO2}) ) (µmol/mol)</th>
<th>U (( \Delta [\text{NO2}] )) (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS (M1)</td>
<td>31.02</td>
<td>0.001</td>
<td>0.0002</td>
<td>0.007</td>
<td>0.010</td>
<td>0.006</td>
<td>0.020</td>
</tr>
<tr>
<td>CSIR-NML (M2)</td>
<td>33.063</td>
<td>0.033215</td>
<td>0.03835</td>
<td>0.278</td>
<td>0.056</td>
<td>0.245</td>
<td>0.135</td>
</tr>
<tr>
<td>CERI (M3)</td>
<td>34.93</td>
<td></td>
<td></td>
<td>0.007</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VALCRM1 (M4)</td>
<td>37.17</td>
<td></td>
<td></td>
<td>0.003</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNE (M5)</td>
<td>39.839</td>
<td>0.00035</td>
<td>0.000025</td>
<td>0.005</td>
<td>0.010</td>
<td>0.004</td>
<td>0.020</td>
</tr>
<tr>
<td>SMU (M6)</td>
<td>40.419</td>
<td>0.086</td>
<td>0.017</td>
<td>0.029</td>
<td>0.010</td>
<td>-0.057</td>
<td>0.039</td>
</tr>
<tr>
<td>CENAM (M7)</td>
<td>40.777</td>
<td></td>
<td></td>
<td>0.003</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VNIIM (M8)</td>
<td>42.18</td>
<td>0.042</td>
<td>0.005</td>
<td>0.033</td>
<td>0.010</td>
<td>-0.009</td>
<td>0.022</td>
</tr>
<tr>
<td>NIST (M9)</td>
<td>43.081</td>
<td>0.0341</td>
<td>0.0031</td>
<td>0.031</td>
<td>0.010</td>
<td>-0.003</td>
<td>0.021</td>
</tr>
<tr>
<td>NMIA (M10)</td>
<td>44.844</td>
<td>0.045</td>
<td>0.026</td>
<td>0.004</td>
<td>0.010</td>
<td>-0.041</td>
<td>0.056</td>
</tr>
<tr>
<td>VALCRM2 (M11)</td>
<td>46.98</td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPQ (M12)</td>
<td>47.001</td>
<td>0.004701</td>
<td>0.00023</td>
<td>0.006</td>
<td>0.010</td>
<td>0.002</td>
<td>0.020</td>
</tr>
<tr>
<td>NMi-VSL (M13)</td>
<td>47.011</td>
<td>0.004</td>
<td>0.0008</td>
<td>0.006</td>
<td>0.010</td>
<td>0.002</td>
<td>0.020</td>
</tr>
<tr>
<td>CERI (M14)</td>
<td>50.91</td>
<td></td>
<td></td>
<td>0.006</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KRISS (M15)</td>
<td>52.984</td>
<td>0.002</td>
<td>0.0003</td>
<td>0.007</td>
<td>0.010</td>
<td>0.005</td>
<td>0.020</td>
</tr>
<tr>
<td>CSIR-NML (M16)</td>
<td>55.111</td>
<td>0.055221</td>
<td>0.06737</td>
<td>0.272</td>
<td>0.054</td>
<td>0.217</td>
<td>0.173</td>
</tr>
<tr>
<td>VALCRM3 (M17)</td>
<td>56.95</td>
<td></td>
<td></td>
<td>0.002</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMU (M18)</td>
<td>59.576</td>
<td>0.127</td>
<td>0.026</td>
<td>0.151</td>
<td>0.030</td>
<td>0.024</td>
<td>0.080</td>
</tr>
<tr>
<td>LNE (M19)</td>
<td>60.58</td>
<td>0.00322</td>
<td>0.0001</td>
<td>0.003</td>
<td>0.010</td>
<td>-0.001</td>
<td>0.020</td>
</tr>
<tr>
<td>CENAM (M20)</td>
<td>60.69</td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMI-VSL (M21)</td>
<td>63.012</td>
<td>0.0054</td>
<td>0.0011</td>
<td>0.010</td>
<td>0.010</td>
<td>0.005</td>
<td>0.020</td>
</tr>
<tr>
<td>VNIIM (M22)</td>
<td>63.32</td>
<td>0.064</td>
<td>0.007</td>
<td>0.032</td>
<td>0.010</td>
<td>-0.032</td>
<td>0.024</td>
</tr>
<tr>
<td>NMIA (M23)</td>
<td>64.84</td>
<td>0.065</td>
<td>0.038</td>
<td>0.007</td>
<td>0.010</td>
<td>-0.058</td>
<td>0.079</td>
</tr>
<tr>
<td>NIST (M24)</td>
<td>67.085</td>
<td>0.0531</td>
<td>0.0048</td>
<td>0.050</td>
<td>0.010</td>
<td>-0.003</td>
<td>0.022</td>
</tr>
<tr>
<td>IPQ (M25)</td>
<td>69.7</td>
<td>0.006975</td>
<td>0.00035</td>
<td>0.006</td>
<td>0.010</td>
<td>-0.001</td>
<td>0.020</td>
</tr>
</tbody>
</table>

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

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acquired across a total wavelength range of (1500 to 2500) cm$^{-1}$, were fitted on two spectral windows according to the impurities of interest: (1400 to 1700) cm$^{-1}$ for H$_2$O and NO$_2$, and (2000 to 2400) cm$^{-1}$ for CO, CO$_2$ and N$_2$O.

**Uncertainty budget for FTIR measurements**

Previous comparisons between mole fraction determinations by FTIR spectroscopy with fitting to synthetic spectra versus gravimetry$^3$, have indicated that the values determined from FTIR measurements could be biased by up to 5 % relative to gravimetric values, although the precision of the measurements were much better than this. A conservative estimate for the measurement uncertainty of results determined from FTIR analysis was adopted, with 10% of the value taken as the standard uncertainty, with a minimum of 10 nmol.mol$^{-1}$. The mass fractions NO$_2$ and N$_2$O measured at the BIPM are shown in figures 3 and 5 respectively. In the cases where the purity tables provided by participating laboratories gave values of mole fractions of NO$_2$ and N$_2$O, the difference between these values and those determined by the BIPM with FTIR analysis ($\Delta$(NO$_2$) and $\Delta$(N$_2$O)) were calculated and shown in figures 4 and 6.

CENAM reported a value for the sum of both NO$_2$ and N$_2$O mole fractions present, and therefore differences for individual components could not be calculated.

LNE and CERI reported N$_2$O and NO$_2$ impurities in their pure nitrogen monoxide gas. CERI did not provide information on the N$_2$O and NO$_2$ mole fractions in the gas standards submitted for analysis in CCQM-P73, and LNE only provided values for nitrogen dioxide in their gas standards.

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

Figure 4: Graph of difference between NMI assigned values and BIPM FTIR measurements of NO₂ mole fractions within gas standards analysed in CCQM-P73
Table 9: NMI assigned and BIPM FTIR measurement results for N₂O mole fractions in gas standards analysed in CCQM-P73

<table>
<thead>
<tr>
<th>Mixture Label</th>
<th>NMI Assigned ( x_{\text{N}_2\text{O}} ) (µmol/mol)</th>
<th>NMI Assigned ( u(x_{\text{N}_2\text{O}}) ) (µmol/mol)</th>
<th>BIPM FTIR ( x_{\text{N}_2\text{O}-\text{FTIR}} ) (µmol/mol)</th>
<th>BIPM FTIR ( u(x_{\text{N}_2\text{O}-\text{FTIR}}) ) (µmol/mol)</th>
<th>( \Delta (N_2O) ) (µmol/mol)</th>
<th>( U(\Delta [N_2O]) ) (µmol/mol) (k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS (M1)</td>
<td>31.02</td>
<td>0.046</td>
<td>0.002</td>
<td>0.089</td>
<td>0.020</td>
<td>0.043</td>
</tr>
<tr>
<td>CSIR-NML (M2)</td>
<td>33.063</td>
<td>0.033</td>
<td>0.0383</td>
<td>0.214</td>
<td>0.043</td>
<td>0.181</td>
</tr>
<tr>
<td>CERI (M3)</td>
<td>34.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VALCRM1 (M4)</td>
<td>37.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNE (M5)</td>
<td>39.839</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMU (M6)</td>
<td>40.419</td>
<td>0.058</td>
<td>0.011</td>
<td>0.272</td>
<td>0.054</td>
<td>0.214</td>
</tr>
<tr>
<td>CENAM (M7)</td>
<td>40.777</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VNIIM (M8)</td>
<td>42.18</td>
<td>0.051</td>
<td>0.006</td>
<td>0.057</td>
<td>0.020</td>
<td>0.006</td>
</tr>
<tr>
<td>NIST (M9)</td>
<td>43.081</td>
<td>0.035</td>
<td>0.0035</td>
<td>0.032</td>
<td>0.020</td>
<td>-0.003</td>
</tr>
<tr>
<td>NMIA (M10)</td>
<td>44.844</td>
<td>0.045</td>
<td>0.026</td>
<td>0.483</td>
<td>0.097</td>
<td>0.438</td>
</tr>
<tr>
<td>VALCRM2 (M11)</td>
<td>46.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPQ (M12)</td>
<td>47.001</td>
<td>0.001</td>
<td>0.000023</td>
<td>0.020</td>
<td>0.020</td>
<td>0.019</td>
</tr>
<tr>
<td>NMi-VSL (M13)</td>
<td>47.011</td>
<td>0.011</td>
<td>0.0012</td>
<td>0.018</td>
<td>0.020</td>
<td>0.007</td>
</tr>
<tr>
<td>CERI (M14)</td>
<td>50.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KRISS (M15)</td>
<td>52.984</td>
<td>0.078</td>
<td>0.004</td>
<td>0.145</td>
<td>0.029</td>
<td>0.067</td>
</tr>
<tr>
<td>CSIR-NML (M16)</td>
<td>55.111</td>
<td>0.055</td>
<td>0.06376</td>
<td>0.356</td>
<td>0.071</td>
<td>0.301</td>
</tr>
<tr>
<td>VALCRM3 (M17)</td>
<td>56.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMU (M18)</td>
<td>59.576</td>
<td>0.085</td>
<td>0.017</td>
<td>0.398</td>
<td>0.080</td>
<td>0.313</td>
</tr>
<tr>
<td>LNE (M19)</td>
<td>60.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CENAM (M20)</td>
<td>60.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMi-VSL (M21)</td>
<td>63.012</td>
<td>0.015</td>
<td>0.0016</td>
<td>0.020</td>
<td>0.020</td>
<td>0.005</td>
</tr>
<tr>
<td>VNIIM (M22)</td>
<td>63.32</td>
<td>0.076</td>
<td>0.009</td>
<td>0.074</td>
<td>0.020</td>
<td>-0.002</td>
</tr>
<tr>
<td>NMIA (M23)</td>
<td>64.84</td>
<td>0.065</td>
<td>0.038</td>
<td>0.897</td>
<td>0.139</td>
<td>0.632</td>
</tr>
<tr>
<td>NIST (M24)</td>
<td>67.085</td>
<td>0.055</td>
<td>0.0055</td>
<td>0.050</td>
<td>0.020</td>
<td>-0.005</td>
</tr>
<tr>
<td>IPQ (M25)</td>
<td>69.7</td>
<td>0.001</td>
<td>0.000035</td>
<td>0.029</td>
<td>0.020</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Figure 5: BIPM FTIR measurement results for N₂O mole fractions in gas standards analysed in CCQM-P73

Figure 6: Graph of difference between NMI assigned values and BIPM FTIR measurements of N₂O mole fractions within gas standards analysed in CCQM-P73
The comparison of NMI assigned values and measured values for NO2 and N2O mole fractions confirmed that the following standards would be omitted from the calculation of the regression line for the nitrogen monoxide measurement data:

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

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

a) the determination of the analysis function \( x = G(y) \), which expressed analyte contents in relation to corresponding measured responses;

b) validation of the analysis function;

c) and prediction of mole fraction values from measured responses and comparison to NMI assigned values. The difference in these quantities \( (D) \) could be compared to degrees of equivalence calculated in previous key comparisons for nitrogen monoxide gas standards.

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

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

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

As no additional information was available to the coordinating laboratory to omit further cylinders from the regression analysis data set, it was decided to increase the values for the analyser measurement uncertainties until the analysis function was consistent with the
calibration data. This approach was consistent with the hypothesis that the analytical uncertainties previously validated by the coordinating laboratory had not included systematic effects within the measurement system. In order to arrive at an analysis function that was consistent with the calibration data, the measurement uncertainty values used were increased from 4.4 a.u. to 11.05 a.u. for the LIMAS 11-UV analyser, and from 29.7 a.u. to 89.1 a.u. for the 42C Chemiluminescence analyser.

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

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

\[ x = b_0 + b_1 y \]

where,

- \( x \) was the mole fraction of nitrogen monoxide, \( \mu mol/mol \)
- \( y \) was the corrected instrument response, a.u.

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LIMAS 11-UV analysis</th>
<th>42C Chemiluminescence analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0 )</td>
<td>-0.30406</td>
<td>-0.37102</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>7.5168 x 10^{-3}</td>
<td>1.0058 x 10^{-3}</td>
</tr>
<tr>
<td>( u(b_0) )</td>
<td>0.10497</td>
<td>0.11265</td>
</tr>
<tr>
<td>( u(b_1) )</td>
<td>1.4964 x 10^{-5}</td>
<td>2.1439 x 10^{-6}</td>
</tr>
<tr>
<td>Covariance</td>
<td>-1.5311 x 10^{-6}</td>
<td>-2.3547 x 10^{-7}</td>
</tr>
<tr>
<td>Remaining SSD</td>
<td>25.01</td>
<td>26.0</td>
</tr>
<tr>
<td>Goodness-of-fit measure</td>
<td>1.844</td>
<td>1.7879</td>
</tr>
</tbody>
</table>

Table 10: Regression analysis parameters for measurement results recorded on 30/08/08 (3008a)
Figure 7: Regression analysis of a sub-set of cylinders from corrected LIMAS 11UV responses recorded on 30/08/06 (3008a), displaying differences between adjusted and assigned mole fraction values for each cylinder in the regression analysis data set.

Figure 8: Regression analysis of a sub-set of cylinders for corrected LIMAS 11UV responses analysed on 30/08/06 (3008a), displaying differences between adjusted and assigned analyser responses for each cylinder in the regression analysis data set.
Figure 9: Regression analysis of a sub-set of cylinders from corrected 42C chemiluminescence analyser responses recorded on 30/08/06 (3008a), displaying differences between adjusted and assigned mole fraction values for each cylinder in the regression analysis data set.

Figure 10: Regression analysis of a sub-set of cylinders for corrected 42C chemiluminescence analyser responses analysed on 30/08/06 (3008a), displaying
differences between adjusted and assigned analyser responses for each cylinder in the regression analysis data set.

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

\[
|\hat{x}_i - x_i| \leq 2u(x_i) \quad \text{and} \quad |\hat{y}_i - y_i| \leq 2u(y_i)
\]

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

**Comparison of predicted and assigned mole fraction values**

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

\[
D = x_{\text{pred}} - x_{\text{grav}}
\]

and

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

The differences between predicted and assigned gravimetric values are in Tables 11 and 12 and plotted in figures 11 and 12. By considering the predicted value as the reference value for each gas standard, the calculated values of \(D\) can be compared to degrees of equivalence calculated in previous key comparisons for nitrogen monoxide. In order for biases to appear in the same sense, the values of \(−D\) from CCQM-K1.c and EUROMET.K1.c are plotted in figure 13 together with the values of \(D\) determined in CCQM-P73.
Mixture & $x_{\text{NO-grav}}$ & $u(x_{\text{NO-grav}})$ & $y_{\text{LIMAS}}$ & $u(y_{\text{LIMAS}})$ & $x_{\text{NO-pred}}$ & $u(x_{\text{NO-pred}})$ & $D$ & $u(D)$ & $U(D)$ \\
KRISS (M1) & 31.020 & 0.007 & 4160.409 & 11.050 & 30.969 & 0.095 & -0.051 & 0.095 & 0.191 \\
CSIR-NML (M2) & 33.063 & 0.062 & 4385.410 & 11.050 & 32.660 & 0.094 & -0.403 & 0.112 & 0.225 \\
CERI (M3) & 34.930 & 0.020 & 4684.796 & 11.050 & 34.911 & 0.092 & -0.019 & 0.094 & 0.189 \\
VALCRM1 (M4) & 37.170 & 0.027 & 4983.457 & 11.050 & 37.156 & 0.091 & -0.014 & 0.095 & 0.189 \\
LNE (M5) & 39.839 & 0.040 & 5279.117 & 11.050 & 39.378 & 0.089 & -0.461 & 0.098 & 0.196 \\
SMU (M6) & 40.419 & 0.031 & 5350.075 & 11.050 & 39.912 & 0.089 & -0.507 & 0.094 & 0.189 \\
CENAM (M7) & 40.777 & 0.088 & 5484.506 & 11.050 & 40.922 & 0.089 & 0.145 & 0.125 & 0.250 \\
VNIIM (M8) & 42.180 & 0.030 & 5639.689 & 11.050 & 42.088 & 0.088 & -0.092 & 0.093 & 0.186 \\
NIST (M9) & 43.081 & 0.032 & 5790.213 & 11.050 & 43.220 & 0.088 & 0.139 & 0.093 & 0.187 \\
NMIA (M10) & 44.844 & 0.074 & 5852.779 & 11.050 & 43.690 & 0.088 & -1.154 & 0.115 & 0.229 \\
VALCRM2 (M11) & 46.980 & 0.028 & 6295.423 & 11.050 & 47.018 & 0.087 & 0.038 & 0.091 & 0.182 \\
IPQ (M12) & 47.001 & 0.004 & 6307.814 & 11.050 & 47.111 & 0.087 & 0.110 & 0.087 & 0.174 \\
NMi-VSL (M13) & 47.011 & 0.111 & 6310.080 & 11.050 & 47.128 & 0.087 & 0.117 & 0.087 & 0.175 \\
CERI (M14) & 50.910 & 0.020 & 6792.274 & 11.050 & 50.752 & 0.086 & -0.158 & 0.089 & 0.177 \\
KRISS (M15) & 52.984 & 0.009 & 7068.559 & 11.050 & 52.829 & 0.086 & -0.155 & 0.087 & 0.174 \\
CSIR-NML (M16) & 55.111 & 0.104 & 7273.698 & 11.050 & 54.371 & 0.087 & -0.740 & 0.135 & 0.271 \\
VALCRM3 (M17) & 56.950 & 0.031 & 7624.182 & 11.050 & 57.006 & 0.087 & 0.056 & 0.092 & 0.185 \\
SMU (M18) & 59.576 & 0.044 & 7861.665 & 11.050 & 58.791 & 0.088 & -0.785 & 0.098 & 0.196 \\
LNE (M19) & 60.580 & 0.065 & 8078.630 & 11.050 & 60.422 & 0.088 & -0.158 & 0.110 & 0.219 \\
CENAM (M20) & 60.690 & 0.104 & 8148.086 & 11.050 & 60.944 & 0.088 & 0.254 & 0.137 & 0.273 \\
NMi-VSL (M21) & 63.012 & 0.023 & 8434.911 & 11.050 & 63.100 & 0.090 & 0.088 & 0.092 & 0.185 \\
VNIIM (M22) & 63.320 & 0.040 & 8447.391 & 11.050 & 63.193 & 0.090 & -0.127 & 0.098 & 0.196 \\
NMIA (M23) & 64.840 & 0.110 & 8428.526 & 11.050 & 63.052 & 0.090 & -1.788 & 0.142 & 0.284 \\
NIST (M24) & 67.085 & 0.047 & 8968.432 & 11.050 & 67.110 & 0.092 & 0.025 & 0.103 & 0.207 \\
IPQ (M25) & 69.700 & 0.007 & 9318.398 & 11.050 & 69.741 & 0.094 & 0.041 & 0.094 & 0.188 \\

Table 11: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 3008a data set)
### Table 12: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 3008a data set)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$x_{\text{NO-grav}}$ μmol/mol</th>
<th>$u(x_{\text{NO-grav}})$ μmol/mol</th>
<th>$y_{42C}$ /a.u.</th>
<th>$u(y_{42C})$ /a.u.</th>
<th>$x_{\text{NO-pred}}$ μmol/mol</th>
<th>$u(x_{\text{NO-pred}})$ μmol/mol</th>
<th>$D$ μmol/mol</th>
<th>$u(D)$ μmol/mol</th>
<th>$U(D)$ μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS (M1)</td>
<td>31.020</td>
<td>0.007</td>
<td>31119.552</td>
<td>89.100</td>
<td>30.929</td>
<td>0.103</td>
<td>-0.091</td>
<td>0.103</td>
<td>0.206</td>
</tr>
<tr>
<td>CSIR-NML (M2)</td>
<td>33.063</td>
<td>0.062</td>
<td>32815.374</td>
<td>89.100</td>
<td>32.634</td>
<td>0.101</td>
<td>-0.429</td>
<td>0.119</td>
<td>0.237</td>
</tr>
<tr>
<td>CERI (M3)</td>
<td>34.930</td>
<td>0.020</td>
<td>35053.785</td>
<td>89.100</td>
<td>34.866</td>
<td>0.099</td>
<td>-0.044</td>
<td>0.101</td>
<td>0.203</td>
</tr>
<tr>
<td>VALCRM1 (M4)</td>
<td>37.170</td>
<td>0.027</td>
<td>37311.350</td>
<td>89.100</td>
<td>37.156</td>
<td>0.098</td>
<td>-0.014</td>
<td>0.101</td>
<td>0.203</td>
</tr>
<tr>
<td>LNE (M5)</td>
<td>39.839</td>
<td>0.040</td>
<td>39531.760</td>
<td>89.100</td>
<td>39.390</td>
<td>0.096</td>
<td>-0.449</td>
<td>0.104</td>
<td>0.209</td>
</tr>
<tr>
<td>SMU (M6)</td>
<td>40.419</td>
<td>0.031</td>
<td>40072.395</td>
<td>89.100</td>
<td>39.933</td>
<td>0.096</td>
<td>-0.486</td>
<td>0.101</td>
<td>0.202</td>
</tr>
<tr>
<td>CENAM (M7)</td>
<td>40.777</td>
<td>0.088</td>
<td>41085.299</td>
<td>89.100</td>
<td>40.952</td>
<td>0.096</td>
<td>0.175</td>
<td>0.130</td>
<td>0.260</td>
</tr>
<tr>
<td>VNIIM (M8)</td>
<td>42.180</td>
<td>0.030</td>
<td>42194.589</td>
<td>89.100</td>
<td>42.068</td>
<td>0.095</td>
<td>-0.112</td>
<td>0.100</td>
<td>0.199</td>
</tr>
<tr>
<td>NIST (M9)</td>
<td>43.081</td>
<td>0.032</td>
<td>43381.451</td>
<td>89.100</td>
<td>43.262</td>
<td>0.095</td>
<td>0.181</td>
<td>0.100</td>
<td>0.200</td>
</tr>
<tr>
<td>NMIA (M10)</td>
<td>44.844</td>
<td>0.074</td>
<td>43802.957</td>
<td>89.100</td>
<td>43.686</td>
<td>0.094</td>
<td>-1.158</td>
<td>0.120</td>
<td>0.240</td>
</tr>
<tr>
<td>VALCRM2 (M11)</td>
<td>46.980</td>
<td>0.028</td>
<td>47076.981</td>
<td>89.100</td>
<td>46.979</td>
<td>0.093</td>
<td>-0.001</td>
<td>0.098</td>
<td>0.195</td>
</tr>
<tr>
<td>IPQ (M12)</td>
<td>47.001</td>
<td>0.004</td>
<td>47218.588</td>
<td>89.100</td>
<td>47.121</td>
<td>0.093</td>
<td>0.120</td>
<td>0.094</td>
<td>0.187</td>
</tr>
<tr>
<td>NMI-VSL (M13)</td>
<td>47.011</td>
<td>0.011</td>
<td>47241.804</td>
<td>89.100</td>
<td>47.144</td>
<td>0.093</td>
<td>0.133</td>
<td>0.094</td>
<td>0.188</td>
</tr>
<tr>
<td>CERI (M14)</td>
<td>50.910</td>
<td>0.020</td>
<td>50858.756</td>
<td>89.100</td>
<td>50.782</td>
<td>0.093</td>
<td>-0.128</td>
<td>0.095</td>
<td>0.190</td>
</tr>
<tr>
<td>KRISS (M15)</td>
<td>52.984</td>
<td>0.009</td>
<td>52913.261</td>
<td>89.100</td>
<td>52.849</td>
<td>0.093</td>
<td>-0.135</td>
<td>0.094</td>
<td>0.187</td>
</tr>
<tr>
<td>CSIR-NML (M16)</td>
<td>55.111</td>
<td>0.104</td>
<td>54386.625</td>
<td>89.100</td>
<td>54.331</td>
<td>0.093</td>
<td>-0.780</td>
<td>0.140</td>
<td>0.279</td>
</tr>
<tr>
<td>VALCRM3 (M17)</td>
<td>56.950</td>
<td>0.031</td>
<td>57059.788</td>
<td>89.100</td>
<td>57.019</td>
<td>0.094</td>
<td>0.069</td>
<td>0.099</td>
<td>0.198</td>
</tr>
<tr>
<td>SMU (M18)</td>
<td>59.576</td>
<td>0.044</td>
<td>58768.379</td>
<td>89.100</td>
<td>58.738</td>
<td>0.094</td>
<td>-0.838</td>
<td>0.104</td>
<td>0.208</td>
</tr>
<tr>
<td>LNE (M19)</td>
<td>60.580</td>
<td>0.065</td>
<td>60439.333</td>
<td>89.100</td>
<td>60.418</td>
<td>0.095</td>
<td>-0.162</td>
<td>0.115</td>
<td>0.230</td>
</tr>
<tr>
<td>CENAM (M20)</td>
<td>60.690</td>
<td>0.014</td>
<td>60966.926</td>
<td>89.100</td>
<td>60.949</td>
<td>0.095</td>
<td>0.259</td>
<td>0.141</td>
<td>0.282</td>
</tr>
<tr>
<td>NMI-VSL (M21)</td>
<td>63.012</td>
<td>0.023</td>
<td>63103.526</td>
<td>89.100</td>
<td>63.098</td>
<td>0.096</td>
<td>0.086</td>
<td>0.099</td>
<td>0.198</td>
</tr>
<tr>
<td>VNIIM (M22)</td>
<td>63.320</td>
<td>0.040</td>
<td>63157.569</td>
<td>89.100</td>
<td>63.152</td>
<td>0.097</td>
<td>-0.168</td>
<td>0.104</td>
<td>0.209</td>
</tr>
<tr>
<td>NMIA (M23)</td>
<td>64.840</td>
<td>0.110</td>
<td>63015.979</td>
<td>89.100</td>
<td>63.010</td>
<td>0.096</td>
<td>-1.830</td>
<td>0.146</td>
<td>0.293</td>
</tr>
<tr>
<td>NIST (M24)</td>
<td>67.085</td>
<td>0.047</td>
<td>67111.452</td>
<td>89.100</td>
<td>67.129</td>
<td>0.099</td>
<td>0.044</td>
<td>0.110</td>
<td>0.219</td>
</tr>
<tr>
<td>IPQ (M25)</td>
<td>69.700</td>
<td>0.007</td>
<td>69676.385</td>
<td>89.100</td>
<td>69.709</td>
<td>0.101</td>
<td>0.009</td>
<td>0.101</td>
<td>0.203</td>
</tr>
</tbody>
</table>
Figure 11: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 3008a data set)

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

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

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

Discussion and Conclusions:

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

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

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

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

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

Acknowledgements:
Special acknowledgement is given to Dr Michael Esler who coordinated the comparison prior to his departure from the BIPM in October 2006.
Appendix 1: Summary of validation studies performed by the coordinating laboratory

In preparation for CCQM-P73 the BIPM conducted a number of studies to validate the performance and uncertainty of its analytical systems. Three gravimetrically prepared standards of nitrogen monoxide in nitrogen were purchased from one NMI and a fourth obtained from another. Both NMIs had successfully participated in CCQM-K1.c and EUROMET-K1.c. Details of these standards are contained in Table A1. The gas standards were analysed on 17/05/2005, (results listed in Table A2 and 3) and regression analysis performed as for all standards compared in CCQM-P73. All four cylinders were used for the determination of the analysis function, and the difference \((D)\) between predicted and gravimetric values for the nitrogen monoxide mole fraction calculated. Excellent agreement between the analysis function and calibration data was observed. This was consistent with estimates of the standard analytical uncertainty of 0.05% (at 37 \(\mu\text{mol/mol}\)) and 0.08% (at 57 \(\mu\text{mol/mol}\)), and predicted average standard uncertainties of the nitrogen monoxide mole fraction of 0.04 \(\mu\text{mol/mol}\).

<table>
<thead>
<tr>
<th>Gas standard</th>
<th>Certification date</th>
<th>(x_{\text{NO-grav}} \mu\text{mol/mol})</th>
<th>(u(x_{\text{NO-grav}}) \mu\text{mol/mol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALCRM1</td>
<td>05/04/04</td>
<td>37.17</td>
<td>0.0267</td>
</tr>
<tr>
<td>NMI-B</td>
<td>Before 08/03/05</td>
<td>40.04</td>
<td>0.0200</td>
</tr>
<tr>
<td>VALCRM2</td>
<td>05/04/04</td>
<td>46.98</td>
<td>0.0282</td>
</tr>
<tr>
<td>VALCRM3</td>
<td>05/04/04</td>
<td>56.95</td>
<td>0.0305</td>
</tr>
</tbody>
</table>

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

Figure A2: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas standards in the validation study set. (42C chemiluminescence analyser)
### Table A2: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the four gas standards in the validation study set. (LIMAS 11-UV analyser)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$x_{\text{NO-grav}}$ $\mu\text{mol/mol}$</th>
<th>$u(x_{\text{NO-grav}})$ $\mu\text{mol/mol}$</th>
<th>$y_{\text{LIMAS}}$ /a.u.</th>
<th>$u(y_{\text{LIMAS}})$ /a.u.</th>
<th>$x_{\text{NO-pred}}$ $\mu\text{mol/mol}$</th>
<th>$u(x_{\text{NO-pred}})$ $\mu\text{mol/mol}$</th>
<th>$D$ $\mu\text{mol/mol}$</th>
<th>$u(D)$ $\mu\text{mol/mol}$</th>
<th>$U(D)$ $\mu\text{mol/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALCRM1</td>
<td>37.17</td>
<td>0.0267</td>
<td>4839.1595</td>
<td>4.4</td>
<td>37.167</td>
<td>0.046</td>
<td>-0.003</td>
<td>0.053</td>
<td>0.106</td>
</tr>
<tr>
<td>NMI-B</td>
<td>40.04</td>
<td>0.0200</td>
<td>5210.694</td>
<td>4.4</td>
<td>40.051</td>
<td>0.043</td>
<td>0.011</td>
<td>0.047</td>
<td>0.094</td>
</tr>
<tr>
<td>VALCRM2</td>
<td>46.98</td>
<td>0.0282</td>
<td>6101.227</td>
<td>4.4</td>
<td>46.964</td>
<td>0.041</td>
<td>-0.016</td>
<td>0.050</td>
<td>0.099</td>
</tr>
<tr>
<td>VALCRM3</td>
<td>56.95</td>
<td>0.0305</td>
<td>7388.5131</td>
<td>4.4</td>
<td>56.957</td>
<td>0.054</td>
<td>0.007</td>
<td>0.082</td>
<td>0.124</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$x_{\text{NO-grav}}$ $\mu\text{mol/mol}$</th>
<th>$u(x_{\text{NO-grav}})$ $\mu\text{mol/mol}$</th>
<th>$y_{42C}$ /a.u.</th>
<th>$u(y_{42C})$ /a.u.</th>
<th>$x_{\text{NO-pred}}$ $\mu\text{mol/mol}$</th>
<th>$u(x_{\text{NO-pred}})$ $\mu\text{mol/mol}$</th>
<th>$D$ $\mu\text{mol/mol}$</th>
<th>$u(D)$ $\mu\text{mol/mol}$</th>
<th>$U(D)$ $\mu\text{mol/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALCRM1</td>
<td>37.17</td>
<td>0.0267</td>
<td>36648.5</td>
<td>29.7</td>
<td>37.167</td>
<td>0.041</td>
<td>-0.003</td>
<td>0.049</td>
<td>0.098</td>
</tr>
<tr>
<td>NMI-B</td>
<td>40.04</td>
<td>0.0200</td>
<td>39498.7</td>
<td>29.7</td>
<td>40.050</td>
<td>0.038</td>
<td>0.010</td>
<td>0.043</td>
<td>0.086</td>
</tr>
<tr>
<td>VALCRM2</td>
<td>46.98</td>
<td>0.0282</td>
<td>46332.9</td>
<td>29.7</td>
<td>46.963</td>
<td>0.037</td>
<td>-0.017</td>
<td>0.046</td>
<td>0.092</td>
</tr>
<tr>
<td>VALCRM3</td>
<td>56.95</td>
<td>0.0305</td>
<td>56212.6</td>
<td>29.7</td>
<td>56.957</td>
<td>0.049</td>
<td>0.007</td>
<td>0.058</td>
<td>0.116</td>
</tr>
</tbody>
</table>
Appendix 2: Results from measurement series 2 and 3

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

Figure A5: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 1409a data set)
Figure A6: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (LIMAS 11-UV analyser with the 0410c data set)

Figure A7: Difference ($D$) of NO mole fractions predicted from the analysis function versus gravimetric values assigned by NMIs for the twenty-five gas standards listed in Table 1. (42C chemiluminescence analyser with the 0410c data set)
Appendix 3: Information submitted by participating laboratories
(See attachment)

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

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

**Complementary informations on the results of LNE (CCQM-P73)**

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

<table>
<thead>
<tr>
<th>Date</th>
<th>Action</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006/05/10</td>
<td>Gravimetric preparation</td>
<td>$C_{\text{grav}}(\text{NO}) = (39.839 \pm 0.080) \mu\text{mol/mol}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_{\text{grav}}(\text{NO}_2) = (0.00036 \pm 0.00005) \mu\text{mol/mol}$</td>
</tr>
<tr>
<td>2006/05/31</td>
<td>Analysis</td>
<td>Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{\text{anal}}(\text{NO}) = (39.82 \pm 0.40) \mu\text{mol/mol}$ Deviation between &quot;Gravimetric concentration&quot; and &quot;Analytical concentration&quot; : - 0.06 %</td>
</tr>
<tr>
<td>2006/06/28</td>
<td>Analysis</td>
<td>Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{\text{anal}}(\text{NO}) = (39.74 \pm 0.40) \mu\text{mol/mol}$ Deviation between &quot;Gravimetric concentration&quot; and &quot;Analytical concentration&quot; : - 0.25 %</td>
</tr>
<tr>
<td>2006/07/25</td>
<td>Analysis</td>
<td>Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR $C_{\text{anal}}(\text{NO}) = (39.85 \pm 0.40) \mu\text{mol/mol}$ Deviation between &quot;Gravimetric concentration&quot; and &quot;Analytical concentration&quot; : + 0.03 %</td>
</tr>
<tr>
<td>Date</td>
<td>Event</td>
<td>Details</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2006/07/26</td>
<td>The gas mixture NO/N2 0040 was sent to BIPM</td>
<td></td>
</tr>
<tr>
<td>2007/04/18</td>
<td>Analysis</td>
<td>Determination of the analytical concentration of the gas mixture NO/N2 0040 with another gas mixture NO/N2 0037 by using FTIR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_{\text{anal}}(\text{NO}) = (39.25 \pm 0.40) \ \mu\text{mol/mol}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deviation between &quot;Gravimetric concentration&quot; and &quot;Analytical concentration&quot; : - 1.48 %</td>
</tr>
</tbody>
</table>
Comments:

- **Before delivery in BIPM**

  The different analyses done on the gas mixture NO/N2 0040 by LNE before delivery to BIPM show a good stability of the NO concentration during the time:
  
  - During 3 months, the results show no significant bias between analytical and gravimetric concentrations; consequently, the NO concentration of the gas mixture can be considered stable during 3 months (May to July 2006);
  
  - The analysis done on the gas mixture the day before delivery to BIPM shows a very small deviation of 0.03% between analytical and gravimetric concentrations: as before, there is no significant bias between analytical and gravimetric concentrations.

- **After its return from BIPM**

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

  On the other hand, an IR analysis has been done and shows that the N$_2$O and CO$_2$ concentrations are higher in April 2007 than in July 2006:
  
  - 2006/07/25: \( C_{\text{N}_2\text{O}} = 56 \text{ nmol/mol} \) \( C_{\text{CO}_2} = 52 \text{ nmol/mol} \)
  
  - 2007/04/18: \( C_{\text{N}_2\text{O}} = 140 \text{ nmol/mol} \) \( C_{\text{CO}_2} = 119 \text{ nmol/mol} \)

  The NO$_2$ concentration measured in April 2007 stays negligible, which confirms the results obtained by BIPM.

**Conclusion:**

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

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

- the delivery of the gas mixture to BIPM at the end of July 2006: the NO concentration was stable during 3 months in LNE (May to July 2006),

- the beginning of the tests done by BIPM in the framework of CCQM-P73 comparison: the NO concentration began to decrease.
Appendix 3: Descriptions of NO/N₂ standards prepared by participating laboratories

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

<table>
<thead>
<tr>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS</td>
</tr>
<tr>
<td>CSIR-NML</td>
</tr>
<tr>
<td>CERI</td>
</tr>
<tr>
<td>LNE</td>
</tr>
<tr>
<td>SMU</td>
</tr>
<tr>
<td>CENAM</td>
</tr>
<tr>
<td>VNIIM</td>
</tr>
<tr>
<td>NIST</td>
</tr>
<tr>
<td>NMIA</td>
</tr>
<tr>
<td>IPQ</td>
</tr>
<tr>
<td>NMI-VSL</td>
</tr>
</tbody>
</table>
Form CCQM-P73_Mixtures: Description of NO/N\textsubscript{2} mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>KRISS (Korea Research Institute of Standards and Science)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>PO box 102, Yuseong, Daejeon, 305-600 KOREA</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Sang Hyub Oh</td>
</tr>
<tr>
<td>Telephone</td>
<td>82-42-868-5341</td>
</tr>
<tr>
<td>Fax</td>
<td>82-42-868-5344</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:shoh@kriss.re.kr">shoh@kriss.re.kr</a></td>
</tr>
</tbody>
</table>
Low range (30-50) μmol/mol mixture

L1. CYLINDER DETAILS

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

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Pure NO gas from Liquid Air Corp.

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (μmol/mol)</th>
<th>Uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td></td>
<td>997,394</td>
<td>96</td>
</tr>
<tr>
<td>H₂</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>O₂</td>
<td>Gas MS</td>
<td>231</td>
<td>25</td>
</tr>
<tr>
<td>N₂</td>
<td>Gas MS</td>
<td>519</td>
<td>25</td>
</tr>
<tr>
<td>He</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>Ar</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>CO</td>
<td>Gas MS</td>
<td>ND</td>
<td>28.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>ND</td>
<td>0.577</td>
</tr>
<tr>
<td>CO₂</td>
<td>Gas MS</td>
<td>ND</td>
<td>28.9</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>32</td>
<td>5</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>1,470</td>
<td>75</td>
</tr>
<tr>
<td>H₂O</td>
<td>FTIR</td>
<td>354</td>
<td>25</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
**L4. Purity Table for Nominally Pure N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td>999,966.6</td>
<td>1.74</td>
</tr>
<tr>
<td>H₂</td>
<td>GC-AED</td>
<td>0.2</td>
<td>0.0289</td>
</tr>
<tr>
<td>O₂</td>
<td>GC-AED</td>
<td>0.0379</td>
<td>0.000577</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-AED</td>
<td>31.2</td>
<td>1.73</td>
</tr>
<tr>
<td>THC</td>
<td>GC-FID</td>
<td>0.98</td>
<td>0.0577</td>
</tr>
<tr>
<td>CO</td>
<td>GC methanizer</td>
<td>0.01</td>
<td>0.00289</td>
</tr>
<tr>
<td>CO₂</td>
<td>GC-AED</td>
<td>0.01</td>
<td>0.00289</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dew point meter</td>
<td>1.0</td>
<td>0.115</td>
</tr>
</tbody>
</table>

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

**L5. Purity Table for Final NO/N₂ Mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999935.56</td>
<td>1.74</td>
</tr>
<tr>
<td>NO</td>
<td>$x_{NO,grav} : 31.02$</td>
<td>$u(x_{NO,grav}) : 0.007$</td>
</tr>
<tr>
<td>H₂</td>
<td>0.2</td>
<td>0.0289</td>
</tr>
<tr>
<td>O₂</td>
<td>0.045</td>
<td>0.001</td>
</tr>
<tr>
<td>Ar</td>
<td>31.2</td>
<td>1.73</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.001</td>
<td>0.0002</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.046</td>
<td>0.002</td>
</tr>
<tr>
<td>THC</td>
<td>0.980</td>
<td>0.058</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.01</td>
<td>0.12</td>
</tr>
<tr>
<td>He</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td>CH₄</td>
<td>negligible</td>
<td>negligible</td>
</tr>
</tbody>
</table>
L6. DILUTION SERIES

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

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

Two cylinders of 2% and 1,000 ppm standards were prepared and compared. And three cylinders of 31 ppm standards were tested. NOx analyzer (Model 42, TEI) and A-B-A methods were used in this test.

What NO mole fraction was predicted from your verification analysis?

\[ x_{\text{NO,anal}} : 31.020 \ \mu\text{mol/mol} \]

What is your estimate of the uncertainty in \( x_{\text{NO,anal}} \)?

\[ u(x_{\text{NO,anal}}) : 0.12 \ \mu\text{mol/mol} \]

(about 0.4 %)

L8. STABILITY TESTING

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

Five cylinders of 20 ppm standards were tested. One was prepared at 03/8/20, two were prepared at 04/6/30, and two were prepared at 05/11/23. In this long term stability test, concentration differences of all five standards from measured value and preparation value were less than 0.34 %. Our uncertainty of NO analysis is about 0.4 %

This results means that NO standards more than 20 ppm concentration are stable more than 2 years.
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of mixture preparation</td>
<td>2006. 6. 20</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>9.5</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>80</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>JIS 8246</td>
</tr>
</tbody>
</table>

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Pure NO gas from Liquid Air Corp.

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td></td>
<td>997,394</td>
<td>96</td>
</tr>
<tr>
<td>H₂</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>O₂</td>
<td>Gas MS</td>
<td>231</td>
<td>25</td>
</tr>
<tr>
<td>N₂</td>
<td>Gas MS</td>
<td>519</td>
<td>25</td>
</tr>
<tr>
<td>He</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>Ar</td>
<td>Gas MS</td>
<td>ND</td>
<td>2.89</td>
</tr>
<tr>
<td>CO</td>
<td>Gas MS</td>
<td>ND</td>
<td>28.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>ND</td>
<td>0.577</td>
</tr>
<tr>
<td>CO₂</td>
<td>Gas MS</td>
<td>ND</td>
<td>28.9</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>32</td>
<td>5</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>1,470</td>
<td>75</td>
</tr>
<tr>
<td>H₂O</td>
<td>FTIR</td>
<td>354</td>
<td>25</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
**H4. PURITY TABLE FOR NOMINALLY PURE N\textsubscript{2}**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td></td>
<td>999,966.6</td>
<td>1.74</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>GC-AED</td>
<td>0.2</td>
<td>0.0289</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>GC-AED</td>
<td>0.0379</td>
<td>0.000577</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-AED</td>
<td>31.2</td>
<td>1.73</td>
</tr>
<tr>
<td>THC</td>
<td>GC-FID</td>
<td>0.98</td>
<td>0.0577</td>
</tr>
<tr>
<td>CO</td>
<td>GC methanizer</td>
<td>0.01</td>
<td>0.00289</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>GC-AED</td>
<td>0.01</td>
<td>0.00289</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>Dew point meter</td>
<td>1.0</td>
<td>0.115</td>
</tr>
</tbody>
</table>

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

**H5. PURITY TABLE FOR FINAL NO/N\textsubscript{2} MIXTURE**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>999,913.61</td>
<td>1.74</td>
</tr>
<tr>
<td>NO</td>
<td>$x_{\text{NO,grav}} : 52.984$</td>
<td>$u(x_{\text{NO,grav}}) : 0.009$</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>0.2</td>
<td>0.0289</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>0.050</td>
<td>0.001</td>
</tr>
<tr>
<td>Ar</td>
<td>31.2</td>
<td>1.73</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>0.002</td>
<td>0.0003</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>0.078</td>
<td>0.004</td>
</tr>
<tr>
<td>THC</td>
<td>0.980</td>
<td>0.058</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>1.02</td>
<td>0.12</td>
</tr>
<tr>
<td>He</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>negligible</td>
<td>negligible</td>
</tr>
</tbody>
</table>

**H6. DILUTION SERIES**
<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction</th>
<th>Expanded Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>0\textsuperscript{th} (Parent NO)</td>
<td>99.7394 % mol/mol</td>
<td>0.019 % mol/mol</td>
</tr>
<tr>
<td>1\textsuperscript{st}</td>
<td>1.9932 % mol/mol</td>
<td>0.0009 % mol/mol</td>
</tr>
<tr>
<td>2\textsuperscript{nd}</td>
<td>1001.3 µmol/mol</td>
<td>0.3 µmol/mol</td>
</tr>
<tr>
<td>3\textsuperscript{rd}</td>
<td>52.984 µmol/mol</td>
<td>0.017 µmol/mol</td>
</tr>
</tbody>
</table>

**H7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N\textsubscript{2} standards; how many such standards; which analytical methods were used?

Two cylinders of 2\% and 1,000 ppm standards were prepared and compared. And three cylinders of 53 ppm standards were tested.

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

What NO mole fraction was predicted from your verification analysis?

\[ x_{\text{NO,anal}} : 52.984 \mu\text{mol/mol} \]

What is your estimate of the uncertainty in \( x_{\text{NO,anal}} \)?

\[ u(x_{\text{NO,anal}}) : 0.21 \mu\text{mol/mol} \]

(about 0.4 \%)

**H8. STABILITY TESTING**

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

Five cylinders of 20 ppm standards were tested. One was prepared at 03/8/20, two were prepared at 04/6/30, and two were prepared at 05/11/23.

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

This results means that NO standards more than 20 ppm concentration are stable more than 2 years.
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

PARTICIPATING INSTITUTE:

<table>
<thead>
<tr>
<th>Institute</th>
<th>CSIR National Metrology Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>CSIR, Building 5</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 395</td>
</tr>
<tr>
<td></td>
<td>Pretoria</td>
</tr>
<tr>
<td></td>
<td>0001</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Angelique Botha</td>
</tr>
<tr>
<td>Telephone</td>
<td>+27 12 841 3800</td>
</tr>
<tr>
<td>Fax</td>
<td>+27 12 841 2131</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:abotha@csir.co.za">abotha@csir.co.za</a></td>
</tr>
</tbody>
</table>
Low range (30-50) μmol/mol mixture

**L1. CYLINDER DETAILS**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of mixture preparation</td>
<td>29 June 2006</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>5 ℓ</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>120 bar</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>CGA 330</td>
</tr>
<tr>
<td>Cylinder number</td>
<td>3775</td>
</tr>
</tbody>
</table>

**L2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

**NO 2.5 (99.5%)** Air Liquide

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction ($x10^{-6}$ mol/mol)</th>
<th>Uncertainty ($x10^{-6}$ mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>Specification</td>
<td>1000</td>
<td>1154700538</td>
</tr>
<tr>
<td>NO</td>
<td>Specification</td>
<td>998000</td>
<td>2309401076</td>
</tr>
<tr>
<td>NO₂</td>
<td>Specification</td>
<td>1000</td>
<td>1154700538</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
### L4. Purity Table for nominally pure \( \text{N}_2 \)

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction ((x10^6 \text{ mol/mol}))</th>
<th>Uncertainty ((x10^6 \text{ mol/mol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>Specification</td>
<td>9999999,375</td>
<td>0,82248650</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>GC-FID</td>
<td>0,02199999998</td>
<td>0,025</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>GC-FID</td>
<td>0,0240000002</td>
<td>0,028</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>Specification</td>
<td>0,5</td>
<td>0,57735</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>Specification</td>
<td>0,0099999997</td>
<td>0,011547</td>
</tr>
<tr>
<td>HC(Hydrocarbons)</td>
<td>Specification</td>
<td>0,0500000007</td>
<td>0,057735</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>Specification</td>
<td>0,0049999998</td>
<td>0,005774</td>
</tr>
</tbody>
</table>

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

### L5. Purity Table for final NO/\( \text{N}_2 \) mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction ((x10^6 \text{ mol/mol}))</th>
<th>Uncertainty ((x10^6 \text{ mol/mol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>9999966,15969</td>
<td>32,46133380</td>
</tr>
<tr>
<td>NO</td>
<td>( x_{\text{NO,grav}} : ) 33,14889796</td>
<td>( U(x_{\text{NO,grav}}) : k=2 ) 0,124956560</td>
</tr>
<tr>
<td>CO</td>
<td>0,21507658</td>
<td>0,022845823</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>0,023996811</td>
<td>0,025502571</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>0,499983392</td>
<td>0,531299356</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0,009999967</td>
<td>0,010625987</td>
</tr>
<tr>
<td>HC(Hydrocarbons)</td>
<td>0,049998399</td>
<td>0,053129935</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>0,033215328</td>
<td>0,038353885</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>0,033215328</td>
<td>0,038353885</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0,004999834</td>
<td>0,00531625</td>
</tr>
</tbody>
</table>
**L6. DILUTION SERIES**

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction ($x10^{-6}$ mol/mol)</th>
<th>Uncertainty ($x10^{-6}$ mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0&lt;sup&gt;th&lt;/sup&gt; (Parent NO)</td>
<td>99,5</td>
<td>2309,401076</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>39916,54862876</td>
<td>149,899614778</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>4000,7181734048</td>
<td>15,0561820537</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>400,27263626564</td>
<td>1,50699076303</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>33,14889796</td>
<td>0,124956560</td>
</tr>
</tbody>
</table>

**L7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N<sub>2</sub> standards; how many such standards; which analytical methods were used?

A set of 7 samples of NO/N<sub>2</sub> mixtures (10 - 100 ppm) was compared with a second set of gravimetrically prepared NO/N<sub>2</sub> standards (10 - 100 ppm). The verification was done using chemiluminescence. The verification runs were performed once a week for three weeks in a row.

What NO mole fraction was predicted from your verification analysis? $x_{NO, anal} : 33,06 \times 10^{-6}$ mol/mol

What is your estimate of the uncertainty in $x_{NO, anal}$? $U(x_{NO, anal}) : k=2$ $0,98 \times 10^{-6}$ mol/mol

**L8. STABILITY TESTING**

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

The stability of the mixture was monitored with a verification run once a week for 3 conservative weeks before shipping.
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>30 June 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5 ℓ</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>120 bar</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>CGA 330</td>
</tr>
<tr>
<td>Cylinder number</td>
<td>3770</td>
</tr>
</tbody>
</table>

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

NO 2.5 (99.5%) Air Liquide

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (x10⁻⁶ mol/mol)</th>
<th>Uncertainty (x10⁻⁶ mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>Specification</td>
<td>1000</td>
<td>1154,700538</td>
</tr>
<tr>
<td>NO</td>
<td>Specification</td>
<td>998000</td>
<td>2309,401076</td>
</tr>
<tr>
<td>NO₂</td>
<td>Specification</td>
<td>1000</td>
<td>1154,700538</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
H4. Purity Table for nominally pure N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (x10⁻⁶ mol/mol)</th>
<th>Uncertainty (x10⁻⁶ mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>Specification</td>
<td>999999,375</td>
<td>0,82248650</td>
</tr>
<tr>
<td>CO</td>
<td>GC-FID</td>
<td>0,02199999998</td>
<td>0,025</td>
</tr>
<tr>
<td>CO₂</td>
<td>GC-FID</td>
<td>0,0240000002</td>
<td>0,028</td>
</tr>
<tr>
<td>H₂</td>
<td>Specification</td>
<td>0,5</td>
<td>0,57735</td>
</tr>
<tr>
<td>H₂O</td>
<td>Specification</td>
<td>0,0099999997</td>
<td>0,011547</td>
</tr>
<tr>
<td>HC(hydrocarbons)</td>
<td>Specification</td>
<td>0,0500000007</td>
<td>0,057735</td>
</tr>
<tr>
<td>O₂</td>
<td>Specification</td>
<td>0,0049999998</td>
<td>0,005774</td>
</tr>
</tbody>
</table>

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

H5. Purity Table for final NO/N₂ mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (x10⁻⁶ mol/mol)</th>
<th>Uncertainty (x10⁻⁶ mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999944,15378252</td>
<td>27,05014665344</td>
</tr>
<tr>
<td>NO</td>
<td>xₙ₀,grav : 55,1108094895</td>
<td>U(xₙ₀,grav) : k=2 0,2077334323</td>
</tr>
<tr>
<td>CO</td>
<td>0,021947386907</td>
<td>0,0227931638</td>
</tr>
<tr>
<td>CO₂</td>
<td>0,023995722945</td>
<td>0,0255276526</td>
</tr>
<tr>
<td>H₂</td>
<td>0,499972389374</td>
<td>0,5264158896</td>
</tr>
<tr>
<td>H₂O</td>
<td>0,009999447564</td>
<td>0,0105283178</td>
</tr>
<tr>
<td>HC(Hydrocarbons)</td>
<td>0,049997239682</td>
<td>0,0526415889</td>
</tr>
<tr>
<td>N₂O</td>
<td>0,055221251994</td>
<td>0,0637642211</td>
</tr>
<tr>
<td>NO₂</td>
<td>0,055221251994</td>
<td>0,0637642211</td>
</tr>
<tr>
<td>O₂</td>
<td>0,004999723782</td>
<td>0,0052646148</td>
</tr>
</tbody>
</table>
### H6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction ((x10^6 \text{ mol/mol}))</th>
<th>Uncertainty ((x10^6 \text{ mol/mol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(^{th}) (Parent NO)</td>
<td>99.5</td>
<td>2309.401076</td>
</tr>
<tr>
<td>1(^{st})</td>
<td>53031.67118599</td>
<td>198.878045087</td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>5991.396112434</td>
<td>22.5465129825</td>
</tr>
<tr>
<td>3(^{rd})</td>
<td>598.8498331181</td>
<td>2.2561669788</td>
</tr>
<tr>
<td>4(^{th})</td>
<td>55.11080948958</td>
<td>0.20773343231</td>
</tr>
</tbody>
</table>

### H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N\(_2\) standards; how many such standards; which analytical methods were used?

A set of 7 samples of NO/N\(_2\) mixtures (10 - 100 ppm) was compared with a second set of gravimetrically prepared NO/N\(_2\) standards (10 - 100 ppm). The verification was done using chemiluminescence. The verification runs were performed once a week for three weeks in a row.

What NO mole fraction was predicted from your verification analysis?

\(x_{\text{NO,anal}} = 55.01 \times 10^{-6} \text{ mol/mol}\)

What is your estimate of the uncertainty in \(x_{\text{NO,anal}}\) ?

\((x_{\text{NO,anal}}) : k=2 \quad 1.52 \times 10^{-6} \text{ mol/mol}\)

### H8. STABILITY TESTING

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

The stability of the mixture was monitored with a verification run once a week for 3 conservative weeks before shipping.
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Chemicals Evaluation and Research Institute, Japan (CERI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1600, Shimo-Takano, Sugito-machi, Kitakatsushika-gun, Saitama 345-0043, Japan</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Masaaki Maruyama</td>
</tr>
<tr>
<td>Telephone</td>
<td>+81-480-37-2601</td>
</tr>
<tr>
<td>Fax</td>
<td>+81-480-37-2521</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:maruyama-masaaki@ceri.jp">maruyama-masaaki@ceri.jp</a></td>
</tr>
</tbody>
</table>
Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

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

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>FT-IR</td>
<td>79</td>
<td>12</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-PID</td>
<td>144.8</td>
<td>6.6</td>
</tr>
<tr>
<td>O₂</td>
<td>GC-PID</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>N₂O</td>
<td>FT-IR</td>
<td>84.85</td>
<td>0.60</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>9.6</td>
<td>5.6</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>GC-FID</td>
<td>1.17</td>
<td>0.67</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dew point measurement with mirror</td>
<td>24.4</td>
<td>5.5</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td>999654</td>
<td>16</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
**L4. Purity Table for nominally pure N\textsubscript{2}**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction ((\mu)mol/mol)</th>
<th>Standard uncertainty ((\mu)mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>GC-MS</td>
<td>&lt;0.1</td>
<td>0.029</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>GC-MS</td>
<td>&lt;0.1</td>
<td>0.029</td>
</tr>
<tr>
<td>CO</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>NOx(NO+NO\textsubscript{2})</td>
<td>Chemiluminescent</td>
<td>&lt;0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>UV fluorescence</td>
<td>&lt;0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>Dew Point meter</td>
<td>&lt;1</td>
<td>0.289</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td></td>
<td>999999.4</td>
<td>0.29</td>
</tr>
</tbody>
</table>

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

**L5. Purity Table for final NO/N\textsubscript{2} mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction ((\mu)mol/mol)</th>
<th>Uncertainty ((\mu)mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>999965.07</td>
<td>71.38</td>
</tr>
<tr>
<td>NO</td>
<td>(x_{NO,grav}:34.93)</td>
<td>(u(x_{NO,grav}):0.02)</td>
</tr>
</tbody>
</table>
**L6. DILUTION SERIES**

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0&lt;sup&gt;th&lt;/sup&gt; (Parent NO)</td>
<td>999654</td>
<td>16</td>
</tr>
<tr>
<td>1st</td>
<td>11921.2</td>
<td>5.3</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>1492.85</td>
<td>0.68</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>34.93</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**L7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N<sub>2</sub> standards; how many such standards; which analytical methods were used?

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

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

What NO mole fraction was predicted from your verification analysis?

\[ x_{NO, anal} : 34.91 \text{ µmol/mol (01/2006)} \]

What is your estimate of the uncertainty in \( x_{NO, anal} \)?

\[ u(x_{NO, anal}) : 0.13 \text{ µmol/mol (0.37%rel)(k=2)} \]

**L8. STABILITY TESTING**

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

The NO mole fraction after preparation is compared with the NO mole fraction before sending to BIPM.
And the stability is evaluated by amount of NO mole fraction of change.

The NO mole fraction after preparation is 34.91 µmol/mol (01/2006)
The NO mole fraction before sending is 34.98 µmol/mol (07/2006)
The NO mole fraction of change is 0.07 µmol/mol (6 months)
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

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

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>FT-IR</td>
<td>79</td>
<td>12</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-PID</td>
<td>144.8</td>
<td>6.6</td>
</tr>
<tr>
<td>O₂</td>
<td>GC-PID</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>N₂O</td>
<td>FT-IR</td>
<td>84.85</td>
<td>0.60</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>9.6</td>
<td>5.6</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>GC-FID</td>
<td>1.17</td>
<td>0.67</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dew point measurement with mirror</td>
<td>24.4</td>
<td>5.5</td>
</tr>
<tr>
<td>NO</td>
<td>999654</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

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


**H4. Purity Table for Nominally Pure $N_2$**

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction ($\mu$mol/mol)</th>
<th>Uncertainty ($\mu$mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>GC-MS</td>
<td>&lt;0.1</td>
<td>0.029</td>
</tr>
<tr>
<td>$O_2$</td>
<td>GC-MS</td>
<td>&lt;0.1</td>
<td>0.029</td>
</tr>
<tr>
<td>$CO$</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>$C_3H_8$</td>
<td>GC-FID</td>
<td>&lt;0.01</td>
<td>0.003</td>
</tr>
<tr>
<td>NOx(NO+NO$_2$)</td>
<td>Chemiluminescent</td>
<td>&lt;0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>UV fluorescence</td>
<td>&lt;0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>Dew Point meter</td>
<td>&lt;1</td>
<td>0.289</td>
</tr>
<tr>
<td>$N_2$</td>
<td></td>
<td>9999949.09</td>
<td>64.64</td>
</tr>
</tbody>
</table>

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

**H5. Purity Table for Final NO/$N_2$ Mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction ($\mu$mol/mol)</th>
<th>Uncertainty ($\mu$mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>999949.09</td>
<td>64.64</td>
</tr>
<tr>
<td>NO</td>
<td>$\chi_{NO,grav} : 50.91$</td>
<td>$\mu(\chi_{NO,grav}) : 0.02$</td>
</tr>
</tbody>
</table>
**H6. DILUTION SERIES**

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction ($\mu$mol/mol)</th>
<th>Uncertainty ($\mu$mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^{th}$ (Parent NO)</td>
<td>999654</td>
<td>16</td>
</tr>
<tr>
<td>1st</td>
<td>11921.2</td>
<td>5.3</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>1492.85</td>
<td>0.68</td>
</tr>
<tr>
<td>3$^{rd}$</td>
<td>50.91</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**H7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N$_2$ standards; how many such standards; which analytical methods were used?

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

Procedure of analysis: R1→Sample→R2→R3

NO mole fraction is determined by calibration curve (R1,R2,R3)

What NO mole fraction was predicted from your verification analysis? $x_{NO,anal} : 50.81 \mu$mol/mol (01/2006)

What is your estimate of the uncertainty in $x_{NO,anal}$? $u(x_{NO,anal}) : 0.19 \mu$mol/mol

(0.37%rel)(k=2)

**H8. STABILITY TESTING**

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

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

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

The NO mole fraction after preparation is 50.81 $\mu$mol/mol (01/2006)

The NO mole fraction before sending is 50.90 $\mu$mol/mol (07/2006)

The NO mole fraction of change is 0.09 $\mu$mol/mol (6 months)
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Laboratoire national de métrologie et d'essais</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>1, rue Gaston Boissier 75724 Paris Cedex 15 France</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Tatiana Macé / Christophe Sutour</td>
</tr>
<tr>
<td>Telephone</td>
<td>33 1 40 43 38 53 / 33 1 40 43 37 49</td>
</tr>
<tr>
<td>Fax</td>
<td>33 1 40 43 37 37</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:tatiana.mace@lne.fr">tatiana.mace@lne.fr</a> / <a href="mailto:christophe.sutour@lne.fr">christophe.sutour@lne.fr</a></td>
</tr>
</tbody>
</table>
**Low range (30-50) µmol/mol mixture**

**L1. CYLINDER DETAILS**

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

**L2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Our pure NO gas comes from Air Liquide

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>9.0</td>
<td>0.5</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>48.0</td>
<td>1.2</td>
</tr>
<tr>
<td>N₂</td>
<td>GC/TCD</td>
<td>149.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>Air Liquide</td>
<td>25.0</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>specifications</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
### L4. Purity Table for nominally pure N\(_2\)

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>Air products specifications</td>
<td>0.0050</td>
<td>0.0029</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>Air products specifications</td>
<td>0.0100</td>
<td>0.0058</td>
</tr>
<tr>
<td>CO+CO(_2)</td>
<td>Air products specifications</td>
<td>0.025</td>
<td>0.014</td>
</tr>
<tr>
<td>THC</td>
<td>Air products specifications</td>
<td>0.050</td>
<td>0.029</td>
</tr>
<tr>
<td>H(_2)</td>
<td>Air products specifications</td>
<td>0.025</td>
<td>0.014</td>
</tr>
</tbody>
</table>

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

### L5. Purity Table for final NO/N\(_2\) mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>(x_{NO,grav} : 39.839)</td>
<td>(u(x_{NO,grav}) : 0.040)</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>(x_{NO2,grav} : 0.000350)</td>
<td>(u(x_{NO2,grav}) : 0.000025)</td>
</tr>
</tbody>
</table>
### L6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>Pure NO and Pure N₂</td>
<td></td>
</tr>
<tr>
<td>1st (SMG 1393 – NO/N₂ 0039)</td>
<td>30380.09</td>
<td>0.03</td>
</tr>
<tr>
<td>2nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4th</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### L7. Verification

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

The verification preparation consists in:

- The preparation of several gas mixtures of NO in N₂ at about 40 µmol/mol by using the gravimetric method,
- The comparison of the prepared gravimetric gas mixtures by spectrophotometry: the used spectrometer is a BIO-RAD and is equipped with a measurement cell of a 4.8 m optical path.

What NO mole fraction was predicted from your verification analysis? \( x_{\text{NO, anal}} : 39.82 \text{ µmol/mol} \)

What is your estimate of the uncertainty in \( x_{\text{NO, anal}} \)? \( u(x_{\text{NO, anal}}) : 0.20 \text{ µmol/mol} \)

### L8. Stability Testing

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

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

31 May 2006 \( 39.82 \text{ µmol/mol with an uncertainty of } 0.20 \text{ µmol/mol (u)} \)
28 June 2006 \( 39.74 \text{ µmol/mol with an uncertainty of } 0.20 \text{ µmol/mol (u)} \)
25 July 2006 \( 39.85 \text{ µmol/mol with an uncertainty of } 0.20 \text{ µmol/mol (u)} \)
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

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

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Our pure NO gas comes from Air Liquide

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>53.0</td>
<td>1.5</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>95.0</td>
<td>2.5</td>
</tr>
<tr>
<td>N₂</td>
<td>GC/TCD</td>
<td>97.80</td>
<td>2.45</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
**H4. Purity Table for Nominally Pure N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Air products specifications</td>
<td>0.0050</td>
<td>0.0029</td>
</tr>
<tr>
<td>H₂O</td>
<td>Air products specifications</td>
<td>0.0100</td>
<td>0.0058</td>
</tr>
<tr>
<td>CO+CO₂</td>
<td>Air products specifications</td>
<td>0.025</td>
<td>0.014</td>
</tr>
<tr>
<td>THC</td>
<td>Air products specifications</td>
<td>0.050</td>
<td>0.029</td>
</tr>
<tr>
<td>H₂</td>
<td>Air products specifications</td>
<td>0.025</td>
<td>0.014</td>
</tr>
</tbody>
</table>

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

**H5. Purity Table for Final NO/N₂ Mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>( x_{\text{NO, grav}} : 60.580 )</td>
<td>( u(x_{\text{NO, grav}}) : 0.065 )</td>
</tr>
<tr>
<td>NO₂</td>
<td>( x_{\text{NO₂, grav}} : 0.00322 )</td>
<td>( u(x_{\text{NO₂, grav}}) : 0.00010 )</td>
</tr>
</tbody>
</table>
H6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (µmol/mol)</th>
<th>Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>Pure NO and Pure N$_2$</td>
<td></td>
</tr>
<tr>
<td>1st (APEO 889 525E – NO/N2 0030)</td>
<td>38298.30</td>
<td>3.55</td>
</tr>
<tr>
<td>2nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4th</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N$_2$ standards; how many such standards; which analytical methods were used?

The verification preparation consists in:

- The preparation of several gas mixtures of NO in N$_2$ at about 60 µmol/mol by using the gravimetric method,
- The comparison of the prepared gravimetric gas mixtures by spectrophotometry: the used spectrometer is a BIO-RAD and is equipped with a measurement cell of a 4.8 m optical path.

What NO mole fraction was predicted from your verification analysis? $x_{\text{NO,anal}}: 60.540$ µmol/mol

What is your estimate of the uncertainty in $x_{\text{NO,anal}}$? $u(x_{\text{NO,anal}}): 0.305$ µmol/mol

H8. STABILITY TESTING

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

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

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

<table>
<thead>
<tr>
<th>Institute</th>
<th>Slovak Institute of Metrology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Karloveska 63</td>
</tr>
<tr>
<td></td>
<td>84255 Bratislava</td>
</tr>
<tr>
<td></td>
<td>Slovak Republic</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Ing. S. Musil, PhD., RNDr. Viliam Štovčík</td>
</tr>
<tr>
<td>Telephone</td>
<td>+421 2 60294 365</td>
</tr>
<tr>
<td>Fax</td>
<td>+421 2 60294 561</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:musil@smu.gov.sk">musil@smu.gov.sk</a>, <a href="mailto:stovcik@smu.gov.sk">stovcik@smu.gov.sk</a></td>
</tr>
</tbody>
</table>
**Low range (30-50) µmol/mol mixture**

**L1. CYLINDER DETAILS**

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>20.IV.2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>10</td>
</tr>
<tr>
<td>Connection type</td>
<td>DIN1</td>
</tr>
</tbody>
</table>

**L2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

Complete for all components considered:

Linde NO 2.5

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>rest</td>
<td>0.9965</td>
<td>0.0010</td>
</tr>
<tr>
<td>NO₂</td>
<td>GC-TCD</td>
<td>0.00213</td>
<td>0.00043</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>1x10⁻⁷</td>
<td>6x10⁻⁸</td>
</tr>
<tr>
<td>N₂O</td>
<td>GC-TCD</td>
<td>0.0014</td>
<td>0.00028</td>
</tr>
</tbody>
</table>
### L4. Purity Table for Nominal Pure N₂

Complete for all components considered:

**N₂ BIP PLUS 6.0 (AIR Products)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>rest</td>
<td>0.999999827</td>
<td>3.5x10⁻⁸</td>
</tr>
<tr>
<td>CO</td>
<td>GC-FID (methanizer)</td>
<td>1.5x10⁻⁸</td>
<td>9x10⁻⁹</td>
</tr>
<tr>
<td>CO₂</td>
<td>GC-FID (methanizer)</td>
<td>3.8x10⁻⁸</td>
<td>2.2x10⁻⁸</td>
</tr>
<tr>
<td>H₂</td>
<td>Air Products decl.</td>
<td>2.5x10⁻⁸</td>
<td>1.4x10⁻⁸</td>
</tr>
<tr>
<td>O₂</td>
<td>Air Products decl.</td>
<td>5x10⁻⁹</td>
<td>3x10⁻⁹</td>
</tr>
<tr>
<td>H₂O</td>
<td>SMU Primary dew point meter</td>
<td>1x10⁻⁸</td>
<td>6x10⁻⁹</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>4x10⁻⁸</td>
<td>1x10⁻⁸</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>GC-FID</td>
<td>2x10⁻⁸</td>
<td>1.2x10⁻⁸</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>GC-FID</td>
<td>2x10⁻⁸</td>
<td>1.2x10⁻⁸</td>
</tr>
</tbody>
</table>

### L5. Purity Table for Final NO/N₂ Mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.999959235</td>
<td>6.5x10⁻⁸</td>
</tr>
<tr>
<td>NO</td>
<td>x₉(NO,grav) : 0.000040419</td>
<td>u(x₉(NO,grav)) : 3.1x10⁻⁸</td>
</tr>
<tr>
<td>N₂O</td>
<td>5.8x10⁻⁸</td>
<td>1.1x10⁻⁸</td>
</tr>
<tr>
<td>NO₂</td>
<td>8.6x10⁻⁸</td>
<td>1.7x10⁻⁸</td>
</tr>
<tr>
<td>Ar</td>
<td>1.83x10⁻¹⁰</td>
<td>7.5x10⁻¹¹</td>
</tr>
<tr>
<td>CO</td>
<td>1.50x10⁻⁸</td>
<td>8.6x10⁻⁹</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.80x10⁻⁸</td>
<td>2.1x10⁻⁸</td>
</tr>
<tr>
<td>H₂</td>
<td>2.5x10⁻⁸</td>
<td>1.3x10⁻⁸</td>
</tr>
<tr>
<td>O₂</td>
<td>5.09x10⁻⁹</td>
<td>2.9x10⁻⁹</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.05x10⁻⁸</td>
<td>5.8x10⁻⁹</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.9x10⁻⁸</td>
<td>1.9x10⁻⁸</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2.0x10⁻⁸</td>
<td>1.2x10⁻⁸</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>2.0x10⁻⁸</td>
<td>1.3x10⁻⁸</td>
</tr>
</tbody>
</table>
### L6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>x(NO) (mol/mol)</th>
<th>u(x) (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0&lt;sup&gt;th&lt;/sup&gt; (Parent NO)</td>
<td>0.99645</td>
<td>10x10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>0.099636</td>
<td>0.000073</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>0.0099566</td>
<td>0.0000070</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>0.0010097</td>
<td>0.00000073</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>0.000040419</td>
<td>0.00000031</td>
</tr>
</tbody>
</table>

### L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N<sub>2</sub> standards; how many such standards; which analytical methods were used?

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

#### Preparation data

<table>
<thead>
<tr>
<th>x&lt;sub&gt;NO,grav&lt;/sub&gt;</th>
<th>40.419 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>u(x&lt;sub&gt;NO,grav&lt;/sub&gt;)</td>
<td>0.031 ppm</td>
</tr>
</tbody>
</table>

#### What NO mole fraction was predicted from your verification analysis?

x<sub>NO,anal</sub> : 40.2 ppm

#### What is your estimate of the uncertainty in x<sub>NO,anal</sub> ?

u(x<sub>NO,anal</sub>) : 0.17 ppm
(from repeatability & calibration & display resolution uncertainties)

- u<sub>A</sub>(x<sub>NO,anal</sub>) : 0.11 ppm
- u<sub>B,cal</sub>(x<sub>NO,anal</sub>) : 0.13 ppm
- u<sub>B,drift</sub>(x<sub>NO,anal</sub>) : 0.00 ppm
- u<sub>B,display resol</sub>(x<sub>NO,anal</sub>) : 0.03 ppm
L8. STABILITY TESTING

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

Every three weeks NO content had been measured by luminiscence method on Thermo Vision 43C
The one-point calibration with NMi PRM 50 ppm was performed just before measurement.

<table>
<thead>
<tr>
<th></th>
<th>April</th>
<th>May</th>
<th>June</th>
<th>July</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY9744</td>
<td>40.2</td>
<td>40.1</td>
<td>40.2</td>
<td>40.1</td>
</tr>
<tr>
<td>Δ</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>NMi</td>
<td>50.1</td>
<td>50.0</td>
<td>50.1</td>
<td>50.1</td>
</tr>
<tr>
<td>Δ</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

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

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

Complete for all components considered:

Linde NO 2.5

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>rest</td>
<td>0.9965</td>
<td>0.0010</td>
</tr>
<tr>
<td>NO₂</td>
<td>GC-TCD</td>
<td>0.00213</td>
<td>0.00043</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>1x10⁻⁷</td>
<td>6x10⁻⁸</td>
</tr>
<tr>
<td>N₂O</td>
<td>GC-TCD</td>
<td>0.0014</td>
<td>0.00028</td>
</tr>
</tbody>
</table>
### H4. Purity Table for Nominally Pure $N_2$

Complete for all components considered:

$N_2$ BIP PLUS 6.0 (AIR Products)

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>rest</td>
<td>0.999999827</td>
<td>3.5x10^-8</td>
</tr>
<tr>
<td>CO</td>
<td>GC-FID (methanizer)</td>
<td>1.5x10^-8</td>
<td>9x10^-9</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>GC-FID (methanizer)</td>
<td>3.8x10^-8</td>
<td>2.2x10^-8</td>
</tr>
<tr>
<td>$H_2$</td>
<td>Air Products decl.</td>
<td>2.5x10^-8</td>
<td>1.4x10^-8</td>
</tr>
<tr>
<td>$O_2$</td>
<td>Air Products decl.</td>
<td>5x10^-9</td>
<td>3x10^-9</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>SMU Primary dew point meter</td>
<td>1x10^-8</td>
<td>6x10^-9</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>GC-FID</td>
<td>4x10^-8</td>
<td>1x10^-8</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>GC-FID</td>
<td>2x10^-8</td>
<td>1.2x10^-8</td>
</tr>
</tbody>
</table>

### H5. Purity Table for Final NO/$N_2$ Mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.99994002</td>
<td>8.2x10^-8</td>
</tr>
<tr>
<td>NO</td>
<td>$x_{NO, grav} = 0.000059576$</td>
<td>$u(x_{NO, grav}) = 0.000000044$</td>
</tr>
<tr>
<td>$N_2O$</td>
<td>0.000000085</td>
<td>0.000000017</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.000000127</td>
<td>0.000000026</td>
</tr>
<tr>
<td>Ar</td>
<td>2.7x10^-10</td>
<td>1.1x10^-10</td>
</tr>
<tr>
<td>CO</td>
<td>1.50x10^-8</td>
<td>6.0x10^-9</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.80x10^-8</td>
<td>1.5x10^-8</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2.51x10^-8</td>
<td>9.4x10^-9</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5.1x10^-9</td>
<td>2.0x10^-9</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>1.07x10^-8</td>
<td>4.0x10^-9</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>5.3x10^-8</td>
<td>1.0x10^-8</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>2.0x10^-8</td>
<td>8.0x10^-9</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>2.0x10^-8</td>
<td>8.0x10^-9</td>
</tr>
</tbody>
</table>
H6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>x(NO) (mol/mol)</th>
<th>u(x) (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>0.99645</td>
<td>10x10^-3</td>
</tr>
<tr>
<td>1st</td>
<td>0.099636</td>
<td>0.000073</td>
</tr>
<tr>
<td>2nd</td>
<td>0.0099566</td>
<td>0.0000070</td>
</tr>
<tr>
<td>3rd</td>
<td>0.0010097</td>
<td>0.00000073</td>
</tr>
<tr>
<td>4th</td>
<td>0.000059576</td>
<td>4.4x10^-8</td>
</tr>
</tbody>
</table>

H7. Verification

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

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

Preparation data

<table>
<thead>
<tr>
<th>x_NO,grav</th>
<th>59.576 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>uc(x_NO,grav)</td>
<td>0.044 ppm</td>
</tr>
</tbody>
</table>

What NO mole fraction was predicted from your verification analysis?

x_NO,anal : 59.7 ppm

What is your estimate of the uncertainty in x_NO,anal ?

u(x_NO,anal) : 0.17 ppm

(from repeatability & calibration & display resolution uncertainties)

u_A(x_NO,anal) : 0.11 ppm

u_B,cal(x_NO,anal) : 0.13 ppm

u_B,drift(x_NO,anal) : 0.00 ppm

u_B,display_resol(x_NO,anal) : 0.03 ppm
**H8. Stability Testing**

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

Every three weeks NO content had been measured by luminiscence method on Thermo Vision 43C. The one-point calibration with NMi PRM 50 ppm was performed just before measurement.

<table>
<thead>
<tr>
<th></th>
<th>March</th>
<th>April</th>
<th>May</th>
<th>June</th>
<th>July</th>
</tr>
</thead>
<tbody>
<tr>
<td>MY9741</td>
<td>59.9</td>
<td>59.7</td>
<td>59.7</td>
<td>59.9</td>
<td>59.7</td>
</tr>
<tr>
<td>Δ</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>NMi</td>
<td>50.2</td>
<td>50.1</td>
<td>50.0</td>
<td>50.1</td>
<td>50.1</td>
</tr>
<tr>
<td>Δ</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**NOTES:**

All uncertainties mentioned are in unextended form.
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>CENTRO NACIONAL DE METROLOGÍA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>KM 4.5 CARRETERA A Los Cués. Municipio El Marques, CP 76241 Querétaro, México.</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Alejandro Pérez Castorena</td>
</tr>
<tr>
<td>Telephone</td>
<td>(442) 211-05-00 Ext. 3907</td>
</tr>
<tr>
<td>Fax</td>
<td>(442) 211-05-69</td>
</tr>
<tr>
<td>Email</td>
<td><a href="mailto:aperezx@cenam.mx">aperezx@cenam.mx</a></td>
</tr>
</tbody>
</table>
Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS  (Cylinder number: FF39556)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of mixture preparation</td>
<td>2006-01-23</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>5,4 L</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>103,4 bar</td>
</tr>
<tr>
<td>Connection type</td>
<td>CGA-660</td>
</tr>
</tbody>
</table>

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N2, what is its source?

Manufacture: CENAM

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty** (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>specification</td>
<td>3,9697x10⁻²</td>
<td>8,9 x10⁻⁵</td>
</tr>
<tr>
<td>N₂</td>
<td>specification</td>
<td>9,60159 x10⁻¹</td>
<td>1,2 x10⁻⁴</td>
</tr>
<tr>
<td>O₂</td>
<td>specification</td>
<td>1,4 x10⁻⁷</td>
<td>2,8 x10⁻⁸</td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>1,9 x10⁻⁶</td>
<td>3,9 x10⁻⁷</td>
</tr>
<tr>
<td>THC</td>
<td>specification</td>
<td>8,8 x10⁻⁷</td>
<td>1,8 x10⁻⁷</td>
</tr>
<tr>
<td>CO</td>
<td>specification</td>
<td>2,9 x10⁻⁷</td>
<td>8,3 x10⁻⁸</td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>7,7 x10⁻⁷</td>
<td>2,2 x10⁻⁷</td>
</tr>
<tr>
<td>NO₂ + N₂O</td>
<td>specification</td>
<td>1,39 x10⁻⁴</td>
<td>4,0 x10⁻⁵</td>
</tr>
</tbody>
</table>

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

**K=1
**L4. Purity Table for nominally pure N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty** (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1-impurity</td>
<td>9,99975 x10⁻¹</td>
<td>7,4 x10⁻⁷</td>
</tr>
<tr>
<td>O₂</td>
<td>Electrochemical cell</td>
<td>6,0 x10⁻⁶</td>
<td>2,0 x10⁻⁶</td>
</tr>
<tr>
<td>H₂O</td>
<td>Electrochemical cell</td>
<td>8,0 x10⁻⁷</td>
<td>2,0 x10⁻⁷</td>
</tr>
<tr>
<td>CO</td>
<td>FTIR</td>
<td>3,0 x10⁻⁷</td>
<td>9,0 x10⁻⁷</td>
</tr>
<tr>
<td>THC</td>
<td>specification</td>
<td>5,0 x10⁻⁷</td>
<td>1,0 x10⁻⁷</td>
</tr>
<tr>
<td>CO₂</td>
<td>FTIR</td>
<td>8,0 x10⁻⁷</td>
<td>2,0 x10⁻⁷</td>
</tr>
</tbody>
</table>

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

**K=1

**L5. Purity Table for final NO/N₂ mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty * (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>9,99957 x10⁻¹</td>
<td>1,4 x10⁻⁶</td>
</tr>
<tr>
<td>NO</td>
<td>x_{NO,grav} : 4,0777 x10⁻⁵</td>
<td>u(x_{NO,grav}) : 8,8 x10⁻⁸</td>
</tr>
<tr>
<td>O₂</td>
<td>6,0 x10⁻⁸</td>
<td>2,0 x10⁻⁸</td>
</tr>
<tr>
<td>H₂O</td>
<td>8,0 x10⁻⁷</td>
<td>2,1 x10⁻⁷</td>
</tr>
<tr>
<td>THC</td>
<td>5,0 x10⁻⁷</td>
<td>1,3 x10⁻⁷</td>
</tr>
<tr>
<td>CO</td>
<td>3,0 x10⁻⁷</td>
<td>8,0 x10⁻⁸</td>
</tr>
<tr>
<td>CO₂</td>
<td>8,0 x10⁻⁷</td>
<td>2,1 x10⁻⁷</td>
</tr>
<tr>
<td>NO₂+N₂O</td>
<td>1,4 x10⁻⁷</td>
<td>4,1 x10⁻⁸</td>
</tr>
</tbody>
</table>

*K=1
L6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty* (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>$3.9697 \times 10^{-2}$</td>
<td>$8.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>1st</td>
<td>$3.9849 \times 10^{-3}$</td>
<td>$8.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>2nd</td>
<td>$3.9770 \times 10^{-4}$</td>
<td>$8.5 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

* $k=1$

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

Verification procedure:
The verification procedure was according to ISO 6142 clause 6.3 incise a, and ISO 6143 clause 6.2. Were prepared and used for verification processes five calibration gas mixtures covering the range $3.0 - 7.0 \times 10^{-5}$ mol/mol.

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

What NO mole fraction was predicted from your verification analysis?

$x_{NO, anal} : 4.075 \times 10^{-5} \text{ mol/mol}$

What is your estimate of the uncertainty in $x_{NO, anal}$?

$u(x_{NO, anal}) : 2.1 \times 10^{-7} \text{ mol/mol } k=2$

L8. STABILITY TESTING

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

The stability of travelling standards was confirmed by repeated analysis using five standards, in the range of $3.0$ to $7.0 \times 10^{-5}$ mol/mol. Before each travelling standard was despatched to the coordinating laboratory it was analysed at least 5 times in the period between their preparation and their shipping.
High range (50-70) µmol/mol mixture

**H1. CYLINDER DETAILS (Cylinder number: FF39527)**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of mixture preparation</td>
<td>2006-01-23</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>5.4 L</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>103.4 bar</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>CGA-660</td>
</tr>
</tbody>
</table>

**H2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Manufacture: CENAM

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty** (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>specification</td>
<td>5.96996 x10⁻²</td>
<td>1.09 x10⁻⁴</td>
</tr>
<tr>
<td>N₂</td>
<td>specification</td>
<td>9.40086 x10⁻¹</td>
<td>1.57 x10⁻⁴</td>
</tr>
<tr>
<td>O₂</td>
<td>specification</td>
<td>1.8 x10⁻⁷</td>
<td>4.0 x10⁻⁸</td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>2.4 x10⁻⁶</td>
<td>5.3 x10⁻⁷</td>
</tr>
<tr>
<td>THC</td>
<td>specification</td>
<td>1.1 x10⁻⁶</td>
<td>2.2 x10⁻⁷</td>
</tr>
<tr>
<td>CO</td>
<td>specification</td>
<td>2.8 x10⁻⁷</td>
<td>8.0 x10⁻⁸</td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>7.5 x10⁻⁷</td>
<td>0.22 x10⁻⁷</td>
</tr>
<tr>
<td>NO₂+N₂O</td>
<td>specification</td>
<td>2.10 x10⁻⁴</td>
<td>6.0 x10⁻⁵</td>
</tr>
</tbody>
</table>

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

**K=1
H4. **Purity Table for Nominally Pure N\(_2\)**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty* (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>1-impurity</td>
<td>9.99975 x 10(^{-1})</td>
<td>7.4 x 10(^{-7})</td>
</tr>
<tr>
<td>O(_2)</td>
<td>Electrochemical cell</td>
<td>6.0 x 10(^{-8})</td>
<td>2.0 x 10(^{-8})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>Electrochemical cell</td>
<td>8.0 x 10(^{-7})</td>
<td>2.0 x 10(^{-7})</td>
</tr>
<tr>
<td>CO</td>
<td>FTIR</td>
<td>3.0 x 10(^{-7})</td>
<td>9.0 x 10(^{-8})</td>
</tr>
<tr>
<td>THC</td>
<td>specification</td>
<td>5.0 x 10(^{-7})</td>
<td>1.0 x 10(^{-7})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>FTIR</td>
<td>8.0 x 10(^{-7})</td>
<td>2.0 x 10(^{-7})</td>
</tr>
</tbody>
</table>

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

**k=1

H5. **Purity Table for Final NO/N\(_2\) Mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>9.999366 x 10(^{-1})</td>
<td>7.0 x 10(^{-7})</td>
</tr>
<tr>
<td>NO</td>
<td>(x_{\text{NO,grav}}) : 6.0690 x 10(^{-5})</td>
<td>(u(x_{\text{NO,grav}})) : 1.04 x 10(^{-7})</td>
</tr>
<tr>
<td>O(_2)</td>
<td>6.0 x 10(^{-8})</td>
<td>2.0 x 10(^{-8})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>8.0 x 10(^{-7})</td>
<td>2.1 x 10(^{-7})</td>
</tr>
<tr>
<td>THC</td>
<td>5.0 x 10(^{-7})</td>
<td>1.3 x 10(^{-7})</td>
</tr>
<tr>
<td>CO</td>
<td>3.0 x 10(^{-7})</td>
<td>8.0 x 10(^{-8})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>8.0 x 10(^{-7})</td>
<td>2.1 x 10(^{-7})</td>
</tr>
<tr>
<td>NO(_2)+N(_2)O</td>
<td>2.1 x 10(^{-7})</td>
<td>6.0 x 10(^{-8})</td>
</tr>
</tbody>
</table>

*\(k=1\)
## H6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty* (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>$5.96996 \times 10^{-2}$</td>
<td>$1.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>1st</td>
<td>$5.9784 \times 10^{-3}$</td>
<td>$1.03 \times 10^{-5}$</td>
</tr>
<tr>
<td>2nd</td>
<td>$5.964 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

*\(k=1\)

## H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

**Verification procedure:**
The verification procedure was according to ISO 6142 clause 6.3 incise a, and ISO 6143 clause 6.2. Were prepared and used for verification processes five calibration gas mixtures covering the range $3.0 - 7.0 \times 10^{-5}$ mol/mol.

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

What NO mole fraction was predicted from your verification analysis?

\[ x_{NO, anal} : 6.079 \times 10^{-5} \text{ mol/mol} \]

What is your estimate of the uncertainty in \(x_{NO, anal}\)?

\[ u(x_{NO, anal}) : 2.6 \times 10^{-7} \text{ mol/mol} \quad k=2 \]

## H8. STABILITY TESTING

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

The stability of travelling standards was confirmed by repeated analysis using five standards, in the range of $3.0$ to $7.0 \times 10^{-5}$ mol/mol. Before each travelling standard was despatched to the coordinating laboratory it was analysed at least 5 times in the period between their preparation and their shipping.
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>VNIIM (D.I. Mendeleyev Institute for Metrology)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>19, Moskovsky pr., St. Petersburg, Russia</td>
</tr>
<tr>
<td>Contact Person</td>
<td>L.A. Konopelko</td>
</tr>
<tr>
<td></td>
<td>Y.A. Kustikov</td>
</tr>
<tr>
<td>Telephone</td>
<td>(812) 315-11-45</td>
</tr>
<tr>
<td>Fax</td>
<td>(812) 327-97-76</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:Ikonop@b10.vniim.ru">Ikonop@b10.vniim.ru</a></td>
</tr>
</tbody>
</table>
Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>30.05.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>73</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>DIN1</td>
</tr>
</tbody>
</table>

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

Pure NO was received from “Pure gases, Inc”. Novosibirsk, Russia

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>-</td>
<td>996800</td>
<td>350</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>1000</td>
<td>120</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>1200</td>
<td>140</td>
</tr>
<tr>
<td>CO₂</td>
<td>FTIR</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>N₂</td>
<td>suppliers specification</td>
<td>500</td>
<td>290</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
### L4. Purity Table for Nominal Pure N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (μmol/mol)</th>
<th>Standard uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>-</td>
<td>999990,6</td>
<td>0,7</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dew-point hygrometry</td>
<td>1,4</td>
<td>0,4</td>
</tr>
<tr>
<td>CO</td>
<td>NDIR</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>CO₂</td>
<td>NDIR</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>O₂</td>
<td>GC-PDHID</td>
<td>0,45</td>
<td>0,10</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PDHID</td>
<td>5,0</td>
<td>0,5</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>0,50</td>
<td>0,20</td>
</tr>
</tbody>
</table>

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

### L5. Purity Table for Final NO/N₂ Mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (μmol/mol)</th>
<th>Standard uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999948,4</td>
<td>0,7</td>
</tr>
<tr>
<td>NO</td>
<td>( x_{\text{NO,grav}} :42,18 )</td>
<td>( u(x_{\text{NO,grav}}) :0,03 )</td>
</tr>
<tr>
<td>NO₂</td>
<td>0,042</td>
<td>0,005</td>
</tr>
<tr>
<td>N₂O</td>
<td>0,051</td>
<td>0,006</td>
</tr>
<tr>
<td>CO₂</td>
<td>1,02</td>
<td>0,20</td>
</tr>
<tr>
<td>H₂O</td>
<td>1,4</td>
<td>0,4</td>
</tr>
<tr>
<td>O₂</td>
<td>0,45</td>
<td>0,10</td>
</tr>
<tr>
<td>Ar</td>
<td>5,0</td>
<td>0,5</td>
</tr>
<tr>
<td>CO</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>CH₄</td>
<td>0,50</td>
<td>0,20</td>
</tr>
</tbody>
</table>
L6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (μmol/mol)</th>
<th>Standard uncertainty (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>996800</td>
<td>350</td>
</tr>
<tr>
<td>1st</td>
<td>24636</td>
<td>11</td>
</tr>
<tr>
<td>2nd</td>
<td>1817.7</td>
<td>0.9</td>
</tr>
<tr>
<td>3rd</td>
<td>42.18</td>
<td>0.03</td>
</tr>
</tbody>
</table>

L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

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

What NO mole fraction was predicted from your verification analysis?  \( X_{NO,anal} : 42.18 \)

What is your estimate of the uncertainty (standard) in \( X_{NO,anal} \)? \( u(X_{NO,anal}) : 0.05 \)

L8. STABILITY TESTING

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

Stability testing was performed by direct comparison with the other traceable PSM (previously prepared). Stability study was carried out during a period of 1.5 month. There were made three measurement series - 05.06.06; 30.06.06; 20.07.06.
High range (50-70) $\mu$mol/mol mixture

H1. CYLINDER DETAILS

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

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N$_2$, what is its source?

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

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Standard uncertainty ($\mu$mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>-</td>
<td>996800</td>
<td>350</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>FTIR</td>
<td>1000</td>
<td>120</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>FTIR</td>
<td>1200</td>
<td>140</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>FTIR</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>N$_2$</td>
<td>suppliers specification</td>
<td>500</td>
<td>290</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
### H4. Purity Table for nominally pure N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>-</td>
<td>999990,6</td>
<td>0,7</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dew-point hygrometry</td>
<td>1,4</td>
<td>0,4</td>
</tr>
<tr>
<td>CO</td>
<td>NDIR</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>CO₂</td>
<td>NDIR</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>O₂</td>
<td>GC-PDHID</td>
<td>0,45</td>
<td>0,10</td>
</tr>
<tr>
<td>Ar</td>
<td>GC-PDHID</td>
<td>5,0</td>
<td>0,5</td>
</tr>
<tr>
<td>CH₄</td>
<td>GC-FID</td>
<td>0,50</td>
<td>0,20</td>
</tr>
</tbody>
</table>

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

### H5. Purity Table for final NO/N₂ Mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999927,2</td>
<td>0,7</td>
</tr>
<tr>
<td>NO</td>
<td>X_{NO, grav} = 63,32</td>
<td>u(X_{NO, grav}) = 0,04</td>
</tr>
<tr>
<td>NO₂</td>
<td>0,064</td>
<td>0,007</td>
</tr>
<tr>
<td>N₂O</td>
<td>0,076</td>
<td>0,009</td>
</tr>
<tr>
<td>CO₂</td>
<td>1,03</td>
<td>0,20</td>
</tr>
<tr>
<td>H₂O</td>
<td>1,4</td>
<td>0,4</td>
</tr>
<tr>
<td>O₂</td>
<td>0,45</td>
<td>0,10</td>
</tr>
<tr>
<td>Ar</td>
<td>5,0</td>
<td>0,5</td>
</tr>
<tr>
<td>CO</td>
<td>1,0</td>
<td>0,20</td>
</tr>
<tr>
<td>CH₄</td>
<td>0,50</td>
<td>0,20</td>
</tr>
</tbody>
</table>
H6. DILUTION SERIES

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0&lt;sup&gt;th&lt;/sup&gt; (Parent NO)</td>
<td>996800</td>
<td>350</td>
</tr>
<tr>
<td>1st</td>
<td>24756</td>
<td>11</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>1823,6</td>
<td>1,0</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>63,32</td>
<td>0,04</td>
</tr>
</tbody>
</table>

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N<sub>2</sub> standards; how many such standards; which analytical methods were used?

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

What NO mole fraction was predicted from your verification analysis? \( x_{\text{NO, anal}} : 63,32 \)

What is your estimate of the uncertainty (standard) in \( x_{\text{NO, anal}} \)? \( u(x_{\text{NO, anal}}) : 0,08 \)

H8. STABILITY TESTING

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

Stability testing was performed by direct comparison with the other traceable PSM (previously prepared). Stability study was carried out during a period of 1,5 month. There were made three measurement series - 06.06.06; 03.07.06; 21.07.06.
**Decision Institute:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Institute of Standards and Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>100 Bureau Drive</td>
</tr>
<tr>
<td></td>
<td>Gaithersburg MD 20899-8393</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Bill Thorn/Franklin Guenther</td>
</tr>
<tr>
<td>Telephone</td>
<td>301-975-3939</td>
</tr>
<tr>
<td>Fax</td>
<td>301-977-8392</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:fguenther@nist.gov">fguenther@nist.gov</a></td>
</tr>
</tbody>
</table>
Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS

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

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?
Takachiho Trading Company, Tokyo Japan

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>FTIR</td>
<td>0.99827</td>
<td>0.00030</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>0.00079</td>
<td>0.00007</td>
</tr>
<tr>
<td>N₂O</td>
<td>FTIR</td>
<td>0.00082</td>
<td>0.00008</td>
</tr>
<tr>
<td>N₂</td>
<td>GC/TCD</td>
<td>0.00012</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
### L4. Purity Table for Nominaly Pure N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td>0.999965</td>
<td>0.000005</td>
</tr>
<tr>
<td>O₂</td>
<td>Delta -F NT</td>
<td>&lt;2 nmol/mol</td>
<td>1 nmol/mol</td>
</tr>
<tr>
<td>H₂O</td>
<td>Spec</td>
<td>&lt;20 nmol/mol</td>
<td>10 nmol/mol</td>
</tr>
<tr>
<td>THC</td>
<td>Spec</td>
<td>&lt;100 nmol/mol</td>
<td>60 nmol/mol</td>
</tr>
<tr>
<td>Argon</td>
<td>GC/TCD</td>
<td>35 µmol/mol</td>
<td>5 µmol/mol</td>
</tr>
</tbody>
</table>

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

### L5. Purity Table for Final NO/N₂ mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>$x_{\text{NO, grav}} : 43.081 \mu\text{mol/mol}$</td>
<td>$u(x_{\text{NO, grav}}) : 0.062 \mu\text{mol/mol}$</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0341 µmol/mol</td>
<td>0.0031 µmol/mol</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0353 µmol/mol</td>
<td>0.0035 µmol/mol</td>
</tr>
</tbody>
</table>
L6. Dilution Series

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

L7. Verification

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

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

What NO mole fraction was predicted from your verification analysis?

\[ x_{\text{NO, anal}} : 43.030 \, \mu\text{mol/mol} \]

What is your estimate of the uncertainty in \( x_{\text{NO, anal}} \)?

\[ u(x_{\text{NO, anal}}) : 0.065 \, \mu\text{mol/mol} \]

L8. Stability Testing

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

Primary standards are monitored over many years by comparing to freshly made PSMs. This mixture was monitored for one month, too short to obtain any meaningful stability data, except to say that it agrees with the gravimetric value.
**High range (50-70) µmol/mol mixture**  
[SEE ABOVE FOR INFORMATION ALL THE SAME EXCEPT WHERE NOTED BELOW IN TABLES]

## H1. CYLINDER DETAILS

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>July 17, 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td></td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td></td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td></td>
</tr>
</tbody>
</table>

## H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
**H4. Purity Table for nominally pure N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

**H5. Purity Table for final NO/N₂ mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>$x_{NO,grav} : 67.082 , \mu\text{mol/mol}$</td>
<td>$u(x_{NO,grav}) : 0.087 , \mu\text{mol/mol}$</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.0531 , \mu\text{mol/mol}</td>
<td>0.0048 , \mu\text{mol/mol}</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0550 , \mu\text{mol/mol}</td>
<td>0.0055 , \mu\text{mol/mol}</td>
</tr>
</tbody>
</table>
**H6. DILUTION SERIES**

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol) (Expanded k=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(^{th}) (Parent NO)</td>
<td>0.9983</td>
<td>0.0003</td>
</tr>
<tr>
<td>1st</td>
<td>0.015468</td>
<td>0.000024</td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>0.0025603</td>
<td>0.0000030</td>
</tr>
<tr>
<td>3(^{rd})</td>
<td>679.29 µmol/mol</td>
<td>0.82 µmol/mol</td>
</tr>
<tr>
<td>4(^{th})</td>
<td>67.085 µmol/mol</td>
<td>0.094 µmol/mol</td>
</tr>
</tbody>
</table>

**H7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N\(_2\) standards; how many such standards; which analytical methods were used?

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

| What NO mole fraction was predicted from your verification analysis? | \(x_{\text{NO,anal}}\) : 67.13 µmol/mol |
| What is your estimate of the uncertainty in \(x_{\text{NO,anal}}\)? | \(u(x_{\text{NO,anal}})\) : 0.15 µmol/mol |

**H8. STABILITY TESTING**

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

See above
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**PARTICIPATING INSTITUTE:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>National Measurement Institute Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Bradfield Rd</td>
</tr>
<tr>
<td></td>
<td>West Lindfield NSW 2070</td>
</tr>
<tr>
<td></td>
<td>Australia</td>
</tr>
<tr>
<td></td>
<td>(PO Box 264, Lindfield NSW 2070)</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Damian Smeulders</td>
</tr>
<tr>
<td>Telephone</td>
<td>+61 2 8467 3534</td>
</tr>
<tr>
<td>Fax</td>
<td>+ 61 2 8467 3752</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:damian.smeulders@measurement.gov.au">damian.smeulders@measurement.gov.au</a></td>
</tr>
</tbody>
</table>
Low range (30-50) µmol/mol mixture

L1. CYLINDER DETAILS [MK0787]

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>26/06/2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5.4L</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>50 Bar</td>
</tr>
<tr>
<td>Connection type</td>
<td>BS14</td>
</tr>
</tbody>
</table>

L2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?
Nominally pure NO – manufactured by Air Liquide Deutschland GMBH Specialty Gases

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Specification</td>
<td>998.0</td>
<td>0.8</td>
</tr>
<tr>
<td>N₂O</td>
<td>Specification</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₂</td>
<td>Specification</td>
<td>1.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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

L4. PURITY TABLE FOR NOMINALLY PURE N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td>999.99825</td>
<td>0.00008</td>
</tr>
<tr>
<td>O₂</td>
<td>Systech/Illinios Model 276 Oxygen analyser (Hersch cell)</td>
<td>0.00015</td>
<td>0.000008</td>
</tr>
<tr>
<td>H₂O</td>
<td>Systech/Illinios Model 510 Moisture analyser (P₂O₅)</td>
<td>0.0016</td>
<td>0.00008</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
### L5. Purity Table for final NO/N₂ Mixture
Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999.95332</td>
<td>0.00010</td>
</tr>
<tr>
<td>NO</td>
<td>(x_{NO,grav} : 0.044844)</td>
<td>(u(x_{NO,grav}) : 0.000074)</td>
</tr>
<tr>
<td>NO₂</td>
<td>(4.5 \times 10^{-5})</td>
<td>(2.6 \times 10^{-5})</td>
</tr>
<tr>
<td>N₂O</td>
<td>(4.5 \times 10^{-5})</td>
<td>(2.6 \times 10^{-5})</td>
</tr>
</tbody>
</table>

### L6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>998.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1st</td>
<td>39.959 (MK0783)</td>
<td>0.065</td>
</tr>
<tr>
<td>2nd</td>
<td>1.5759 (MK0784)</td>
<td>0.0026</td>
</tr>
<tr>
<td>3rd</td>
<td>0.044844 (MK0787)</td>
<td>0.000074</td>
</tr>
</tbody>
</table>
L7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

Mixtures were verified using chemiluminescence. A Thermo 42i NOx analyser was used to check mixtures after manufacture. The concentration of the mixture was tested with respect to other NO/N₂ gravimetric mixtures manufactured at NMIA. An additional 10 mixtures near the target concentrations were used in the verification process.

<table>
<thead>
<tr>
<th>What NO mole fraction was predicted from your verification analysis?</th>
<th>( x_{\text{NO,anal}} : 0.04485 \text{ mmol/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>What is your estimate of the uncertainty in ( x_{\text{NO,anal}} )?</td>
<td>( u(x_{\text{NO,anal}}) : 0.00021 \text{ mmol/mol} )</td>
</tr>
</tbody>
</table>

L8. STABILITY TESTING

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

- No stability testing was performed due to the short period of time between manufacture and shipping.
High range (50-70) µmol/mol mixture

**H1. CYLINDER DETAILS [MK0781]**

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

**H2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?
Nominally pure NO – manufactured by Air Liquide Deutschland GMBH Specialty Gases

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Specification</td>
<td>998.0</td>
<td>0.8</td>
</tr>
<tr>
<td>N₂O</td>
<td>Specification</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₂</td>
<td>Specification</td>
<td>1.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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

**H4. PURITY TABLE FOR NOMINALLY PURE N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td>999.99825</td>
<td>0.00008</td>
</tr>
<tr>
<td>O₂</td>
<td>Systech/Illinios Model 276 Oxygen analyser (Hersch cell)</td>
<td>0.00015</td>
<td>0.000008</td>
</tr>
<tr>
<td>H₂O</td>
<td>Systech/Illinios Model 510 Moisture analyser (P₂O₅)</td>
<td>0.0016</td>
<td>0.00008</td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
### H5. Purity Table for final NO/N₂ mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>999.93328</td>
<td>0.00012</td>
</tr>
<tr>
<td>NO</td>
<td>( x_{\text{NO,grav}} : 0.06484 )</td>
<td>( u(x_{\text{NO,grav}}) : 0.00011 )</td>
</tr>
<tr>
<td>NO₂</td>
<td>( 6.5 \times 10^{-5} )</td>
<td>( 3.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>N₂O</td>
<td>( 6.5 \times 10^{-5} )</td>
<td>( 3.8 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

### H6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mmol/mol)</th>
<th>Uncertainty (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(^{th}) (Parent NO)</td>
<td>998.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1st</td>
<td>39.811 (MK0776)</td>
<td>0.065</td>
</tr>
<tr>
<td>2nd</td>
<td>1.5898 (MK0778)</td>
<td>0.0026</td>
</tr>
<tr>
<td>3rd</td>
<td>0.06484 (MK0781)</td>
<td>0.00011</td>
</tr>
</tbody>
</table>
**H7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

Mixtures were verified using chemiluminescence. A Thermo 42i NOx analyser was used to check mixtures after manufacture. The concentration of the mixture was tested with respect to other NO/N₂ gravimetric mixtures manufactured at NMIA. An additional 10 mixtures near the target concentrations were used in the verification process.

<table>
<thead>
<tr>
<th>What NO mole fraction was predicted from your verification analysis?</th>
<th>$x_{\text{NO,anal}} : 0.06497 \text{ mmol/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>What is your estimate of the uncertainty in $x_{\text{NO,anal}}$?</td>
<td>$u(x_{\text{NO,anal}}) : 0.00020 \text{ mmol/mol}$</td>
</tr>
</tbody>
</table>

**H8. STABILITY TESTING**

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

- No stability testing was performed due to the short period of time between manufacture and shipping.
**Participating Institute:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Instituto Portugês da Qualidade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>R. António Gião, 2, 2829-513 Caparica, Portugal</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Florbela Dias</td>
</tr>
<tr>
<td>Telephone</td>
<td>00351 212 948 175</td>
</tr>
<tr>
<td>Fax</td>
<td>00351 212 948 188</td>
</tr>
<tr>
<td>email</td>
<td><a href="mailto:florbela@mail.ipq.pt">florbela@mail.ipq.pt</a></td>
</tr>
</tbody>
</table>
**Low range (30-50) µmol/mol mixture**

**L1. CYLINDER DETAILS – PSM 103453**

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>17-11-2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>100</td>
</tr>
<tr>
<td>Connection type</td>
<td>DIN1</td>
</tr>
</tbody>
</table>

**L2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

The source of our nominally pure NO is Air Liquide.

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>specification</td>
<td>&gt; 99,9 x10⁻²</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>&lt; 20 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>specification</td>
<td>&lt; 100 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>&lt; 100 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>specification</td>
<td>&lt; 200 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>specification</td>
<td>&lt; 500 x10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
### L4. Purity Table for Nominally Pure N₂
Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>specification</td>
<td>&gt; 99,9999 x10⁻²</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>&lt; 0,5 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CₙHₘ</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

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

### L5. Purity Table for Final NO/N₂ Mixture
Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>99,995203 x10⁻²</td>
<td>0,000091 x10⁻²</td>
</tr>
<tr>
<td>NO</td>
<td>x_{NO,grav} : 47,0014 x10⁻⁶</td>
<td>μ(x_{NO,grav}) : 0,0044 x10⁻⁶</td>
</tr>
<tr>
<td>CO</td>
<td>1,00 x10⁻⁷</td>
<td>0,45 x10⁻⁷</td>
</tr>
<tr>
<td>CO₂</td>
<td>5,5 x10⁻⁸</td>
<td>2,3 x10⁻⁸</td>
</tr>
<tr>
<td>NO₂</td>
<td>4,704 x10⁻⁹</td>
<td>0,023 x10⁻⁹</td>
</tr>
<tr>
<td>N₂O</td>
<td>6,58 x10⁻¹⁰</td>
<td>0,23 x10⁻¹⁰</td>
</tr>
<tr>
<td>H₂O</td>
<td>6,0 x10⁻⁷</td>
<td>2,7 x10⁻⁷</td>
</tr>
<tr>
<td>H₂</td>
<td>1,00 x10⁻⁷</td>
<td>0,45 x10⁻⁷</td>
</tr>
<tr>
<td>O₂</td>
<td>1,00 x10⁻⁷</td>
<td>0,45 x10⁻⁷</td>
</tr>
<tr>
<td>CₙHₘ</td>
<td>1,00 x10⁻⁸</td>
<td>0,45 x10⁻⁸</td>
</tr>
</tbody>
</table>
**L6. DILUTION SERIES**

<table>
<thead>
<tr>
<th>Dilution Step (Parent NO)</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th</td>
<td>99,9 x10^{-2}</td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>4,98934 x10^{-2}</td>
<td>0,00035 x10^{-2}</td>
</tr>
<tr>
<td>2nd</td>
<td>5,00018 x10^{-3}</td>
<td>0,00042 x10^{-3}</td>
</tr>
<tr>
<td>3rd</td>
<td>499,315 x10^{-6}</td>
<td>0,044 x10^{-6}</td>
</tr>
<tr>
<td>4th</td>
<td>47,0014 x10^{-6}</td>
<td>0,0044 x10^{-6}</td>
</tr>
</tbody>
</table>

**L7. VERIFICATION**

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N2 standards; how many such standards; which analytical methods were used?

We did the verification procedure according to the international standard ISO 6143. The verification was done by comparison with other traceable NO/N2 standards. We used five NMi standards. The analytical method used was Chemiluminescence.

What NO mole fraction was predicted from your verification analysis? \( x_{\text{NO,anal}} : 47,04 x10^{-6} \text{ mol/mol} \)

What is your estimate of the uncertainty in \( x_{\text{NO,anal}} \)? \( U(x_{\text{NO,anal}}) : 0,71 x10^{-6} \text{ mol/mol} \)

**L8. STABILITY TESTING**

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

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>( x_{\text{NO,grav/mol}} )</th>
<th>Date</th>
<th>( x_{\text{NO,anal/mol}} )</th>
<th>( U(x_{\text{NO,anal/mol}}) )</th>
<th>( En )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSM103453</td>
<td>47,00 x 10^{-6}</td>
<td>18-11-2005</td>
<td>47,04 x10^{-6}</td>
<td>0,71 x10^{-6}</td>
<td>0,1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17-01-2006</td>
<td>46,74 x10^{-6}</td>
<td>0,75 x10^{-6}</td>
<td>-0,4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14-03-2006</td>
<td>47,17 x10^{-6}</td>
<td>0,85 x10^{-6}</td>
<td>0,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25-05-2006</td>
<td>47,17 x10^{-6}</td>
<td>0,83 x10^{-6}</td>
<td>0,2</td>
</tr>
</tbody>
</table>
High range (50-70) µmol/mol mixture PSM 103406

H1. CYLINDER DETAILS

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

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

The source of our nominally pure NO is Air Liquide.

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>specification</td>
<td>&gt; 99,9 x10⁻²</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>&lt; 20 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>specification</td>
<td>&lt; 100 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>&lt; 100 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>specification</td>
<td>&lt; 200 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>specification</td>
<td>&lt; 500 x10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".
### H4. Purity Table for Nominally Pure N₂

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>specification</td>
<td>&gt; 99,9999 x10⁻²</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>specification</td>
<td>&lt; 0,5 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CₙHₘ</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>specification</td>
<td>&lt; 0,1 x10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

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

### H5. Purity Table for Final NO/N₂ Mixture

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>99,992932 x10⁻²</td>
<td>0,000087 x10⁻²</td>
</tr>
<tr>
<td>NO</td>
<td>x_{NO,grav} : 69,7000 x10⁻⁶</td>
<td>(\mu(x_{NO,grav}) : 0,0065 x10⁻⁶)</td>
</tr>
<tr>
<td>CO</td>
<td>1,00 x10⁻⁷</td>
<td>0,43 x10⁻⁷</td>
</tr>
<tr>
<td>CO₂</td>
<td>5,7 x10⁻⁸</td>
<td>2,2 x10⁻⁸</td>
</tr>
<tr>
<td>NO₂</td>
<td>6,975 x10⁻⁹</td>
<td>0,035 x10⁻⁹</td>
</tr>
<tr>
<td>N₂O</td>
<td>9,76 x10⁻¹⁰</td>
<td>0,35 x10⁻¹⁰</td>
</tr>
<tr>
<td>H₂O</td>
<td>6,0 x10⁻⁷</td>
<td>2,6 x10⁻⁷</td>
</tr>
<tr>
<td>H₂</td>
<td>1,00 x10⁻⁷</td>
<td>0,43 x10⁻⁷</td>
</tr>
<tr>
<td>O₂</td>
<td>1,00 x10⁻⁷</td>
<td>0,43 x10⁻⁷</td>
</tr>
<tr>
<td>CₙHₘ</td>
<td>1,00 x10⁻⁸</td>
<td>0,43 x10⁻⁸</td>
</tr>
</tbody>
</table>
## H6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>99,9 x10^{-2}</td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>4,98934 x10^{-2}</td>
<td>0,00035 x10^{-2}</td>
</tr>
<tr>
<td>2nd</td>
<td>5,00018 x10^{-3}</td>
<td>0,00042 x10^{-3}</td>
</tr>
<tr>
<td>3rd</td>
<td>499,315 x10^{-6}</td>
<td>0,044 x10^{-6}</td>
</tr>
<tr>
<td>4th</td>
<td>69,7000 x10^{-6}</td>
<td>0,0065 x10^{-6}</td>
</tr>
</tbody>
</table>

## H7. Verification

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N2 standards; how many such standards; which analytical methods were used?

We did the verification procedure according to the international standard ISO 6143. The verification was done by comparison with other traceable NO/N2 standards. We used five NMi standards. The analytical method used was Chemiluminescence.

What NO mole fraction was predicted from your verification analysis?

\[ x_{\text{NO,anal}} : 69,84 \times 10^{-6} \text{ mol/mol} \]

What is your estimate of the uncertainty in \( x_{\text{NO,anal}} \)?

\[ U(x_{\text{NO,anal}}) : 0,63 \times 10^{-6} \text{ mol/mol} \]

## H8. Stability Testing

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

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>( x_{\text{NO,grav}} ) / mol/mol</th>
<th>Date</th>
<th>( x_{\text{NO,anal}} ) / mol/mol</th>
<th>( U(x_{\text{NO,anal}}) ) / mol/mol</th>
<th>En</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSM103406</td>
<td>69,70 \times 10^{-6}</td>
<td>18-11-2005</td>
<td>69,84 \times 10^{-6}</td>
<td>0,63 \times 10^{-6}</td>
<td>0,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17-01-2006</td>
<td>69,68 \times 10^{-6}</td>
<td>0,62 \times 10^{-6}</td>
<td>0,0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14-03-2006</td>
<td>69,86 \times 10^{-6}</td>
<td>0,68 \times 10^{-6}</td>
<td>0,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25-05-2006</td>
<td>69,46 \times 10^{-6}</td>
<td>0,76 \times 10^{-6}</td>
<td>-0,3</td>
</tr>
</tbody>
</table>
Form CCQM-P73_Mixtures: Description of NO/N₂ mixtures, to be completed by participants and forwarded to the BIPM

**Participating Institute:**

<table>
<thead>
<tr>
<th>Institute</th>
<th>Nederlands Meetinstituut (NMi) Van Swinden Laboratorium (VSL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Thijsseweg 11 2629 JA Delft The Netherlands</td>
</tr>
<tr>
<td>Contact Person</td>
<td>Gerard Nieuwenkamp / Rob Wessel</td>
</tr>
<tr>
<td>Telephone</td>
<td>+31 15 2691682 / +31 15 2691677</td>
</tr>
<tr>
<td>Fax</td>
<td>+31 15 2612971</td>
</tr>
<tr>
<td>Email</td>
<td><a href="mailto:gnieuwenkamp@nmi.nl">gnieuwenkamp@nmi.nl</a> <a href="mailto:rwessel@nmi.nl">rwessel@nmi.nl</a></td>
</tr>
</tbody>
</table>
**Low range (30-50) µmol/mol mixture**

**L1. CYLINDER DETAILS**

<table>
<thead>
<tr>
<th>Date of mixture preparation</th>
<th>2006-06-23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (L)</td>
<td>5 liter</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>100 bar</td>
</tr>
<tr>
<td>Connection type (e.g. DIN1, BS14 etc.)</td>
<td>DIN1</td>
</tr>
</tbody>
</table>

**L2. SOURCE OF NO**

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>1 - impurities</td>
<td>0.999402</td>
<td>0.000043</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-TCD</td>
<td>165 · 10⁻⁶</td>
<td>10 · 10⁻⁶</td>
</tr>
<tr>
<td>N₂O</td>
<td>average GC/FTIR *</td>
<td>232 · 10⁻⁶</td>
<td>25 · 10⁻⁶</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>86 · 10⁻⁶</td>
<td>17 · 10⁻⁶</td>
</tr>
<tr>
<td>HNO₂</td>
<td>FTIR</td>
<td>40 · 10⁻⁶</td>
<td>15 · 10⁻⁶</td>
</tr>
<tr>
<td>HNO₃</td>
<td>FTIR</td>
<td>75 · 10⁻⁶</td>
<td>25 · 10⁻⁶</td>
</tr>
</tbody>
</table>

* N₂O GC-TCD | 238 · 10⁻⁶ | 30 · 10⁻⁶ |
* N₂O FTIR | 226 · 10⁻⁶ | 30 · 10⁻⁶ |

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.
**L4. PURITY TABLE FOR NOMINALLY PURE N\textsubscript{2}**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>1 - impurities</td>
<td>0.999996912</td>
<td>0.0000011</td>
</tr>
<tr>
<td>Ar</td>
<td>GC (random check)</td>
<td>$3 \cdot 10^{-6}$</td>
<td>$1 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>FTIR (random check)</td>
<td>$8 \cdot 10^{-9}$</td>
<td>$5 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>CO</td>
<td>FTIR (random check)</td>
<td>$15 \cdot 10^{-9}$</td>
<td>$9 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>FTIR (random check)</td>
<td>$10 \cdot 10^{-9}$</td>
<td>$6 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>specification</td>
<td>$25 \cdot 10^{-9}$</td>
<td>$14 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>CRDS (random check)</td>
<td>$20 \cdot 10^{-9}$</td>
<td>$10 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>specification</td>
<td>$10 \cdot 10^{-9}$</td>
<td>$10 \cdot 10^{-9}$</td>
</tr>
</tbody>
</table>

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

**L5. PURITY TABLE FOR FINAL NO/N\textsubscript{2} MIXTURE**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>0.99994986</td>
<td>0.00000105</td>
</tr>
<tr>
<td>NO</td>
<td>$x_{NO,grav} : 47.0105 \cdot 10^{-6}$ \quad $u(x_{NO,grav}) : 0.0112 \cdot 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>$3.00 \cdot 10^{-6}$</td>
<td>$0.95 \cdot 10^{-6}$</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>$8.0 \cdot 10^{-9}$</td>
<td>$4.8 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>CO</td>
<td>$15.0 \cdot 10^{-9}$</td>
<td>$8.6 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>$10.0 \cdot 10^{-9}$</td>
<td>$5.7 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>HNO\textsubscript{2}</td>
<td>$1.9 \cdot 10^{-9}$</td>
<td>$0.7 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>$3.5 \cdot 10^{-9}$</td>
<td>$1.2 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>$25.0 \cdot 10^{-9}$</td>
<td>$13.4 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>$31.0 \cdot 10^{-9}$</td>
<td>$11.2 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>$4.0 \cdot 10^{-9}$</td>
<td>$0.8 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>$10.9 \cdot 10^{-9}$</td>
<td>$1.2 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>$18.8 \cdot 10^{-9}$</td>
<td>$10.8 \cdot 10^{-9}$</td>
</tr>
</tbody>
</table>
L6. Dilution Series

<table>
<thead>
<tr>
<th>Dilution Step</th>
<th>NO Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0th (Parent NO)</td>
<td>0.999402</td>
<td>0.000043</td>
</tr>
<tr>
<td>1st</td>
<td>0.059907</td>
<td>0.0000079</td>
</tr>
<tr>
<td>2nd</td>
<td>0.010005</td>
<td>0.0000013</td>
</tr>
<tr>
<td>3rd</td>
<td>997.77 · 10^{-6}</td>
<td>0.15 · 10^{-6}</td>
</tr>
<tr>
<td>4th</td>
<td>47.011 · 10^{-6}</td>
<td>0.011 · 10^{-6}</td>
</tr>
</tbody>
</table>

L7. Verification

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N2 standards; how many such standards; which analytical methods were used?

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

What NO mole fraction was predicted from your verification analysis? $x_{\text{NO, anal}} : 46.97 \cdot 10^{-6}$ (mol/mol)

What is your estimate of the uncertainty in $x_{\text{NO, anal}}$? $u(x_{\text{NO, anal}}) : 0.08 \cdot 10^{-6}$ (mol/mol)

L8. Stability Testing

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

- The mixture has been analysed twice in a three weeks period.
- Similar mixtures prepared in similar treated cylinders have shown no instability in a period of two years.
High range (50-70) µmol/mol mixture

H1. CYLINDER DETAILS

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Date of mixture preparation</td>
<td>2006-06-22</td>
</tr>
<tr>
<td>Volume (L)</td>
<td>5 Liter</td>
</tr>
<tr>
<td>Total Pressure (bar)</td>
<td>100 bar</td>
</tr>
<tr>
<td>Connection type</td>
<td>DIN1</td>
</tr>
</tbody>
</table>

H2. SOURCE OF NO

What is the source of your nominally pure NO gas? Or, if you started with a mixture of NO already diluted in N₂, what is its source?

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

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

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>1 - impurities</td>
<td>0.999402</td>
<td>0.000043</td>
</tr>
<tr>
<td>N₂</td>
<td>GC-TCD</td>
<td>165 · 10⁻⁶</td>
<td>10 · 10⁻⁶</td>
</tr>
<tr>
<td>N₂O</td>
<td>average GC/FTIR *</td>
<td>232 · 10⁻⁶</td>
<td>25 · 10⁻⁶</td>
</tr>
<tr>
<td>NO₂</td>
<td>FTIR</td>
<td>86 · 10⁻⁶</td>
<td>17 · 10⁻⁶</td>
</tr>
<tr>
<td>HNO₂</td>
<td>FTIR</td>
<td>40 · 10⁻⁶</td>
<td>15 · 10⁻⁶</td>
</tr>
<tr>
<td>HNO₃</td>
<td>FTIR</td>
<td>75 · 10⁻⁶</td>
<td>25 · 10⁻⁶</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* N₂O         | GC-TCD    | 238 · 10⁻⁶         | 30 · 10⁻⁶             |

* N₂O        | FTIR     | 226 · 10⁻⁶         | 30 · 10⁻⁶             |

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

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**H4. Purity Table for Nominally Pure N₂**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Method*</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1 - impurities</td>
<td>0.999996912</td>
<td>0.0000011</td>
</tr>
<tr>
<td>Ar</td>
<td>GC (random check)</td>
<td>3 · 10⁻⁶</td>
<td>1 · 10⁻⁶</td>
</tr>
<tr>
<td>CH₄</td>
<td>FTIR (random check)</td>
<td>8 · 10⁻⁹</td>
<td>5 · 10⁻⁹</td>
</tr>
<tr>
<td>CO</td>
<td>FTIR (random check)</td>
<td>15 · 10⁻⁹</td>
<td>9 · 10⁻⁹</td>
</tr>
<tr>
<td>CO₂</td>
<td>FTIR (random check)</td>
<td>10 · 10⁻⁹</td>
<td>6 · 10⁻⁹</td>
</tr>
<tr>
<td>H₂</td>
<td>specification</td>
<td>25 · 10⁻⁹</td>
<td>14 · 10⁻⁹</td>
</tr>
<tr>
<td>H₂O</td>
<td>CRDS (random check)</td>
<td>20 · 10⁻⁹</td>
<td>10 · 10⁻⁹</td>
</tr>
<tr>
<td>O₂</td>
<td>specification</td>
<td>10 · 10⁻⁹</td>
<td>10 · 10⁻⁹</td>
</tr>
</tbody>
</table>

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

**H5. Purity Table for Final NO/N₂ Mixture**

Complete for all components considered:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Fraction (mol/mol)</th>
<th>Uncertainty (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.99993387</td>
<td>0.00000107</td>
</tr>
<tr>
<td>NO</td>
<td>X_{NO,grav} : 63.0119 · 10⁻⁶</td>
<td>u(X_{NO,grav}) : 0.0226 · 10⁻⁶</td>
</tr>
<tr>
<td>Ar</td>
<td>3.00 · 10⁻⁶</td>
<td>0.97 · 10⁻⁶</td>
</tr>
<tr>
<td>CH₄</td>
<td>8.5 · 10⁻⁹</td>
<td>4.9 · 10⁻⁹</td>
</tr>
<tr>
<td>CO</td>
<td>15.0 · 10⁻⁹</td>
<td>8.7 · 10⁻⁹</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.0 · 10⁻⁹</td>
<td>5.8 · 10⁻⁹</td>
</tr>
<tr>
<td>HNO₂</td>
<td>2.5 · 10⁻⁹</td>
<td>0.9 · 10⁻⁹</td>
</tr>
<tr>
<td>HNO₃</td>
<td>4.7 · 10⁻⁹</td>
<td>1.6 · 10⁻⁹</td>
</tr>
<tr>
<td>H₂</td>
<td>25.0 · 10⁻⁹</td>
<td>13.6 · 10⁻⁹</td>
</tr>
<tr>
<td>H₂O</td>
<td>20.0 · 10⁻⁹</td>
<td>9.7 · 10⁻⁹</td>
</tr>
<tr>
<td>NO₂</td>
<td>5.4 · 10⁻⁹</td>
<td>1.1 · 10⁻⁹</td>
</tr>
<tr>
<td>N₂O</td>
<td>14.6 · 10⁻⁹</td>
<td>1.6 · 10⁻⁹</td>
</tr>
<tr>
<td>O₂</td>
<td>10.0 · 10⁻⁹</td>
<td>9.7 · 10⁻⁹</td>
</tr>
</tbody>
</table>
H6. DILUTION SERIES

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

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable NO/N₂ standards; how many such standards; which analytical methods were used?

- Verification to 11 primary standard gas mixtures (PSMs) in a concentration range of 10 · 10⁻⁶ - 100 · 10⁻⁶.
- Analysis with ND-UV
- Quadratic curve fitting, according to ISO-6143

What NO mole fraction was predicted from your verification analysis?

\[ x_{\text{NO,anal}} : 63.11 \cdot 10^{-6} \text{ (mol/mol)} \]

What is your estimate of the uncertainty in \( x_{\text{NO,anal}} \)?

\[ u(x_{\text{NO,anal}}) : 0.11 \cdot 10^{-6} \text{ (mol/mol)} \]

H8. STABILITY TESTING

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

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