CCQM-K68 Final Report

International Comparison CCQM K68

Nitrous Oxide in synthetic air

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Field
Amount of substance

Subject
Nitrous Oxide in synthetic air

Participants
KRISS, VSL, NMIJ, NIST, VNIIM, NIM, ESRL/NOAA

Organizing body
CCQM-GAWG
Introduction
Nitrous oxide (N\textsubscript{2}O), as one of six greenhouse gases that are regulated by Kyoto protocol, is known as the third largest greenhouse gas contributor to overall global warming. N\textsubscript{2}O has increased at a rate of 0.25 \%/yr (0.8 ppb/yr) during the last 10 years (1994 ~ 2004) and its warming potential (GWP) is 296 times more than that of carbon dioxide. In order to control effectively the global emission of N\textsubscript{2}O in the atmosphere, it is necessary to demonstrate measurement equivalence at the highest level of accuracy for the assigned values of standards.

This report describes the results of a key comparison of nitrous oxide in synthetic air. The objective of this key comparison is to compare the measurement capability of N\textsubscript{2}O at a trace level of 320 nmol/mol. This key comparison can be seen as related to CCQM-K15 and P41 [1 - 3], considering that they are connected to the measurement of different greenhouse gases. Consequently, this key comparison will support the development of measurement capability at NMIs for N\textsubscript{2}O at trace levels at an uncertainty level within the target set for the NOAA Global Monitoring Division (GMD) calibration scale.

Supported claims
This key comparison can be used to support CMC claims for nitrous oxide in the range from 200 nmol/mol to 20 µmol/mol in synthetic air.

Participants
A total of 7 laboratories took part in this key comparison under the auspices of the CIPM-MRA. One of the WMO facilities us a designated institute under the MRA. The participants are listed in Table 1.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Country</th>
<th>Institute</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS</td>
<td>KR</td>
<td>Korea Research Institute of Standards and Science, Daejeon, Republic of Korea</td>
</tr>
<tr>
<td>NIM</td>
<td>CR</td>
<td>National Institute of Metrology, Beijing, P.R.China</td>
</tr>
<tr>
<td>NIST</td>
<td>US</td>
<td>National Institute of Standards and Technology, Gaithersburg, United States of America</td>
</tr>
<tr>
<td>NMII</td>
<td>JP</td>
<td>National Metrology Institute of Japan, Tsukuba, Japan</td>
</tr>
<tr>
<td>VNIIM</td>
<td>RU</td>
<td>D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia</td>
</tr>
<tr>
<td>VSL</td>
<td>NL</td>
<td>VSL, Delft, the Netherlands</td>
</tr>
</tbody>
</table>
Schedule
The schedule for this key comparison reads as follows

March 2008  Registration and protocol circulation
Until April 30, 2008  Shipment of cylinders to participating laboratories
May - September 2008  Measurement of cylinders by participants and report due to coordinating laboratory
November 30 2008  Second verification measurement
September 30, 2009  Draft A report
April 15, 2010  Draft B report

Measurement protocol
A set of nitrous oxide in synthetic air mixtures with the nominal value of approx. 320 nmol/mol were prepared gravimetrically [4] through a 4 step dilution process and verified with a GC/ECD system against PSMs with amount of substance fractions between 270 to 340 nmol/mol. The amount of substance fractions were adopted as key comparison reference value (KCRV). Before preparation the constituent gases were analyzed for impurities.

Table 2: Composition and its nominal amount of substance fraction of standard gas mixtures

<table>
<thead>
<tr>
<th>component</th>
<th>x (nominal value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous oxide [nmol/mol]</td>
<td>320</td>
</tr>
<tr>
<td>Oxygen [%mol/mol]</td>
<td>21</td>
</tr>
<tr>
<td>Nitrogen [%mol/mol]</td>
<td>balance</td>
</tr>
</tbody>
</table>

The pressure in the cylinders was approximately 100 bar; cylinders of 5 dm³ (Al. Luxfer co.) were used.

Participating laboratories were requested to specify in detail which analytical method(s) were used and how the evaluation of the measurement uncertainty was performed.

Each participating laboratory was responsible for the calibration of its own equipment. For a
proper evaluation of the data, it was necessary that the calibration method, as well as the way in which the calibration mixtures were prepared was well established and reported to KRISS.

After each calibration, the measurements of the gas mixture must be recorded.

Each laboratory was required to express the uncertainty on all results submitted, as expanded uncertainty. The evaluation of the measurement uncertainty was required to be performed in accordance with the “Guide to the expression of uncertainty in measurement” (ISO GUM). The participants were required to provide a detailed description of the uncertainty budget, including method of evaluation (type A or type B)

- (assumed) probability distribution
- standard uncertainties and sensitivity coefficients
- (effective) degrees of equivalence (if applicable/used)
- (statistical) reasoning behind the coverage factor

After the measurements, the participants are responsible for return shipment of the cylinders leaving a sufficient amount of gas (pressure at least 30 bar) for re-analysis.

The measurement report required at least three independent measurements per cylinder, obtained under repeatability conditions with (at least) three independent calibrations, e.g. calibration (A) → measurement (B) → calibration (A) → measurement (B) → calibration (A) → measurement (B) → calibration (A) (etc.). This was a strict requirement to come to proper statistical analysis of the reported data.

One single measurement result was usually obtained from multiple readings (sub measurements), without recalibrations. Its standard deviation provided information about the performance of the measurement system.

**Measurement standards**

A total of 10 mixtures of nitrous oxide in synthetic air composed of nitrogen and oxygen were prepared gravimetrically and verified with a GC/ECD system against PSMs. The amount-of-substance fractions as obtained from gravimetry and purity analysis of the parent gases were used as reference values. Accordingly each cylinder had its own reference value.

For purity analysis of an O\textsubscript{2} and N\textsubscript{2} matrix gas, a GC/ECD analyzer with a pre-concentration device was used and its detection limit for nitrous oxide was 0.024 nmol/mol (3\textsigma). SF\subscript{6} with a strong peak signal was detected during the purity analysis of O\textsubscript{2} or N\textsubscript{2} and its amount of
substance fraction was about 0.1 pmol/mol. However, the well controlled GC/ECD analyzer separates \( \text{N}_2\text{O} \) peak from \( \text{SF}_6 \) peak as well as the main peaks of \( \text{O}_2 \) or \( \text{N}_2 \). As a result, a noticeable amount of substance fraction of nitrous oxide as impurity and calculated as 0.12 nmol/mol in nitrogen and 0.11 nmol/mol in oxygen, respectively. Based on the purity analysis, these values were considered during gravimetric preparation of the 4 step dilution.

To validate the stability of the primary standard mixtures prepared by the coordinating laboratory, mixtures prepared in 2003 were compared with mixtures prepared in 2007. As shown in Table 3, the difference between the two periods was within 0.02 % for the short term as well as 0.04 % for the long term. The stability of the primary standard mixtures was checked to be in the range of analysis uncertainty and therefore the uncertainty component from stability was considered to be negligible during this key comparison. Cylinder used for the calibration was EB63097 prepared in 2009.

Table 3: Results of stability test between \( \text{N}_2\text{O} \) standard gas mixtures

<table>
<thead>
<tr>
<th>Cyl. No.</th>
<th>Preparation Date</th>
<th>Prepared Conc. [nmol/mol]</th>
<th>Peak area [arb. unit]</th>
<th>Cal. Conc. (at present) [nmol/mol]</th>
<th>difference [nmol/mol], [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME5567</td>
<td>Dec.24, 2003</td>
<td>300.57</td>
<td>1622.55</td>
<td>300.51</td>
<td>-0.06, [-0.02]</td>
</tr>
<tr>
<td>ME5544</td>
<td>Sep.25, 2003</td>
<td>303.70</td>
<td>1639.34</td>
<td>303.57</td>
<td>-0.13, [-0.04]</td>
</tr>
<tr>
<td>ME5583</td>
<td>Dec.24, 2003</td>
<td>315.02</td>
<td>1699.38</td>
<td>315.04</td>
<td>0.02, [0.01]</td>
</tr>
<tr>
<td>FF43167</td>
<td>Oct.9, 2007</td>
<td>333.21</td>
<td>1785.80</td>
<td>333.28</td>
<td>0.07, [0.02]</td>
</tr>
</tbody>
</table>

Finally a total of 10 cylinders were prepared for this comparison. Their preparation uncertainties were set to 0.06 % of the relative standard uncertainty. In order to verify the mole fraction of \( \text{N}_2\text{O} \) in the primary standard gases a modified gas chromatograph (GC) with micro-electron capture detector(\( \mu \)-ECD) was used. The column used was a Restek Porapak Q with 4 m long, OD 1/8", 80-100 mesh, SS Packed. Pure Ar with 5% of \( \text{CH}_4 \) as dopent gas was used as carrier gas, with a flow of 26 ml/min. Samples passed through a Multi Position Valve (MPV) directly connected to each cylinder, then through a mass flow controller to be finally introduced in the sample loop (2 mL). Two pressure restrictors were adopted to maintain a constant pressure in the ECD detector and in the sample loop by providing a damping effect for pressure before venting to the atmosphere. During the measurement of each cylinder, the pressure restrictors were adjusted to a pressure of 1.9 bar, which ensured the pressure in the sample loop to be constant. The sample loop was continuously rinsed (except when injecting). The reference cylinder A was measured between each cylinder to correct the analyzer for the drift during the
comparison experiment (in sequence A-B-A-C-A-...). The amount of N\textsubscript{2}O was verified according to ISO6143 [5]. The analyzer response \((y_{\text{response}Cor,i,j})\) of \(i\)-th NMI cylinder is expressed as Eq. 3 after taking into account the repeatability, drift and reproducibility.

\[
y_{\text{response}Cor,i,j} = \left( \sum_{j=1}^{J} y_{\text{response},i,j} \right) / \left( \frac{y_{\text{ref},i,j} + y_{\text{ref},i+1,j}}{2} - \frac{y_{\text{ref},i,j} + y_{\text{ref},i+2,j}}{2} \right) / J ,
\]  
(Eq. 1)

Where \(y_{\text{response},i,j}\) is the measurement response of the \(i\)-th NMI during \(S_j\)-th series measurement; \(y_{\text{ref},i,j}\) and \(y_{\text{ref},i+1,j}\) denote the response of the reference cylinder A (here we used a reference cylinder of EB6397) before and after measurement of the \(i\)-th NMI to control drift. All measurements for any \(j\)-th series measurement were rescaled with the first set of reference measurements, \(\frac{y_{\text{ref},i,j} + y_{\text{ref},i+2,j}}{2}\) to compensate for drift during any \(j\)-th series measurement. \(j\) denotes \(j\)-th series measurement and \(j\) ranges from 1 to \(J\). It means in detail that a series of measurements was repeated \(J\) times for reproducibility before obtaining the final response value. In addition, the last \(J\)-th measurement was fulfilled after receiving the cylinder back from each NMI. Then the amount of the standards mixtures were determined by solving a quadratic equation on the basis of a relation between gravimetric value \((x_i)\) and corrected response \((y_{\text{response}Cor,i,j})\) [5]. The analysis uncertainty was set as 0.22 nmol/mol for all cylinders.

Finally the mole fractions of N\textsubscript{2}O listed at the result section were adopted as key comparison reference value (KCRV). So each cylinder had its own reference value.

**Measurement equation**

To assign the amount of substance fraction to a gravimetrically prepared cylinder, the following four groups of uncertainty components have been considered [6]:

1. gravimetric preparation (weighing process) \((x_{i,grav})\)
2. purity of the parent gases \((\Delta x_{i,purity})\)
3. stability of the gas mixture \((\Delta x_{i,stab})\)
4. non-recovered data \((\Delta x_{i,nr})\)

The amount of substance fraction \(x_{i,prep}\) of a particular component in mixture \(i\), as it appears
during use of the cylinder, can now be expressed as

\[ x_{i,\text{prep}} = x_{i,\text{grav}} + \Delta x_{i,\text{purity}} + \Delta x_{i,\text{stab}} + \Delta x_{i,\text{nr}} \quad (2) \]

The value obtained from equation (2) is sometimes referred to as the gravimetric value. Assuming independence between errors of the terms of equation (2), the expression for the combined standard uncertainty becomes

\[ u_{i,\text{prep}}^2 = u_{i,\text{grav}}^2 + u_{i,\text{purity}}^2 + u_{i,\text{stab}}^2 + u_{i,\text{nr}}^2 \quad (3) \]

For the mixtures used in this key comparison, the preparation method has been designed in such a way that long-term stability and a non-recovered data have been shown as;

\[ x_{i,\text{stab}} = x_{i,\text{nr}} = 0 \quad (4) \]

as well as their standard uncertainty. On this basis, using the theory of analysis of variance [6,7] the uncertainty can be set to zero due to long-term stability. Accordingly Eq. (2 to 4) reduce to

\[ x_{i,\text{prep}} = x_{i,\text{grav}} + \Delta x_{i,\text{purity}} \quad (5) \]

\[ u_{i,\text{prep}}^2 = u_{i,\text{grav}}^2 + u_{i,\text{purity}}^2 \quad (6) \]

ISO 6143 describes the general procedure for comparison. For the purpose of assigning values to a gas mixture the verification procedure requires the validity of \( x_{i,\text{prep}} \) and its uncertainty so that

\[ \left| x_{i,\text{prep}} - x_{i,\text{ver}} \right| \leq 2 \sqrt{u_{i,\text{prep}}^2 + u_{i,\text{ver}}^2} \quad (7) \]

The factor 2 is a coverage factor. The assumption must be made that both preparation and verification are unbiased. The uncertainty associated with the verification relies on the measurement capability and experimental design. Returning to the definition on the reference value, the reference value of mixture \( i \) in a key comparison can be expressed as

\[ x_{i,\text{ref}} = \langle x_{i,\text{ref}} \rangle + \delta x_{i,\text{ref}}, \quad \text{where} \quad x_{i,\text{ref}} = x_{i,\text{prep}} + \Delta x_{i,\text{ver}}. \quad (8) \]

As far as the verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards, the reference value in Eq. (8) comes to the preparation value. As a result, the standard uncertainty of a reference value is expressed as

\[ u_{i,\text{ref}}^2 = u_{i,\text{prep}}^2 + u_{i,\text{ver}}^2 \quad (9) \]
In this comparison, the verification uncertainty \( (k = 1) \) was set as 0.22 nmol/mol based on the uncertainties of drift, repeatability, and reproducibility during the measurement.

### Measurement method

The details on the measurement methods used by the participants are described in annex B of this report. A summary of the calibration method, date of measurement, and the way in which metrological traceability is established is given in table 4.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Cylinder</th>
<th>Measurement period</th>
<th>Calibration standards</th>
<th>Instrument calibration</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS</td>
<td>ME5524</td>
<td>Feb. 1-Mar. 30, 2009</td>
<td>Own standards</td>
<td>two point calibration</td>
<td>GC-µECD</td>
</tr>
<tr>
<td>NIM</td>
<td>ME5622</td>
<td>Feb. 27-Mar. 6, 2009</td>
<td>Own standards</td>
<td>single point calibration</td>
<td>GC-µECD</td>
</tr>
<tr>
<td>NIST</td>
<td>ME5591</td>
<td>Dec. 22-Dec. 30, 2008</td>
<td>Own standards</td>
<td>multi point calibration</td>
<td>GC-ECD</td>
</tr>
<tr>
<td>VNIIM</td>
<td>ME5563</td>
<td>Mar. 2-17, 2009</td>
<td>Own standards</td>
<td>ISO 6143</td>
<td>GC-ECD</td>
</tr>
<tr>
<td>VSL</td>
<td>ME5589</td>
<td>Feb. 19-20, 2009</td>
<td>Own standards</td>
<td>ISO6143</td>
<td>GC-DID</td>
</tr>
<tr>
<td>ESRL/NOAA</td>
<td>ME5572</td>
<td>Nov. 10-Dec. 29, 2008</td>
<td>WMO</td>
<td>multi point calibration</td>
<td>no information</td>
</tr>
</tbody>
</table>

### Degrees of equivalence (DoE)

A unilateral degree of equivalence is defined as \([6]\)

\[
d_i = x_i - x_i,KCRV, \tag{10}
\]

\(x_i,KCRV\) denotes the key comparison reference value and \(x_i\) the result of laboratory \(i\). Therefore the standard uncertainty of \(d_i\) based on equations of \((8) \sim (10)\) can be expressed as

\[
u^2(d_i) = u^2_{i,lab} + u^2_{i,prep} + u^2_{i,ver} \tag{11}
\]
assuming that the aggregated error terms are uncorrelated. A bilateral degree of equivalence is defined as the difference and its combined uncertainty at 95 % level of confidence under the assumption of independence of \( d_j \) and \( d_j' \).

\[
d_{ij} = d_j - d_j' \text{ and } u^2(d_{ij}) = u^2_{i,\text{lab}} + u^2_{i,\text{prep}} + u^2_{i,\text{ver}} + u^2_{j,\text{lab}} + u^2_{j,\text{prep}} + u^2_{j,\text{ver}}.
\]

(12)

In fact the two parameters are not clearly independent. However, the uncertainty of a degree of equivalence is so dominated by the uncertainty of the laboratory that their correlation can be neglected.

Results and Discussion

The results of the key comparison are summarized in Table 5.

- \( x_{\text{prep}} \): amount of substance fraction, from preparation \((10^{-9} \text{ mol/mol})\).
- \( x_{i,\text{grav}} \): purity \( i_{\text{grav}} \), where \( \Delta x_{i,\text{grav}} = 0.15 \) for this comparison.
- \( u_{\text{ref}} \): uncertainty of reference value \((10^{-9} \text{ mol/mol})\), \( u^2_{i,\text{ref}} = u^2_{i,\text{prep}} + u^2_{i,\text{ver}} \) for this comparison \( u_{i,\text{prep}} = 0.10 \) and \( u_{i,\text{ver}} = 0.22 \).
- \( x_{\text{lab}} \): result of laboratory \((10^{-9} \text{ mol/mol})\).
- \( u_{\text{lab}} \): uncertainty \((k = 1)\) obtained from the value of \( U_{\text{lab}} \) submitted uncertainty by laboratory, at 95 % level of confidence \((10^{-9} \text{ mol/mol})\).
- \( k_{\text{lab}} \): coverage factor \((k = 2)\).
- \( \Delta x \): difference between laboratory result and reference value \((10^{-9} \text{ mol/mol})\).
- \( k \): coverage factor for degree of equivalence, \( k = 2 \) for this comparison.
- \( U(Dx) \): Expanded uncertainty of difference \( Dx \), at 95% level of confidences \((10^{-9} \text{ mol/mol})\).

### Table 5: Summary of the results for CCQM-K68

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Cylinder</th>
<th>( x_{\text{KCRV}} )</th>
<th>( u_{\text{KCRV}} )</th>
<th>( x_{\text{lab}} )</th>
<th>( u_{\text{lab}} ) ( k = 1 )</th>
<th>( D_x ) ( k = 1 )</th>
<th>( u(D_x) ) ( k = 1 )</th>
<th>( U(D_x) ) ( k = 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRISS</td>
<td>ME5524</td>
<td>310.44</td>
<td>0.24</td>
<td>310.55</td>
<td>0.17</td>
<td>0.11</td>
<td>0.29</td>
<td>0.59</td>
</tr>
<tr>
<td>NIM</td>
<td>ME5622</td>
<td>315.40</td>
<td>0.24</td>
<td>314</td>
<td>1.3</td>
<td>-1.40</td>
<td>1.27</td>
<td>2.55</td>
</tr>
<tr>
<td>NIST</td>
<td>ME5591</td>
<td>325.02</td>
<td>0.24</td>
<td>324.5</td>
<td>0.8</td>
<td>-0.52</td>
<td>0.84</td>
<td>1.67</td>
</tr>
<tr>
<td>NMIJ</td>
<td>ME5547</td>
<td>312.93</td>
<td>0.24</td>
<td>313.19</td>
<td>0.21</td>
<td>0.26</td>
<td>0.32</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Table. 5 shows the relative deviation and its uncertainty of each laboratory. The table indicates that the reported results agree well with the KCRV within 0.5 % relative difference (1.5 nmol/mol).

In figure 1, the relative deviation from the reference value for all participating laboratories is shown. The uncertainties given are the relative standard uncertainty of difference ($D_x$) between the laboratory result and the reference value. The distance from the KCRV is smaller than the associated uncertainty in most cases. Average value of deviation from the KCRV was about -0.5 nmol/mol below zero. It implicates that the participating laboratories underestimated the amount of substance fractions.

![Figure 1. Relative Deviation from the reference value](image-url)

In figure 2 the degrees of equivalence for the participants are given relative to the reference value whose uncertainties are given at approximately 95% confidence intervals for a coverage factor $k = 2$. 
Figure 2. Degree of Equivalence for the CCQM-K68.

**Conclusion**

The results of all the participants in this key comparison are consistent with their KCRV. All NMI results agree within 0.5% (or better) with the key comparison reference value.

This key comparison compares the measurement capability of N₂O at a trace level of 320 nmol/mol. The results of the comparison show measurement equivalence between NMIs and WMO which is in charge of global observation of N₂O at ambient. Accordingly, it is possible for this key comparison to offer a good traceability and a harmonization among the global distribution data of N₂O. This key comparison supports the measurement capability of N₂O in the range of 200 nmol/mol to 20 μmol/mol in synthetic air.

**Acknowledgement**

This work was funded by the Korea Meteorological Administration Research and Development Program under Grant RACS_2010_1004 and National Agenda Program (NAP).
References
Annex 1: Measurement raw data set of CCQM-K68

Table 7: Raw data of N$_2$O for CCQM-K68

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>gravimetric value [µmol/mol]</th>
<th>Unc$_{prep}$ (k=2)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>after return</th>
<th>mean</th>
<th>Standard uncertainty</th>
<th>Relative standard uncertainty [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME5524</td>
<td>310.44</td>
<td>0.19</td>
<td>310.48</td>
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<td>325.06</td>
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<td>325.14</td>
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<td>325.16</td>
<td>325.11</td>
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<td>0.016</td>
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<tr>
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<td>331.01</td>
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<td>330.86</td>
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</tbody>
</table>
Annex 2:

International Key Comparison Report
On CCQM-K68 of N₂O in Synthetic Air

Lab Information

Lab Name: National Institute of Metrology (NIM), China
Cylinder No.: ME5622

Measurement Report

Table 1. Measurement Report by GC-µECD

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result ($\times 10^{-9}$ mol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>27/02/09</td>
<td>314.01</td>
<td>0.32%</td>
<td>6</td>
</tr>
<tr>
<td>N₂O</td>
<td>05/03/09</td>
<td>313.83</td>
<td>0.26%</td>
<td>8</td>
</tr>
<tr>
<td>N₂O</td>
<td>05/03/09</td>
<td>313.42</td>
<td>0.29%</td>
<td>6</td>
</tr>
<tr>
<td>N₂O</td>
<td>06/03/09</td>
<td>314.72</td>
<td>0.23%</td>
<td>5</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>313.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Result

Table 2. Measurement Result

<table>
<thead>
<tr>
<th>Component</th>
<th>Result ($\times 10^{-9}$ mol/mol)</th>
<th>Exp.Uncertainty ($\times 10^{-9}$ mol/mol)</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>314.0</td>
<td>2.5*</td>
<td>2**</td>
</tr>
</tbody>
</table>

* Which is equal to a relative expanded uncertainty of 0.8%;
** The coverage factor was based on approximately 95% confidence.

1 Instrumentation

A GC-µECD (Agilent 6890, Agilent) was used to analyze the gas mixtures. A capillary column of HP PLOT-Q (30m×0.52mm) was adopted to separate the N₂O from other gas components.

The gas mixtures in both comparison cylinder and the reference cylinder, via regulators and Teflon tube, were introduced into a 6-port valve. The 6-port valve was driven by compressed air. The size of sample loop used here was 1mL and the gas flow rate though the sample loop was controlled at 60mL/min continuously by an upstream mass flow controller. A restrictor was set at the end of the sample loop in order to increase the injected sample amount and
reduce the ambient pressure interferences.

Here single point calibration method was taken to perform the measurement. The comparison cylinder and our reference cylinders were measured in the order of Reference-Sample-Reference-Sample……

2 Comparison Cylinder handling

When package box including comparison cylinder arrived at our lab, it was in good state. Then the box was unpacked and the comparison cylinder was stored at room temperature. When a SS regulator was connected to the cylinder, an inner pressure of about 7.5MPa was read by the gauge.

3 Calibration Standards

3.1 Impurity analysis

The calibration standards of CO in nitrogen were prepared by gravimetric method according to ISO 6142-2001. Of the parent gases, the measured purity data were listed in Table 3-5.

Table 3. Purity of the High purity N₂ (Cylinder No.1208321,1032453)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Standard Uncertainty (µmol/mol)</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.310</td>
<td>0.031</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.631</td>
<td>0.063</td>
<td>GC-MEN-FID</td>
</tr>
<tr>
<td>N₂O</td>
<td>&lt;0.001</td>
<td>0.00029</td>
<td>GC-µECD</td>
</tr>
<tr>
<td>O₂</td>
<td>0.5</td>
<td>0.05</td>
<td>O2 Analyzer</td>
</tr>
<tr>
<td>N₂</td>
<td>999985.2</td>
<td>1.4</td>
<td>/</td>
</tr>
<tr>
<td>H₂</td>
<td>0.02</td>
<td>0.004</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>Ar</td>
<td>12.3</td>
<td>1.23</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt;2</td>
<td>0.58</td>
<td>Dew point Meter</td>
</tr>
</tbody>
</table>

Table 4. Purity data of the High purity O₂ (Cylinder No. 448054)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Standard Uncertainty (µmol/mol)</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.010</td>
<td>0.002</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.0</td>
<td>0.2</td>
<td>GC-MEN-FID</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.004</td>
<td>0.002</td>
<td>GC-µECD</td>
</tr>
<tr>
<td>O₂</td>
<td>999994,5</td>
<td>0.7</td>
<td>/</td>
</tr>
<tr>
<td>N₂</td>
<td>3.0</td>
<td>0.3</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>H₂</td>
<td>0.02</td>
<td>0.004</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>Ar</td>
<td>0.5</td>
<td>0.1</td>
<td>GC-PDHID</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt;2</td>
<td>0.58</td>
<td>Dew point Meter</td>
</tr>
</tbody>
</table>

Table 5. Purity data of the Pure N₂O (Cylinder No. 05908)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Standard Uncertainty (µmol/mol)</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
3.2 Gravimetric Preparation

The calibration gas mixtures of N₂O in air of about 320µmol/mol were gravimetrically prepared by 5-step dilution. From the pure gases, the N₂O / N₂ gas mixtures of 2.8%mol/mol, 0.17%mol/mol, 110µmol/mol, and 5µmol/mol were prepared in sequence. In the final dilution step, O₂ was added to the final gas mixtures in order to obtain the N₂O/air of about 320µmol/mol. Figure 1 shows the dilution flow chart.

![Dilution Flow Chart](image)

Figure 1. Stepwise dilution for preparation of N₂O/air

3.3 Evaluation of the uncertainty sources in gravimetric preparation

Regarding the uncertainty of our own prepared reference gas mixtures, it was evaluated according to ISO6142-2001 and GUM.

Balance description: Chyo Balance (made in Japan), which is a equal arm balance with capacity of 30Kg and resolution of 1mg.

Weighing Method: Substitution method.

Table 6. Uncertainty in the balance system and weights used

<table>
<thead>
<tr>
<th>Uncertainty in the balance system and weights((u_i))</th>
<th>Value(mg)</th>
<th>Distr.</th>
<th>St. u(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Uncertainty in balance reading</td>
<td>0.645</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Resolution of the balance</td>
<td>1</td>
<td>Rect.</td>
<td>0.289</td>
</tr>
<tr>
<td>1.2 Accuracy of balance including non-linearity</td>
<td>1</td>
<td>Rect.</td>
<td>0.577</td>
</tr>
</tbody>
</table>

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Table 7. Uncertainty related to the cylinders

<table>
<thead>
<tr>
<th>Uncertainty related to the cylinders ($u_2$)</th>
<th>Value(mg)</th>
<th>Distr.</th>
<th>St. u(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Buoyancy effects</td>
<td></td>
<td></td>
<td>13.603</td>
</tr>
<tr>
<td>1.1 Due to volume difference between sample and tare cylinders</td>
<td>2.720</td>
<td>Rect.</td>
<td>1.577</td>
</tr>
<tr>
<td>1.2 Volume change due to filling gas</td>
<td>23.286</td>
<td>Rect.</td>
<td>13.444</td>
</tr>
<tr>
<td>1.3 Volume change due to cylinder temperature rise</td>
<td>2.328</td>
<td>Rect.</td>
<td>1.344</td>
</tr>
<tr>
<td>2. Uncertainty due to handle of sample cylinder</td>
<td>3.267</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Loss of metal, paints or labels from surface of cylinder</td>
<td>5</td>
<td>Rect.</td>
<td>2.887</td>
</tr>
<tr>
<td>2.2 Loss of metal from threads of valve/fitting</td>
<td>5</td>
<td>Rect.</td>
<td>2.887</td>
</tr>
<tr>
<td>3. Uncertainty due to adsorption</td>
<td>0.082</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Dirt on cylinder, valves or associated fittings</td>
<td>4</td>
<td>Rect.</td>
<td>2.309</td>
</tr>
<tr>
<td>3.2 Moisture adsorption onto surface cylinders</td>
<td>0.1</td>
<td>Rect.</td>
<td>0.058</td>
</tr>
</tbody>
</table>

**Total**

<table>
<thead>
<tr>
<th>Value(mg)</th>
<th>Distr.</th>
<th>St. u(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major component</td>
<td>13.99</td>
<td></td>
</tr>
<tr>
<td>Minor Component</td>
<td>3.87</td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Uncertainties related to the component gases

<table>
<thead>
<tr>
<th>Uncertainties related to the component gases ($u_3$)</th>
<th>Value(mg)</th>
<th>Distr.</th>
<th>St. u(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Residual gases in cylinder</td>
<td>0.108</td>
<td>Rect.</td>
<td>0.062</td>
</tr>
<tr>
<td>2. Uncertainties of leakage of gas</td>
<td></td>
<td></td>
<td>0.409</td>
</tr>
<tr>
<td>2.1 Leakage of air into the cylinder after evacuation</td>
<td>1</td>
<td>Rect.</td>
<td>0.289</td>
</tr>
<tr>
<td>2.2 Leakage of gas from the cylinder valve during filling</td>
<td>1</td>
<td>Rect.</td>
<td>0.289</td>
</tr>
<tr>
<td>2.3 Escape of gas from cylinder into transport lines</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Gas remaining in transfer system for weight-loss method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Absorption/reaction of components on Cyl. internal surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Reaction between components</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Insufficient homogenization</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Total (mg)**

<table>
<thead>
<tr>
<th>Value(mg)</th>
<th>Distr.</th>
<th>St. u(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For each filled gas component, the standard uncertainty could calculate from $u_1$, $u_2$, and $u_3$ in Table 6-8.

\[
\begin{align*}
    u_{\text{major comp}} &= \sqrt{u_1^2 + u_2^2 + u_3^2} \\
    u_{\text{min comp}} &= \sqrt{u_1^2 + u_2^2 + u_3^2}
\end{align*}
\]

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Table 9. Primary Standards list

<table>
<thead>
<tr>
<th>Cyl#</th>
<th>N₂O Conc. (x10⁻⁹ mol/mol)</th>
<th>Exp. Relative Uncertainty(N₂O)</th>
<th>O₂ Conc. (mol/mol)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>434679#</td>
<td>305.93</td>
<td>0.4%</td>
<td>21.56%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>435319#</td>
<td>307.65</td>
<td>0.4%</td>
<td>21.63%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>435279#</td>
<td>308.42</td>
<td>0.4%</td>
<td>20.99%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>435258#</td>
<td>310.30</td>
<td>0.4%</td>
<td>21.00%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>411378#</td>
<td>311.92</td>
<td>0.4%</td>
<td>21.11%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>434874#</td>
<td>312.97</td>
<td>0.4%</td>
<td>20.69%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>434959#</td>
<td>314.19</td>
<td>0.4%</td>
<td>20.74%</td>
<td>N₂O/Air</td>
</tr>
<tr>
<td>434952#</td>
<td>312.74</td>
<td>0.4%</td>
<td>20.56%</td>
<td>N₂O/Air</td>
</tr>
</tbody>
</table>

4 Model equation for the measurement of comparison cylinder

\[
c_{\text{CCQM}} = \frac{H_{\text{CCQM}}}{H_{\text{PRM}}} \cdot c_{\text{PRM}} \cdot f_r
\]

- \(c_{\text{CCQM}}\): Concentration of the N₂O in the comparison cylinder, in unit of 10⁻⁹ mol/mol;
- \(H_{\text{CCQM}}\): Peak height of the comparison cylinder on GC-µECD, in unit of pA;
- \(H_{\text{PRM}}\): Peak height of the PRM cylinder on GC-µECD, in unit of pA;
- \(c_{\text{PRM}}\): Concentration of the N₂O in PRM cylinder, in unit of 10⁻⁹ mol/mol;
- \(f_r\): Reproducibility between run and run.

For the \(H_{\text{CCQM}}\) and \(H_{\text{PRM}}\), the relative standard uncertainty could be calculated from the relative standard deviation (RSD). Take the maximum RSD of 0.61% basing on 7 replicates, the relative standard uncertainty is 0.61% / sqrt(7) = 0.23%.

For \(c_{\text{PRM}}\), the relative standard uncertainty was 0.20%.

The relative standard uncertainty of \(f_r\) could be calculated from the 4 measurements on different run, and was RSD / sqrt(6) = 0.18% / sqrt(3) = 0.10%.

Table 10. Uncertainty estimation for the results.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Standard uncertainty</th>
<th>Type</th>
<th>Sensitivity Coefficient</th>
<th>Uncertainty Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_{\text{PRM}})</td>
<td>314.19</td>
<td>0.63</td>
<td>B</td>
<td>1.000987</td>
<td>0.63062</td>
</tr>
<tr>
<td>(H_{\text{CCQM}})</td>
<td>20.228</td>
<td>0.046</td>
<td>A</td>
<td>15.54775</td>
<td>0.71520</td>
</tr>
<tr>
<td>(H_{\text{PRM}})</td>
<td>20.196</td>
<td>0.046</td>
<td>A</td>
<td>-15.57239</td>
<td>0.71633</td>
</tr>
<tr>
<td>(f_r)</td>
<td>0.997795</td>
<td>0.00998</td>
<td>A</td>
<td>314.688</td>
<td>0.31399</td>
</tr>
<tr>
<td>(c_{\text{CCQM}})</td>
<td>313.99</td>
<td>1.23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Result:

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Quantity: $c_{CCQM}$
Value: $314.0 \times 10^{-9}$ mol/mol
Expanded Uncertainty: $2.5 \times 10^{-9}$ mol/mol (Relative Expanded U=0.8%)
$k=2$ (95% confidence level)
Report Form CCQM-K68 Nitrous oxide in synthetic air

Laboratory name: KRISS
Cylinder number: ME5524

*Measurement*

<table>
<thead>
<tr>
<th># of measurement</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>310.53</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>310.56</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>310.50</td>
<td>0.06</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>310.59</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>310.33</td>
<td>0.06</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>310.68</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>310.81</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>310.39</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>310.58</td>
<td>0.06</td>
<td>4</td>
</tr>
</tbody>
</table>

*Results*

This value was calculated by the method described in section of instrument calibration.

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (nmol/mol)</th>
<th>Expanded Uncertainty (nmol/mol)</th>
<th>Coverage factor¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>310.55</td>
<td>0.34</td>
<td>k = 2</td>
</tr>
</tbody>
</table>

*Method Description Forms*

**Details of the measurement method used:**

Trace level of N₂O in synthetic air has been analyzed using GC-μECD. Table 1 shows analytical condition of analyzing system.

Configuration of analysis system: gas cylinder >> regulator >> MFC >> sample injection valve >> column >> detector >> integrator >> area comparison >> results

*Table 1. Analytical condition of instrument used to measure N₂O in Air*

¹ The coverage factor shall be based on approximately 95% confidence.

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Calibration standards:

Preparation of standards

The calibration standards for CCQM K-68 were prepared by gravimetric method in our institute (KRISS). All impurities in each individual source gas were analyzed for purity analysis. For obtaining the nominal value of N₂O mixture, 4step dilutions carried out. The uncertainty of the primary standards prepared during the independent step are within 0.06 %, k=2.

Purity O₂ and N₂ mother gases were analyzed with a GC/ECD analyzer with a pre-concentration device. An amount of substance fraction of Nitrous oxide as impurity was measured by 0.12 nmol/mol in nitrogen mother gas and by 0.11 nmol/mol in oxygen mother gas, respectively. Based on the purity analysis, the amount of 0.15 nmol/mol was finally added as an impurity existed in the mother gases after preparation of primary standard mixtures. Four-step dilution was used to make the mixtures, with nitrous oxide concentration of 13000 µmol/mol, 300 µmol/mol, 9 µmol/mol, and 0.3 µmol/mol. Oxygen was added in the last-step dilution. Table 2 shows characteristics of the calibration standards.

Table 2. Primary standard mixtures for calibration

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Grabimetric Value (nmol/mol)</th>
<th>Expanded uncertainty [k=2] (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME5559</td>
<td>311.88</td>
<td>0.1</td>
</tr>
<tr>
<td>ME5578</td>
<td>310.01</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Purity analysis

The impurities of nitrous oxide, nitrogen, and oxygen were determined by analytical methods and the amount of the major component is conventionally determined from the following equation,

\[ x_{\text{pure}} = 1 - \sum_{i=1}^{N} x_i \]

where

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
\( x_i \): the mole fraction of impurity I, determined by analysis;

N: the number of impurities likely to be present in the final mixture;

\( x_{\text{pure}} \): the mole fraction “purity” of the “pure” parent gas.

Table 3-5 shows the results of purity analyses.

### Table 3. Purity table in pure nitrous oxide mother gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Distribution</th>
<th>Applied concentration (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;0.1</td>
<td>Rectangular</td>
<td>0.05</td>
<td>0.0289</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>Normal</td>
<td>0.2</td>
<td>0.006</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.3</td>
<td>Normal</td>
<td>0.3</td>
<td>0.009</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.52</td>
<td>Normal</td>
<td>0.52</td>
<td>0.010</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>&lt;0.05</td>
<td>Rectangular</td>
<td>0.0025</td>
<td>0.0144</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;0.05</td>
<td>Rectangular</td>
<td>0.0025</td>
<td>0.0144</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.3</td>
<td>Normal</td>
<td>0.3</td>
<td>0.15</td>
</tr>
<tr>
<td>THC</td>
<td>&lt;0.01</td>
<td>Rectangular</td>
<td>0.005</td>
<td>0.0029</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O</td>
<td></td>
<td></td>
<td>999998.6</td>
<td>0.156</td>
</tr>
</tbody>
</table>

### Table 4. Purity analysis in pure nitrogen mother gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Distribution</th>
<th>Applied concentration (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;0.05</td>
<td>rectangular</td>
<td>0.025</td>
<td>0.0144</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.35</td>
<td>normal</td>
<td>0.35</td>
<td>0.035</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;0.1</td>
<td>rectangular</td>
<td>0.05</td>
<td>0.029</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&lt;0.01</td>
<td>rectangular</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.0013</td>
<td>normal</td>
<td>0.0013</td>
<td>0.00065</td>
</tr>
<tr>
<td>Ar</td>
<td>&lt;0.1</td>
<td>rectangular</td>
<td>0.05</td>
<td>0.029</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.2</td>
<td>normal</td>
<td>1.2</td>
<td>0.24</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.00012</td>
<td>normal</td>
<td>0.00012</td>
<td>0.000012</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>purity</td>
<td>999998.3</td>
<td>0.246</td>
</tr>
</tbody>
</table>

### Table 5. Purity analysis in pure oxygen mother gas

Protocol: CCQM-K68 N<sub>2</sub>O 320 nmol/mol in synthetic air
### Table 1: Concentration and Distribution of Components

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (µmol/mol)</th>
<th>Distribution</th>
<th>Applied Concentration (µmol/mol)</th>
<th>Standard Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>&lt;0.05</td>
<td>rectangular</td>
<td>0.025</td>
<td>0.0144</td>
</tr>
<tr>
<td>Ar</td>
<td>&lt;1</td>
<td>rectangular</td>
<td>0.5</td>
<td>0.289</td>
</tr>
<tr>
<td>N₂</td>
<td>2.8</td>
<td>normal</td>
<td>2.8</td>
<td>0.280</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt;0.01</td>
<td>rectangular</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>CH₄</td>
<td>&lt;0.03</td>
<td>rectangular</td>
<td>0.0015</td>
<td>0.001</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;0.1</td>
<td>rectangular</td>
<td>0.05</td>
<td>0.029</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.1</td>
<td>normal</td>
<td>1.1</td>
<td>0.22</td>
</tr>
<tr>
<td>THC</td>
<td>&lt;0.1</td>
<td>rectangular</td>
<td>0.05</td>
<td>0.029</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.00011</td>
<td>normal</td>
<td>0.00011</td>
<td>0.00011</td>
</tr>
<tr>
<td>O₂</td>
<td>purity</td>
<td></td>
<td>999995.5</td>
<td>0.3576</td>
</tr>
</tbody>
</table>

### Instrument Calibration:

One set of 10 standard gases with similar concentration was prepared by gravimetric method and verified by GC/ECD to make sure their accuracy. Finally we used 2 standard gases (ME5559 and ME5578) for a reference during N₂O measurements.

In order to obtain an instrument calibration relation 2 points calibration method with two standard mixtures was used.

### Sample Handling:

The sample cylinders were stood for more than one week at room temperature to equilibrate temperature.

### Uncertainty:

We estimated the uncertainty in the gravimetric methods and measurements. The uncertainties are given in Table 6.

#### Table 6. Total Uncertainties

<table>
<thead>
<tr>
<th>Uncertainty Item</th>
<th>Type</th>
<th>Standard Uncertainty (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetry uncertainty</td>
<td>B</td>
<td>0.1</td>
</tr>
<tr>
<td>Verification uncertainty</td>
<td>A</td>
<td>0.14</td>
</tr>
<tr>
<td>Total expanded uncertainty (k=2)</td>
<td></td>
<td>0.34</td>
</tr>
</tbody>
</table>
Appendix A.

**Report Form CCQM-K68 Nitrous oxide in synthetic air**

Laboratory name: NMIJ

Cylinder number: ME5547

### Measurement

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>28/01/09</td>
<td>313.40</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>28/01/09</td>
<td>313.47</td>
<td>0.06</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>29/01/09</td>
<td>313.06</td>
<td>0.08</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>30/01/09</td>
<td>313.69</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>02/02/09</td>
<td>313.15</td>
<td>0.06</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>03/02/09</td>
<td>313.69</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>04/02/09</td>
<td>313.89</td>
<td>0.04</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>04/02/09</td>
<td>313.02</td>
<td>0.05</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>05/02/09</td>
<td>312.54</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>09/02/09</td>
<td>312.93</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>10/02/09</td>
<td>313.34</td>
<td>0.07</td>
<td>6</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>10/02/09</td>
<td>313.00</td>
<td>0.06</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>13/02/09</td>
<td>312.21</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>17/02/09</td>
<td>313.60</td>
<td>0.11</td>
<td>7</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>17/02/09</td>
<td>312.29</td>
<td>0.14</td>
<td>7</td>
</tr>
</tbody>
</table>

### Results

This values was calculated by the method described in section of instrument calibration.

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (nmol/mol)</th>
<th>Expanded Uncertainty</th>
<th>Coverage factor$^2$</th>
</tr>
</thead>
</table>

---

$^2$ The coverage factor shall be based on approximately 95% confidence.

Protocol: CCQM-K68 N$_2$O 320 nmol/mol in synthetic air
N₂O & 313.19 & 0.13 % & 2 \\

Method Description Forms

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Agilent 5890</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>micro-Electron capture detector</td>
</tr>
<tr>
<td>Detector temp.</td>
<td>345 °C</td>
</tr>
<tr>
<td>Oven temp.</td>
<td>30 °C, isothermal</td>
</tr>
<tr>
<td>column</td>
<td>Porapak Q 80/100 mesh (1/8 inches × 120 cm SUS)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>N₂</td>
</tr>
<tr>
<td>Carrier flow</td>
<td>60 kPa (8 mL/min)</td>
</tr>
<tr>
<td>Make up gas</td>
<td>Ar+CH₄ (10 mL/min)</td>
</tr>
<tr>
<td>Sample Flow</td>
<td>20 mL/min</td>
</tr>
<tr>
<td>Sample loop</td>
<td>2 mL</td>
</tr>
</tbody>
</table>

Details of the measurement method used:

Reference Method:
Trace level of N₂O in synthetic air has been quantified using GC-ECD. Table 1 shows analytical condition of measurement.

Table 1. Analytical condition of instrument used to measure N₂O in Air
Calibration standards:

Preparation method

Five calibration standards were used for the determination of nitrous oxide concentration in synthetic air. The standards were prepared from pure nitrous oxide, pure nitrogen, and pure oxygen in accordance with ISO6142:2001 (Gas analysis-Preparation of calibration gases-Gravimetric method). Pure nitrous oxide was from Sumitomo Seika Chemicals Company Limited and pure nitrogen and oxygen from Japan Fine Products. Four-step dilution was used to make the mixtures, with nitrous oxide concentration of 13000 µmol/mol, 300 µmol/mol, 9 µmol/mol, and 0.3 µmol/mol. Oxygen was added in the last-step dilution. Table 2 shows characteristics of the calibration standards.

Table 2. Gravimetric value and expanded uncertainty in calibration standards

<table>
<thead>
<tr>
<th>Cylinder number</th>
<th>Gravimetric Value (nmol/mol)</th>
<th>Expanded uncertainty [k=2] (nmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPB00877</td>
<td>303.57</td>
<td>0.13</td>
</tr>
<tr>
<td>CPB31362</td>
<td>312.77</td>
<td>0.19</td>
</tr>
<tr>
<td>CPB16468</td>
<td>326.44</td>
<td>0.20</td>
</tr>
<tr>
<td>CPC00415</td>
<td>338.20</td>
<td>0.20</td>
</tr>
<tr>
<td>CPB16463</td>
<td>343.73</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Purity analysis

The impurities of nitrous oxide, nitrogen, and oxygen were determined by analytical methods and the amount of the major component is conventionally determined from the following equation,

\[ x_{\text{pure}} = 1 - \sum_{i=1}^{N} x_i \]

where

\[ x_i \]: the mole fraction of impurity I, determined by analysis;

\[ N \]: the number of impurities likely to be present in the final mixture;

\[ x_{\text{pure}} \]: the mole fraction “purity” of the “pure” parent gas.

Table 3-5 shows the results of purity analyses.

Table 3. Purity table of high-purity nitrous oxide as parent gas

<table>
<thead>
<tr>
<th>Components</th>
<th>Applied concentration (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
<th>Distribution</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Components</td>
<td>Applied concentration (µmol/mol)</td>
<td>Standard uncertainty (µmol/mol)</td>
<td>Distribution</td>
<td>Analytical method</td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------</td>
<td>---------------------------------</td>
<td>--------------</td>
<td>------------------</td>
</tr>
<tr>
<td>N₂</td>
<td>0.983</td>
<td>0.567</td>
<td>Rectangular</td>
<td>Micro GC</td>
</tr>
<tr>
<td>O₂</td>
<td>1.020</td>
<td>0.589</td>
<td>Rectangular</td>
<td>Micro GC</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.128</td>
<td>0.006</td>
<td>Normal</td>
<td>GC-FID with methanizer</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.019</td>
<td>0.003</td>
<td>Normal</td>
<td>GC-FID</td>
</tr>
<tr>
<td>CO</td>
<td>0.056</td>
<td>0.032</td>
<td>Rectangular</td>
<td>GC-FID with methanizer</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.439</td>
<td>0.253</td>
<td>Rectangular</td>
<td>Capacitance-type moisture meter</td>
</tr>
<tr>
<td>N₂O</td>
<td>999997.36</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Purity table of high-purity nitrogen as parent gas

<table>
<thead>
<tr>
<th>Components</th>
<th>Applied concentration (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
<th>Distribution</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.819</td>
<td>0.473</td>
<td>Rectangular</td>
<td>Micro GC</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.010</td>
<td>0.006</td>
<td>Rectangular</td>
<td>FT-IR</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.026</td>
<td>0.015</td>
<td>Rectangular</td>
<td>FT-IR</td>
</tr>
<tr>
<td>CO</td>
<td>0.175</td>
<td>0.101</td>
<td>Rectangular</td>
<td>FT-IR</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.439</td>
<td>0.253</td>
<td>Rectangular</td>
<td>Capacitance-type moisture meter</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.00002</td>
<td>0.00001</td>
<td>Rectangular</td>
<td>Clyo. conc. /GC/MS</td>
</tr>
<tr>
<td>N₂</td>
<td>999998.53</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Purity table of high-purity oxygen as parent gas

<table>
<thead>
<tr>
<th>Components</th>
<th>Applied concentration (µmol/mol)</th>
<th>Standard uncertainty (µmol/mol)</th>
<th>Distribution</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.090</td>
<td>0.052</td>
<td>Rectangular</td>
<td>GC-TCD</td>
</tr>
<tr>
<td>Ar</td>
<td>0.087</td>
<td>0.050</td>
<td>Rectangular</td>
<td>GC-TCD</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.056</td>
<td>0.004</td>
<td>Normal</td>
<td>FT-IR</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.003</td>
<td>0.002</td>
<td>Rectangular</td>
<td>FT-IR</td>
</tr>
<tr>
<td>CO</td>
<td>0.005</td>
<td>0.003</td>
<td>Rectangular</td>
<td>FT-IR</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.439</td>
<td>0.253</td>
<td>Rectangular</td>
<td>Capacitance-type moisture meter</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.00002</td>
<td>0.00001</td>
<td>Rectangular</td>
<td>Clyo. conc. /GC/MS</td>
</tr>
<tr>
<td>O₂</td>
<td>999999.32</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Instrument calibration:

The following measurement cycle was repeated 15 times for the determination of nitrous oxide concentration in air:

\[ \text{STD}_1 - \text{STD}_2 - \text{DC}(\text{drift control sample}) - \text{sample} - \text{STD}_3 - \text{STD}_4 - \text{STD}_5 \]

Where drift control sample was used for correction of sensitivity difference between each cycle. The response \( (y_i) \) to analyte content in each cycle used the mean value of seven individual responses.

\[
y'_i = \frac{1}{7} \sum_{j=1}^{7} y'_{i,j}
\]

Calibration data \( (y_{\text{STD}_1}, y_{\text{STD}_2}, \ldots, y_{\text{STD}_5}, y_{\text{sample}}) \) can be obtained from the mean value of fifteen cycles response \( (y'_1, y'_2, y'_3, \ldots, y'_5) \) divided by the response to drift control sample.

\[
y_i = \frac{\sum_{i=1}^{15} (y'_i / y'_{\text{DC}})}{15}
\]

The calibration data was used in order to determine the concentration of nitrous oxide in synthetic air. The determination process was according to ISO 6143 using the Deming’s generalized least-square method. The five calibration standards listed in table 2 were used for instrument calibration.

Sample handling:

The sample cylinder was stood at room temperature after arrival. Each cylinder was equipped with a stainless steel pressure regulator that was purged three times by sequential evacuation and pressurisation with the gas mixture used. Samples were transferred to sample loop with mass-flow controller.

Uncertainty:

The Deming’s generalized least-square method estimates the uncertainties associated with composition of calibration standards and the measured responses. The over-all standard uncertainty is estimated to be 0.21 nmol/mol.

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Report Form CCQM-K68 Nitrous oxide in synthetic air

Laboratory name: VSL

Cylinder number: ME5589

**Measurement #1**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>19-02-2009</td>
<td>327.2</td>
<td>0.4</td>
<td>3</td>
</tr>
</tbody>
</table>

**Measurement #2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>20-02-2009</td>
<td>333.3</td>
<td>0.6</td>
<td>3</td>
</tr>
</tbody>
</table>

**Results**

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (nmol/mol)</th>
<th>Expanded Uncertainty (nmol/mol)</th>
<th>Coverage factor³</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>330</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

**Method Description Forms**

**Details of the measurement method used:**

**Reference Method:**

Measurements have been performed with an HP6890 GC equipped with a Discharge Ionisation Detector. A Porapak-Q column was used at 35°C and with He as carrier gas. On

³ The coverage factor shall be based on approximately 95% confidence.
each measurement day, the samples were injected three times. Manual integration of the area was performed. The average of the three areas was used as one data point.

**Calibration standards:**

Calibration is performed using the Dutch Primary Standard gas Mixtures (PSM’s). A total of 9 PSM’s, all prepared by the gravimetric method according to ISO 6142:2001 (Gas Analysis-Preparation of calibration gas mixtures-Gravimetric method), have been used in this exercise. These PSM’s were prepared during normal maintenance work over the past years. High-purity N₂O, O₂ and high-purity N₂ are used to prepare high concentration mother mixtures of N₂O in air. With the same method these mixtures are diluted to daughters and granddaughters to achieve the appropriate concentrations. Prior to mixture preparation the pure gases have been analysed for impurities. The detection limit for N₂O in N₂ and O₂ is 0.5 nmol/mol.

**Instrument calibration:**

A linear calibration curve was made between 100 and 1000 nmol/mol by measuring PSM’s with a molar fraction of 100, 200(2), 300, 400(2), 600, 800 and 1000 nmol/mol N₂O in air. The measurements were performed in reverse concentration order starting with the 1000 nmol/mol mixture. For each mixture three injections were made and the average was taken as one data point. Because the injections are at ambient pressure, corrections were made for difference in atmospheric pressure.

**Sample handling:**

All cylinders were stored at 21°C in the laboratory for at least 24 hours before analysis. Each cylinder was equipped with a pressure reducer and individually connected to the sampling line of the GC. Before the measurement, the line was flushed for at least 10 minutes before injection. The flow was kept stable by using a high performance needle valve.

**Uncertainty:**

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
The uncertainty used for the calibration mixtures contains all sources of gravimetric preparation. No uncertainty for lack of stability was introduced because no instability has been recorded. The major source of the uncertainty in the measurement is the determination of the area in the chromatogram and this uncertainty on the response was used to determine the molar fraction of the unknown by comparison with the calibration mixtures according to ISO6143. The reported uncertainty is the combined uncertainty of the 2 analyses (as calculated via ISO6143) and multiplied by the coverage factor k=2.
**Report Form CCQM-K68 Nitrous oxide in synthetic air**

**Laboratory name: NIST**

**Cylinder number: ME5591**

**Measurement #1**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>22/12/08</td>
<td>324.28</td>
<td>0.16 %</td>
<td>6</td>
</tr>
</tbody>
</table>

**Measurement #2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>23/12/08</td>
<td>324.05</td>
<td>0.10 %</td>
<td>8</td>
</tr>
</tbody>
</table>

**Measurement #3**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>29/12/08</td>
<td>324.85</td>
<td>0.10 %</td>
<td>4</td>
</tr>
</tbody>
</table>

**Measurement #4**

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>30/12/08</td>
<td>324.66</td>
<td>0.18 %</td>
<td>7</td>
</tr>
</tbody>
</table>
### Results

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (nmol/mol)</th>
<th>Expanded Uncertainty (nmol/mol)</th>
<th>Coverage factor¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>324.5</td>
<td>1.6</td>
<td>2</td>
</tr>
</tbody>
</table>

### Method Description Forms

Please complete the following data regarding the description of the methods and the uncertainty evaluation.

### Details of the measurement method used:

#### Reference Method:

Describe your instrument(s). (principles, make, type, configuration, data collection, and etc.)

HP 5890 Gas Chromatograph, Electron Capture Detector (ECD) @ 330°C, 3.66 m x 0.32 cm stainless steel column packed with Porapak Q, 38.8 mL/min Argon/Methane carrier flow rate; HPChemstation data system used for peak area integration, data transferred to Excel

#### Calibration standards:

Describe your calibration standards for the measurements. (preparation method, purity analyses, estimated uncertainty, and etc.)

New (within the last 5 years) NIST N₂O in air primary gravimetric standards suite and NIST SRMS were used in the analysis. A bias has been seen between the current NIST N₂O primary standards suite, and those of NOAA and KRISS. However, the NOAA and KRISS standards are in agreement with the NIST SRMs. The NIST primary standards used to certify the SRM have long been expended, therefore the new set was produced. Since the NIST SRMs support the WMO N₂O scale, and NOAA and KRISS agree with the SRM, we are basing our K-68 sample value using the NIST SRMs. We will continue to investigate this bias.

SRM estimated uncertainty = 0.2 % relative standard uncertainty.

Purity analyses by GC/ECD, GC/TCD: N₂O = 99.937 % ± 0.001 %; N₂O in Air = 1.1 ppb ± 0.1 ppb

#### Instrument calibration:

Describe your calibration procedure. (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)
8 Standards used: PSM CAL014811 (447.8 ± 0.0.9) nmol/mol; PSM CAL014823 (383.0 ± 0.8) nmol/mol; PSM CAL014827 (380.8 ± 0.7) nmol/mol; PSM CAL014822 (360.9 ± 0.7) nmol/mol; PSM CAL014810 (313.4 ± 0.6) nmol/mol; PSM CAL014821 (309.8 ± 0.6) nmol/mol; PSM CAL014101 (233.8 ± 0.8) nmol/mol; PSM CAL014139 (207.0 ± 0.5) nmol/mol; SRM 17-35-B (333.0 ± 0.7) nmol/mol; SRM 16-30-B (301.0 ± 0.6) nmol/mol.

General calibration scale 2nd order for 8 PSMs; 2-point calibration using SRMs

Measurement sequence: PSM CAL014827 used as a control with each PSM/SRM and K-68 (ME5591) sample bracketed by PSM CAL014827; PSM CAL014827, PSM CAL014827, etc.

**Sample handling:**

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass flow controller, dilution, and etc.)

All standards and the K-68 sample were brought into the lab and set next to the GC to be used. They were allowed to stabilize over 2 days. The samples were flushed through the sample loop at 40 mL/min flow but then dropped to ambient pressure 5 seconds before automatic injection onto the GC column.

**Uncertainty:**

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method, and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty.

a. Uncertainty related to the standards

b. Uncertainties related to the analysis

**Detailed uncertainty budget:**

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Typical evaluation of the measurement uncertainty for N₂O:

<table>
<thead>
<tr>
<th>Quantity ( X_i )</th>
<th>Estimate ( x_i )</th>
<th>Evaluation Type (A or B)</th>
<th>Distribution</th>
<th>Standard uncertainty ( u(x_i) )</th>
<th>Sensitivity coefficient ( c_i )</th>
<th>Contribution ( u(y) )</th>
</tr>
</thead>
</table>

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
<table>
<thead>
<tr>
<th>Standards</th>
<th>A</th>
<th>Gaussian</th>
<th>0.2 % relative</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response repeatability</td>
<td>A</td>
<td>Gaussian</td>
<td>0.10 %</td>
<td>1</td>
</tr>
<tr>
<td>Value reproducibility</td>
<td>A</td>
<td>Gaussian</td>
<td>0.11 %</td>
<td>1</td>
</tr>
</tbody>
</table>
REPORT

Date: 18.03.09

L.A. Konopelko, Y.A. Kustikov, V.V. Pankratov, I.M. Vishnyakov,
M.V. Pavlov, E.V. Gromova

Report form:

Cylinder number: ME5563

### Measurement #1

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (10^7 mol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>02/03/09</td>
<td>324.14</td>
<td>0.3</td>
<td>4</td>
</tr>
</tbody>
</table>

### Measurement #2

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (10^9 mol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
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<tbody>
<tr>
<td>N₂O</td>
<td>06/03/09</td>
<td>323.93</td>
<td>0.5</td>
<td>4</td>
</tr>
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</table>

### Measurement #3

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (10^9 mol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>11/03/09</td>
<td>323.75</td>
<td>0.5</td>
<td>4</td>
</tr>
</tbody>
</table>

### Measurement #4

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (10^7 mol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>17/03/09</td>
<td>323.50</td>
<td>0.3</td>
<td>4</td>
</tr>
</tbody>
</table>

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
### Results

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (10^9 mol/mol)</th>
<th>Expanded Uncertainty (10^9 mol/mol)</th>
<th>Relative Expanded Uncertainty (%)</th>
<th>Coverage factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>323.83</td>
<td>2.46</td>
<td>0.76</td>
<td>2</td>
</tr>
</tbody>
</table>
Details of the measurement method used:

Reference method: GC-ECD
Instrument: gas chromatograph with ECD “Crystal 5000.2” (“Chromatec”, Russia) included in the set of National Primary Measurement Standard GET 154-01.

Calibration standards:

The calibration standards were prepared from pre-mixtures in accordance with ISO 6142: 2001 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method).

After preparation the composition was verified. The verification process is used to confirm the gravimetric composition as checking internal consistency between prepared cylinders, in accordance with requirements of ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures).

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

Table 1 – Description of pure components

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction $10^4$ mol/mol</th>
<th>Standard uncertainty $10^4$ mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>999948.70</td>
<td>3.18</td>
</tr>
<tr>
<td>N$_2$</td>
<td>999996.75</td>
<td>0.51</td>
</tr>
<tr>
<td>O$_2$</td>
<td>999991.78</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The calibration standards were prepared in aluminium cylinders with Aculife IV treatment, $V=5$ L. Preparation of the calibration standards was carried out in 4 stages.

1 stage:
Preparation of the first gas pre-mixtures N$_2$O/N$_2$ with N$_2$O mole fraction of $\approx 1.2$ %.
Verification of mole fraction was carried out by “Lambda 900” (“Perkin Elmer”, USA) spectrophotometer with gas cell. Relative standard deviation for each measurement series was not more than 0.05 %.

2 stage:
Preparation of the second gas pre-mixtures N$_2$O/N$_2$ with N$_2$O mole fraction of $\approx 220$ ppm.
Verification of mole fraction was carried out by FTIR analyzer “FSM-1201” (“Monitoring Ltd”, Russia). Relative standard deviation for each measurement series was not more than 0.2 %.

3 stage:
Preparation of the third gas pre-mixtures N$_2$O/N$_2$ with N$_2$O mole fraction of $\approx 8$ ppm.
Verification of mole fraction was carried out by gas chromatograph “Crystal-5000.2” (“Chromatec”, Russia) with ECD. Relative standard deviation for each measurement series was not more than 0.2 %.

4 stage:
Preparation of the calibration gas mixtures N$_2$O/N$_2$ with N$_2$O mole fraction of $\approx 320$ ppb.
There were prepared 3 standard gas mixtures.
Verification of mole fraction was carried out by gas chromatograph “Crystal-5000.2” (“Chromatec”, Russia) with ECD. Standard deviation for each measurement series was not more than 0.3 %.

Weighing was performed on the balances 81-V-HCE-20kg (Hum-Voland, USA). Experimental standard deviation for 5 L cylinders: 8 mg.

Protocol: CCQM-K68 N$_2$O 320 nmol/mol in synthetic air
Instrument calibration

The characteristics of the calibration standards are shown in Table 2.

Table 2 – Characteristics of calibration standards

<table>
<thead>
<tr>
<th>Standard gas mixture N</th>
<th>Component</th>
<th>Assigned value, $10^3 \text{ mol/mol}$</th>
<th>Standard uncertainty (gravimetry), $10^3 \text{ mol/mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$O</td>
<td>320.29</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>air balance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>N$_2$O</td>
<td>321.59</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>air balance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N$_2$O</td>
<td>330.69</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>air balance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Linear regression by 3 calibration points (3 standard gas mixtures) was used for instrument calibration.

There were made 4 independent measurements under repeatability conditions with 4 independent calibrations. One single measurement consisted of 4 sub-measurements.

Sample handling

Prior to measurements the cylinder was stabilized to room temperature.

Evaluation of uncertainty of measurements

Total standard uncertainty of nitrous oxide mole fraction was calculated on the base of the following constituents:
- total standard uncertainty of nitrous oxide fraction in standard gas mixture (including uncertainty of weighing of parent gases and pre-mixtures, uncertainty of the purity of the parent gases);
- standard deviation of linear regression;
- standard deviation of the measurement result of nitrous oxide mole fraction in the investigated gas mixture in cylinder № ME5563.

Uncertainty budget for nitrous oxide mole fraction in gas mixture in the cylinder № ME5563 is shown in the Table 3.

Table 3 – Uncertainty budget for nitrous oxide mole fraction in gas mixture in cylinder № ME5563

<table>
<thead>
<tr>
<th>№</th>
<th>Source of uncertainty</th>
<th>Type of evaluation</th>
<th>Standard uncertainty, % relative</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Preparation of the calibration gas mixtures</td>
<td>A,B</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>Standard uncertainty of calibration</td>
<td>A</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>Standard deviation of measurement result</td>
<td>A</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Combined standard uncertainty</td>
<td></td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>Expanded uncertainty</td>
<td></td>
<td>0.76</td>
</tr>
</tbody>
</table>

Protocol: CCQM-K68 N$_2$O 320 nmol/mol in synthetic air
Report Form CCQM-K68 Nitrous oxide in synthetic air

Laboratory name: NOAA-ESRL

Cylinder number: ME5572

---

Report Form CCQM-K68: Nitrous Oxide in Synthetic Air

Laboratory: NOAA Earth System Research Lab, Boulder, Colorado USA
Cylinder Number: ME5572

Measurement #1:
Date: Nov. 10, 2008
Result: 319.38 nmol mol⁻¹
Std. Dev.: 0.022%
No. Replicates: 14

Measurement #2:
Date: Nov. 18, 2008
Result: 319.47 nmol mol⁻¹
Std. Dev.: 0.031%
No. Replicates: 14

Measurement #3:
Date: Dec. 29, 2008
Result: 319.33 nmol mol⁻¹
Std. Dev.: 0.025%
No. Replicates: 14

---

Final Result:
Result: 319.39 nmol mol⁻¹ (ppb)
Std. Dev.: 0.022%
Expanded Unc.¹: -1.06 ppb, +1.01 ppb (-0.33%, +0.32%)
Coverage Factor: 2
Reproducibility²: 0.18 ppb

¹See text.
²A critical parameter for atmospheric measurement is reproducibility, or the 95% C.L. on measurements performed over the long term. Based on repeated analysis of tertiary standards (natural air), we estimate our reproducibility to be 2×0.09 = 0.18 ppb. The WMO/GAW target is 0.1 ppb.

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Reference Method:

N₂O analysis is performed by gas chromatography with electron capture detection. We use an Agilent 6890 GC with an anode-purged ECD (model G1533A). A 9-ml sample of air is injected onto a 3/16"x 1-m Porapak Q pre-column held at 90 deg C. The O₂/N₂ peak is vented and not allowed to reach the ECD. Then the valve is switched and the N₂O/SF₆ peaks are transferred to a 3/16"x 2-m Porapak Q main column (90 °C) and then to a 1/8”x 1-m molecular sieve 5Å column (185 °C). Upon the valve switch, unwanted compounds are “backflushed” off the pre-column.

CO₂-doped nitrogen is used as the carrier gas. The CO₂ is added following the molecular sieve 5Å column upstream of the ECD. Pure CO₂ is added at a flowrate of approx. 0.1 cm³/min. The carrier gas flowrate is 40 cm³/min and the ECD temperature is 340 °C. N₂O elutes at ~410 seconds. The run time is 12 minutes.

The system is controlled by custom software on the Linux operating system. A custom integration packaged developed by P. Salameh at Scripps Institution of Oceanography is used for peak integration.

Calibration standards

The NOAA-2006 N₂O scale has been described by Hall et al. (2007). Briefly, reagent grade N₂O (99.9%) was diluted by gravimetric methods into four 5.9-L aluminum cylinders (1460-2350 ppm). The purity of the N₂O was tested using GC-MS. No significant impurities were found at levels greater than 0.1%. Aliquots of each ppm-level standard were then added gravimetrically to evacuated aluminum cylinders and diluted to ppb-level. All ppb-level standards also contain SF₆ and CO₂ at near-ambient levels. The dilution gas consists of commercially available ultra-pure air (synthetic O₂/N₂ blend). The molecular weight of the dilution air was determined by measuring the O₂ content relative to natural air. The dilution gas typically contains less than 0.3 ppb N₂O. The dilution gas was further scrubbed using activated charcoal and molecular sieve at -78 °C. Grab samples of the dilution gas were taken during the dilution process. The grab samples contained between 0.1 and 0.5 ppb. Because there was not a
consistent measure of N₂O in the grab samples throughout the transfer process, we have not attempted to correct the gravimetric assignments for N₂O in the dilution gas. The upper limit for a possible bias in the NOAA-2006 scale is estimated to be 0.5 ppb (meaning that one or more standards could contain as much as 0.5 ppb N₂O more than specified).

The gravimetric uncertainty of the standards (based only on weighing uncertainties) varies from 0.10-0.48%. Newer standards have lower uncertainties than older standards. The scale is defined in terms of dry air mole-fraction and covers a range of 261 - 371 nmol mol⁻¹ (ppb) N₂O.

The scale is defined by the response ratio of 13 gravimetric standards to a particular working standard (natural air) on a particular GC. The data were fit by a 2nd order polynomial using orthogonal distance regression. Each standard was then assigned a value based on the polynomial. The standards are consistent to within 0.33 ppb (one standard of the residuals from the polynomial fit). There is no relationship between the residuals and the parent standards. There is also no relationship between the residuals and CO₂ concentration, which suggests that CO₂ does not interfere with the N₂O analysis at typical ambient CO₂ levels.

**Instrument Calibration**

The gravimetric standards were used to generate a calibration curve (2nd order polynomial). Five secondary standards containing modified natural air (262-347 ppb N₂O) were compared to the working standard and values assigned. The working standard is regularly compared to the secondary standards (~ once per month). The secondary standards form the basis for maintaining instrument calibration. The gravimetric standards are analyzed once each year.

Samples are run in ABABA... mode in which A is the working standard and B is the unknown. Working standards consist of dried continental background natural air stored in aluminum cylinders. Each working standard is used for approximately 2 years. The sample loop is flushed at 100 cm³/min for 2.5 minutes prior to injection. Injection is performed at room temperature and pressure. It is assumed room temperature and pressure vary slowly with respect to the frequency of standard injections. All samples (unknowns and working standards) are passed through a 3-ml Mg(ClO₄)₂ scrubber to remove water vapor.

A typical run consists of 8 injections of the unknown, each bracketed by working standard. This is repeated on consecutive days and the average of 14-16 injections (peak area) is used to determine the concentration according the calibration curve.

**Sample handling**

Cylinder #ME5572 was connected to a stainless steel pressure regulator using the adapter fitting provided. The regulator was flushed 10 times and allowed to equilibrate at low pressure overnight. The regulator was then flushed 10 times prior to analysis. Samples were transferred to the instrument using 1/16" stainless steel tubing.

Protocol: CCQM-K68 N₂O 320 nmol/mol in synthetic air
Uncertainties

We calculate expanded uncertainty as follows: Even though some of our standards have uncertainties as high as 0.48%, all ppb-level gravimetric standards agree to within 0.33 ppb (1 s.d. of residuals). Thus analysis reveals that the standards are closer in agreement than the combination of random weighing errors would suggest. We multiply this 0.33 ppb uncertainty by 2 to account for all random errors. For bias errors we consider three sources: (1) N\textsubscript{2}O in the dilution gas, (2) impurities in the N\textsubscript{2}O starting material, and (2) a difference in assigned values based on using peak area or height.

(1) Although it is considered unlikely, we cannot rule out the possibility that a critical standard at near-ambient concentration is biased due to N\textsubscript{2}O in the dilution air. The largest amount of N\textsubscript{2}O measured in the dilution gas was 0.5 ppb. The error introduced by having a small number of standards underestimated by 0.5 ppb N\textsubscript{2}O was estimated by recalculating assigned values with 0.5 ppb added to standards at random. An upper limit of 0.35 ppb was estimated.

(2) The purity of the N\textsubscript{2}O source gas is listed as 99.9%. We did not correct for purity and assumed 100%. If this N\textsubscript{2}O were indeed 99.9%, our scale would be 0.1% too high.

(3) There is a consistent difference in assigned values using peak area and peak height. Using peak height results in concentrations that are 0.05-0.1 ppb lower.

Thus, we include 0.35 ppb as a possible negative bias due to impure dilution gas, a 0.1% potential positive bias due to uncertainties in the purity of the starting material, and a 0.08 ppb potential positive bias because we use peak area instead of height. Our expanded uncertainties are estimated to be −(2\times0.33+0.001\times X+0.08) = -1.06 ppb, and + (2\times0.33+0.35) = 1.01 ppb, where X is the measured concentration.

Annex 3. – CCQM-P131 Report

Report Form CCQM-K68 Nitrous oxide in synthetic air

Laboratory name: WCC-N₂O (WMO/GAW World Calibration Centre for Nitrous Oxide)
Cylinder number: ME 5529

### Measurement #1

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>31/10/08</td>
<td>320.52</td>
<td>0.058</td>
<td>9</td>
</tr>
</tbody>
</table>

### Measurement #2

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>03/11/08</td>
<td>320.66</td>
<td>0.070</td>
<td>14</td>
</tr>
</tbody>
</table>

### Measurement #3

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>05/11/08</td>
<td>320.77</td>
<td>0.062</td>
<td>14</td>
</tr>
</tbody>
</table>

### Measurement #4

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>17/11/08</td>
<td>320.67</td>
<td>0.042</td>
<td>14</td>
</tr>
</tbody>
</table>

### Measurement #5

<table>
<thead>
<tr>
<th>Component</th>
<th>Date (dd/mm/yy)</th>
<th>Result (nmol/mol)</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>19/11/08</td>
<td>320.54</td>
<td>0.064</td>
<td>14</td>
</tr>
</tbody>
</table>

---

1 If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary.
**Results**

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (nmol/mol)</th>
<th>Expanded Uncertainty (analysis statistics only)</th>
<th>Coverage factor$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>320.64</td>
<td>0.05</td>
<td>2</td>
</tr>
</tbody>
</table>

The overall uncertainty of the result \(u_{\text{meas}}\) is determined using the following equation:

\[
u_{\text{meas}} = 2 \sqrt{\left(\frac{u_{\text{sample}}}{\text{standard}}\right)^2 + u_{\text{standard( propagation)}} + u_{\text{standard(calibration)}}} = 0.1 + 0.18 +1.06 = 1.34 \text{ ppb}.
\]

This corresponds to \(0.42 \%\) at 320.64 ppb.

In detail:

\(u_{\text{sample}}\) is the expanded uncertainty of the average analysis result (only based on statistics of the individual analyses), as given in the Table above.

\(u_{\text{standard( propagation)}}\) is the uncertainty of the propagation of the calibration scale as estimated by NOAA (in accordance with the NOAA report of results, first page).

\(u_{\text{standard(calibration)}}\) is the expanded uncertainty of the NOAA calibration scale (relevant for the NOAA-calibrated laboratory standards used at the WCC-N$_2$O) as determined by NOAA (see NOAA report of results, last page).

**Method Description Forms**

Please complete the following data regarding the description of the methods and the uncertainty evaluation.

**Details of the measurement method used:**

**Reference Method:**

Describe your instrument(s). (principles, make, type, configuration, data collection, and etc.)

The analytical equipment of the WCC-N$_2$O for comparisons of N$_2$O gas mixtures is based on a Varian model 3800 gas chromatographic system with electron capture detector (ECD).

Gas chromatographic parameters:

- **Oven:** 55 °C
- **Column:** HayeSep Q (80/100 mesh), 1/8" x 3 m main column
  HayeSep Q (80/100 mesh), 1/8" x 2 m backflush
- **Carrier gas:** Ar/CH$_4$ (95/5 \%)
- **ECD:** 390 °C
- **Gas sampling valve:** Valco 10-port (in separate oven at 50 °C)
- **Sample loop:** 10 mL at present (previously 5 mL)

$^5$ The coverage factor shall be based on approximately 95% confidence.
The schematic below describes details of the gas flows. Standards and unknown gas mixtures, such as the KRISS cylinder, are connected to an inlet port of the stream selection valve. Chromatograms are recorded and processed using Varian Star software.

**GC System for N₂O at ambient levels**

**Load Position**

**Inject Position**

**GC System of the WCC-N₂O**

Original design by VARIAN, Inc.
Calibration standards:

The Laboratory Standards (standards of the highest rank) of the WCC-N\textsubscript{2}O consist of a suite of seven gas mixtures of N\textsubscript{2}O in ultra-pure air stored in high-pressure aluminium cylinders. The gas mixtures were manufactured by Scott-Marrin Inc. (Riverside, CA, USA, \url{http://www.scottmarrin.com/})\textsubscript{N}2\textsubscript{O} mole fraction are ranging from 254 to 359 ppb. The cylinders are directly linked to the WMO Global Atmosphere Watch N\textsubscript{2}O scale through calibration by the Central Calibration Laboratory operated by NOAA ESRL GMD in Boulder (CO, USA).

The most recent version of the standard scale is the NOAA-2006 scale (Hall, B. D., G. S. Dutton, and J. W. Elkins (2007), The NOAA nitrous oxide standard scale for atmospheric observations, J. Geophys. Res., 112, D09305, doi:10.1029/2006JD007954). For brief information on the scale see: \url{http://www.esrl.noaa.gov/gmd/hats/standard/N2O_scale.html}. According to Hall et al. (2007), the scale can currently be propagated with an uncertainty of 0.3 ppb.

The last recalibration of the WCC-N\textsubscript{2}O cylinders dates from the February 2009 and has confirmed the previously assigned mole fractions. All mole fractions are expressed in the NOAA-2006 scale.

Instrument calibration:

For the determination of the N\textsubscript{2}O content in the KRISS cylinder \# ME 5529, two of the laboratory standards were employed: These were \#4785 with 312.42 ppb N\textsubscript{2}O, and \#4800 with 325.95 ppb N\textsubscript{2}O. Based on a 2-level calibration with these standards (here denoted s\textsubscript{1} and s\textsubscript{2}), the mole fractions of the unknown sample (u) were calculated from linear interpolation. The measurement sequence was s\textsubscript{1}/s\textsubscript{1}/s\textsubscript{2}/s\textsubscript{2}/u/u/s\textsubscript{1}/s\textsubscript{1}/s\textsubscript{2}/s\textsubscript{2}/u ... Peak areas were averaged over four bracketing analyses of the s\textsubscript{1} and s\textsubscript{2} standards, respectively, with the average value at the time of the analysis of the unknown sample being used for the mole fraction calculation. Each analysis run took 10 min.

Sample handling:

One day after arrival of the cylinder, it was unpacked from its wooden box and a pressure regulator (stainless steel) was connected. After flushing the regulator five times, it was left under pressure during one day for conditioning (stabilization). Before an analysis sequence was started, the regulator was flushed again three time. After that it was connected to a sample inlet of the SSV (see schematic above). Due to a slight overpressure, the sample loop was flushed and filled when the respective magnetic valve (Event 2) was open. The flow was stabilized by the mass flow controller at the outlet. 15 sec before switching the gas sampling valve, the flow was stopped to allow for pressure equilibration in the sample loop. All steps of the analysis were fully automated by PC control.
Result of CCQM-P131

Results of IMK-IFU (WMO WCC laboratory) in the Pilot Study CCQM-P131

Author:
H.E. Scheel, Forschungszentrum Karlsruhe, IMK-IFU, Kreuzeckbahnstr. 19, 82467 Garmisch-Partenkirchen, Germany

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Cylinder</th>
<th>( x_{\text{prep}} )</th>
<th>( u_{\text{ref}} )</th>
<th>( x_{\text{lab}} )</th>
<th>( u_{\text{lab}} )</th>
<th>( D_k )</th>
<th>( U(D_k) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMK-IFU</td>
<td>ME5529</td>
<td>319.88</td>
<td>0.24</td>
<td>320.64</td>
<td>0.67</td>
<td>0.76</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure - Relative deviation from the reference value
In CCQM-K68 and CCQM-P131