Accuracy requirements for interchangeability of gas standards for greenhouse gas and precursor atmospheric monitoring

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HIGHGAS Stakeholder Workshop,
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Bureau International des Poids et Mesures (BIPM)

The International Bureau of Weights and Measures

- Intergovernmental organization with 56 Member States and 41 Associate States/economies, Established in 1875 to:
  ... ensure and promote the global comparability of measurements, including providing a coherent international system of units for:

  - **Scientific discovery and innovation,**
  - **Industrial manufacturing and international trade,**
  - **Sustaining the quality of life and the global environment.**

5 scientific departments:
- Chemistry
- Electricity
- Ionizing Radiation
- Mass
- Time
CIPM Mutual Recognition Arrangement

Definition

Realization

Comparisons

Dissemination
# International Gas Standard Comparisons coordinated by the BIPM Chemistry Department

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Description</th>
<th>Nominal mole fraction</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCQM-P28</td>
<td>Ozone (ground-level)</td>
<td>80 nmol/mol; 400 nmol/mol</td>
<td>2003</td>
</tr>
<tr>
<td>CCQM-P73</td>
<td>Nitrogen Monoxide</td>
<td>50 µmol/mol</td>
<td>2006</td>
</tr>
<tr>
<td>BIPM.QM-K1</td>
<td>Ozone (ground-level)</td>
<td>80 nmol/mol; 400 nmol/mol</td>
<td>2007</td>
</tr>
<tr>
<td>CCQM-K74</td>
<td>Nitrogen Dioxide</td>
<td>10 µmol/mol</td>
<td>2009</td>
</tr>
<tr>
<td>CCQM-P110.B1</td>
<td>Nitrogen Dioxide</td>
<td>10 µmol/mol</td>
<td>2009</td>
</tr>
<tr>
<td>CCQM-K82</td>
<td>Methane</td>
<td>2000 nmol/mol</td>
<td>2012</td>
</tr>
<tr>
<td>CCQM-K90</td>
<td>Formaldehyde</td>
<td>2000 nmol/mol</td>
<td>2014</td>
</tr>
<tr>
<td>CCQM-K120.a</td>
<td>Carbon dioxide</td>
<td>380 µmol/mol – 480 µmol/mol</td>
<td>2015</td>
</tr>
<tr>
<td>CCQM-K120.b</td>
<td>Carbon dioxide</td>
<td>380 µmol/mol – 800 µmol/mol</td>
<td>2015</td>
</tr>
<tr>
<td>CCQM-K68.2018</td>
<td>Nitrous oxide</td>
<td>350 nmol/mol</td>
<td>2018</td>
</tr>
</tbody>
</table>
Essential Climate Variables

<table>
<thead>
<tr>
<th>Domain</th>
<th>Essential Climate Variables</th>
</tr>
</thead>
</table>
| **Atmospheric** (over land, sea and ice) | **Surface:** Air temperature, Wind speed and direction, Water vapour, Pressure, Precipitation, Surface radiation budget.  
**Upper-air:** Temperature, Wind speed and direction, Water vapour, Cloud properties, Earth radiation budget (including solar irradiance).  
**Composition:** Carbon dioxide, Methane, and other long-lived greenhouse gases, Ozone and Aerosol, supported by their precursors. |
| **Oceanic**                  | **Surface:** Sea-surface temperature, Sea-surface salinity, Sea level, Sea state, Sea Ice, Surface current, Ocean colour, Carbon dioxide partial pressure, Ocean acidity, Phytoplankton.  
**Sub-surface:** Temperature, Salinity, Current, Nutrients, Carbon dioxide partial pressure, Ocean acidity, Oxygen, Tracers. |
| **Terrestrial**              | River discharge, Water use, Groundwater, Lakes, Snow cover, Glaciers and ice caps, Ice sheets, Permafrost, Albedo, Land cover (including vegetation type), Fraction of absorbed photosynthetically active radiation (FAPAR), Leaf area index (LAI), Above-ground biomass, Soil carbon, Fire disturbance, Soil moisture. |

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8. Including measurements at standardized, but globally varying heights in close proximity to the surface.
9. Up to the stratopause.
10. Including N₂O, CFCs, HCFCs, HFCs, SF₆ and PFCs.
11. In particular NO₂, SO₂, HCHO and CO₂.
12. Including measurements within the surface mixed layer, usually within the upper 15 m.
Target uncertainties for primary standards

<table>
<thead>
<tr>
<th>Component</th>
<th>Nominal Mole fraction</th>
<th>Primary Standard: target standard uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>400 µmol/mol</td>
<td>0.025 µmol/mol</td>
</tr>
<tr>
<td>CH₄</td>
<td>2000 nmol/mol</td>
<td>0.5 nmol/mol</td>
</tr>
<tr>
<td>N₂O</td>
<td>350 nmol/mol</td>
<td>0.025 nmol/mol</td>
</tr>
</tbody>
</table>

Based on primary standard contributing to less than 5% of measurement uncertainty for monitoring based on most stringent data compatibility requirements.
International comparison of methane in air standards (2012)

**Aims/Deliverables:**

Demonstrate the degree of equivalence of national methane in air gas standards in support of greenhouse gas monitoring *(CCQM-K82, CH₄ in air)*

Matrix: Synthetic air (N₂, O₂, Ar, CO₂)

Matrix: real air scrubbed of methane

BIPM analytical instruments under repeatability conditions

Analysis made by cavity ring down spectroscopy and gas chromatography-flame ionization detector
Accounting for potential biases in CRDS measurements

Uncertainty component included in BIPM measurement Results

Pressure broadening:

CRDS measurements and matrix gas composition

Target mole fractions:

1800±10 nmol/mol and 2200±10 nmol/mol.

Matrix composition

To minimize pressure broadening effects

<table>
<thead>
<tr>
<th>Component in Air</th>
<th>Minimum mole fraction permitted within submitted cylinder</th>
<th>Maximum mole fraction permitted within submitted cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.77849 mol/mol</td>
<td>0.78317 mol/mol</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.20776 mol/mol</td>
<td>0.21111 mol/mol</td>
</tr>
<tr>
<td>Argon</td>
<td>8.865 mmol/mol</td>
<td>9.799 mmol/mol</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>360 µmol/mol</td>
<td>400 µmol/mol</td>
</tr>
</tbody>
</table>
Comparison of GC-GID and CRDS methods for methane in air

Validation of method using NIST real air and synthetic air standards

Matrix composition adapted to minimize broadening effects
Validation of BIPM’s Measurements facility with NIST standards

\[ U(x_{\text{target}}) = \pm 1.0 \text{ nmol/mol} \]
Improvements in global compatibility of methane in air standards

Comparison results vs. Data Compatibility Goals

DQO = ± 2 nmol/mol

For CCQM-K82:

Smallest $u(x) = 0.5$ nmol/mol

$\sigma_{(CCQM-K82)} = 1.17$ nmol/mol

Negligible impact of standards when:

$u(x), \sigma_{(CCQM-Kxx)} \leq DQO/4$

$u(x), \sigma_{(CCQM-Kxx)} \leq 0.5$ nmol/mol
Development for future improvements in CH$_4$ in air standards

Accurate measurements of CH$_4$ in balance gas at 1 nmol/mol levels with $u(x) < 0.1$ nmol/mol required

Trace CH$_4$ mole fractions in balance gas as reported by participating laboratories in CCQM-K82
CCQM-K82 results accounting potential isotope ratio variation in CH$_4$

Method CRDS 2

$D_{2000}/ \text{nmol mol}^{-1}$ vs. $D_{1800}/ \text{nmol mol}^{-1}$
CCQM-K82 results including uncertainty component for potential isotope ratio variation in CH$_4$

Pure methane from natural gas:
–(43±7) ‰ for $\delta^{13}$C (VPDB);
–(185±20) ‰ for $\delta$D (VSMOW)

Bias in the CRDS:
+0.34 nmol/mol and
-0.38 nmol/mol;

Uncertainty component $u_\delta = 0.21$ nmol/mol
Preparing for the repeat ambient CO$_2$ in air key comparison (2015)

Preparation for CCQM-K120 (2015)

Coordinated by: BIPM/NIST

Agreed comparison (November 2013):

**Comparison of NMI capabilities**

**CCQM-K120.a**

CO$_2$ in air (380 µmol/mol to 480 µmol/mol)

Matrix: Scrubbed real air within 0.1% of atmospheric balance gases

**CCQM-K120.b**

CO$_2$ in air (380 µmol/mol to 800 µmol/mol)

Matrix: Air composition within 1% of atmospheric balance gases
Preparing for the repeat ambient CO$_2$ in air key comparison (2015)


Results show good agreement, but...

Uncertainties on all standards > DQO for ambient monitoring community
Measuring mole fractions of CO$_2$ isotopologues

Target relative standard uncertainty $u(x) < 0.01\%$

$1 \, \% \ \delta^{13}C = 4 \, \text{ppb}$

$1 \, \% \ \delta^{18}O = 2 \, \text{ppb}$

Region: 2085-2300 cm$^{-1}$
Preparing for the repeat ambient $\text{CO}_2$ in air key comparison (2015)

Preparation for CCQM-K120 (2015)

Coordinated by: BIPM/NIST

BIPM comparison facilities

Isotope ratio measurements for corrections to $\text{CO}_2$ concentration measurements required at the $\pm 1$‰ level.
Preparing for the repeat ambient CO$_2$ in air key comparison (2015)

- Optimized volumes and wall thicknesses for pressure measurements
- Automated system for cryogens
- Residual Gas Analyser for monitoring efficiency of cryogenic steps

\[
x_{CO_2} = \frac{P_{CO_2}}{P_{air}} \frac{V_a}{V_{tot}} \left( 1 + \frac{B_{air} (T_{air}) P_{air}}{RT_{air}} \right) \left( 1 + \frac{B_{CO_2} (T_{CO_2}) P_{CO_2}}{RT_{CO_2}} \right)
\]
Preparing for the repeat ambient CO\textsubscript{2} in air key comparison (2015)

Preparation for CCQM-K120 (2015)
BIPM comparison facilities

Coordinated by: BIPM/NIST

Manometric System for CO\textsubscript{2}

Volume ratio in system
1:1000

Mole fraction ratios (CO\textsubscript{2}: air)
1:2500 to 1:1000

\[
\chi_{CO_2} = \frac{P_{CO_2}}{P_{air}} \frac{V_a}{V_{tot}} \left( \frac{T_{air}}{T_{CO_2}} \left( 1 + \frac{B_{air} \left( T_{air} \right) P_{air}}{RT_{air}} \right) \right) \left( 1 + \frac{B_{CO_2} \left( T_{CO_2} \right) P_{CO_2}}{RT_{CO_2}} \right)
\]
### Preparation of Validation Standards (Mole fraction)

<table>
<thead>
<tr>
<th>CO$_2$ Mole Fraction</th>
<th>CH$_4$ Mole Fraction</th>
<th>N$_2$O mole fraction</th>
<th>Balance Gas*</th>
</tr>
</thead>
<tbody>
<tr>
<td>380 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>400 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>425 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>450 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>500 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>650 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
<tr>
<td>800 ppm</td>
<td>1850 ppb</td>
<td>&lt; 1ppb</td>
<td>Cryogenic Ultra-Pure Air</td>
</tr>
</tbody>
</table>

| 380 ppm              | 1850 ppb             | 325 ppb              | Cryogenic Ultra-Pure Air |
| 400 ppm              | 1850 ppb             | 325 ppb              | Cryogenic Ultra-Pure Air |
| 425 ppm              | 1850 ppb             | 325 ppb              | Cryogenic Ultra-Pure Air |

**Standards prepared: October 2013; Value assigned by NIST July 2014;**

**Subset sent to MPI BGC JENA for isotope ratio measurement (August 2014)**
Validation standards with a range of isotopic compositions

Selected pure CO₂ sources to span δ¹³C in set of gravimetric standards

- **Clean Air, Niwot Ridge, USA**: ~ -8 ‰
- **Isotopic mixing, NPL, UK**: ~ -8 ‰
- **Natural gas well, Greece**: -7 ‰ to -2 ‰
- **Fermentation, France**: -20 ‰ to -10 ‰
- **Clean Air, New Zealand**: ~ -8 ‰
- **CH₄ combustion, Morocco**: ~ -40 ‰
- **CO₂/air by gravimetry, NPL**: δ¹³C assigned
- **δ¹³C – VPDB by IRMS**: assigned
### IAEA-BIPM Collaboration
### IAEA Workshop on Stable Isotopes (3-5 Sept 2014)

<table>
<thead>
<tr>
<th>Organization</th>
<th>Quantity and types of standard</th>
<th>Calibrated/Measurement Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA</td>
<td>$\delta^{13}C$, $\delta^{18}O$ Carbonates</td>
<td>Mass Spec.</td>
</tr>
<tr>
<td>Max Planck Institute for Biogeochemistry</td>
<td>$\delta^{13}C$, $\delta^{18}O$ CO$_2$ from carbonates in real air</td>
<td>Mass Spec.</td>
</tr>
<tr>
<td>Bureau International des Poids et Mesures</td>
<td>CO$_2$ mole fraction ($\delta^{13}C$, $\delta^{18}O$) CCQM-K120</td>
<td>Optical Spectroscopic methods</td>
</tr>
</tbody>
</table>

- **Carbonates**
- **Pure CO$_2$**
- **CO$_2$ from carbonates in real air**
- **CO$_2$ mole fraction ($\delta^{13}C$, $\delta^{18}O$) CCQM-K120**
- **CO$_2$ in real/synthetic air**
- **Optical Spectroscopic methods**

**Calibrated/Measurement Instrument**

- Mass Spec.
Comparisons of CO$_2$ standards with FTIR

Under repeatability conditions with $u(x_{\text{FTIR}}) = 0.015 \, \mu\text{mol/mol}$
Acknowledgements

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