**COOMET TECHNICAL COMMITTEE 1.8**

**“PHYSICAL CHEMISTRY”**

**Protocol for the Key Comparison:**

**COOMET.QM‐K120.b (COOMET project № 772/RU/18)**

**Carbon dioxide in Air at urban level (480‐800) µmol/mol**

- December 2018 -

## 1 Background

COOMET key comparison COOMET.QM-K120.b is designed as linking to the appropriate CCQM comparison - CCQM-K120.b (2016-2018, Flores et al. 2018, [1]) and is intended to support CMCs of National Metrological Institutes of the countries – mainly members of COOMET.

The CCQM‐K120.b was a gravimetric comparison which evaluated the level of compatibility of NMI preparative capabilities for carbon dioxide in air primary reference mixtures in the range (480‐800) µmol/mol.

CCQM-K120.b is considered as a Track A comparison and tests core skills and competencies required in gravimetric preparation, analytical certification and purity analysis. Participants succesful in CCQM-K120.b and the linked COOMET.QM-K120.b comparison may use their results in the flexible scheme and underpin claims for all core mixtures in accordance with the GAWG strategy document [2].

# 2 Carbon dioxide mixtures and Air Matrix

Each participant will be asked to submit two high pressure cylinder standards at the nominal mole fraction of 480 µmol/mol and other at the mole fraction 800 µmol/mol. The mole fraction of carbon dioxide shall be within ± 10 µmol/mol of the nominal mole fractions of the cylinders.

The CO2 mole fractions and limit values for the composition of the air matrix for standards to be prepared by participating NMIs are listed in the Table 1.

The carbon dioxide shall be produced in a dry air matrix, which can be produced from scrubbed real air or synthetic air that has been blended from pure gases that are the main constituents of air (nitrogen, oxygen, argon) and that can contain the other two major greenhouse gases (nitrous oxide and methane).

Table 1:CCQM‐K120.b Matrix gas composition limits (480 µmol/mol and 800 µmol/mol CO2 in air)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Species | ‘Ambient’  level mole fraction | Unit | Min mole fraction | Unit | Max mole fraction | Unit |
| N2 | 0.780876 | mol/mol | 0.7789 | mol/mol | 0.7829 | mol/mol |
| O2 | 0.2093335 | mol/mol | 0.2073 | mol/mol | 0.2113 | mol/mol |
| Ar | 0.0093332 | mol/mol | 0.0078 | mol/mol | 0.0108 | mol/mol |
| CH4 | 1900 | nmol/mol | 0 | nmol/mol | 1900 | nmol/mol |
| N2O | 330 | nmol/mol | 0 | nmol/mol | 330 | nmol/mol |

The tolerance limits for air composition have been chosen to ensure that any biases arising from matrix composition variation and its effect on pressure broadening of CO2 lines and their quantification is smaller 0.1 µmol/mol for CCQM‐K120.b (for further details see Nara et al. [3] and Flores et al. [1])

The cylinders will be submitted together with the following information:

In the case of standards produced with synthetic air:

* CO2 mole fraction and uncertainty for the submitted standards
* composition of the matrix gas in the submitted standards with mole fraction values of the components and their uncertainties
* a purity table with uncertainties for the nominally pure CO2 parent gas;
* a purity table with uncertainties for the nominally pure N2, O2, Ar, parent gas (and any other parent gas if relevant);
* a brief outline of the dilution series undertaken to produce the final mixtures;
* a brief outline of the verification procedure applied to the final mixtures;
* a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to VNIIM;
* isotope ratios of the CO2 (if known).

In the case of standards produced with scrubbed ‘real’ air:

* CO2 mole fraction and uncertainty for the submitted standards
* composition of the matrix gas in the submitted standards with mole fraction values of the components and their uncertainties
* a purity table with uncertainties for the nominally pure CO2 parent gas;
* results of the analysis and mole fractions and uncertainties of CO2, N2, O2, Ar, N2O and CH4 in the scrubbed real air (if performed);
* a brief outline of the preparation procedure of the final mixtures;
* a composition table for each of the final mixtures, including gravimetric uncertainties when relevant;
* a brief outline of the verification procedure applied to the final mixtures;
* a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to VNIIM;
* isotope ratios of the CO2 (if known).

Pressure in cylinders, before shipping to coordinating laboratory should be not less than 9 MPa as VNIIM analysis will use at maximum 150 L of gas.

**3 Comparison procedure**

The standards are to be sent to VNIIM where the comparison measurements will be performed. The prepared gas mixtures should be tested for stability by participants before shipping to VNIIM and after their return.

Measurements at VNIIM will be performed by Cavity ring-down spectroscopy (CRDS).

The reference value for a given gas standard will be set by the pilot laboratory by measurements against VNIIM primary reference gas mixtures.

After analysis the cylinders will be shipped back to the participants.

Transport of the cylinders from and back to the participants will be paid by the participating laboratories.

**4 Timetable**

|  |  |
| --- | --- |
| **1st Stage** |  |
| December 2018 | Draft protocol distributed to potential participants. |
| January 2019 – May 2019 | The participating laboratories prepare the mixtures and carry out their verification and stability tests. |
| **2nd Stage** |  |
| June 2019 | Shipment of cylinders to VNIIM (to arrive by 1 of July) |
| July 2019‐ October 2019 | Analysis of mixtures in VNIIM |
| November 2019 | Shipment of cylinders from VNIIM to participants |
| **3th Stage** |  |
| December 2019‐ March 2020 | Analysis of mixtures by the participants |
| March 2020 | Reports on stability оf standards to VNIIM |
| **4th Stage** |  |
| June 2020 | Report Draft A |

References:

[1] Edgar Flores, Joële Viallon et al. CCQM-K120 (Carbon dioxide at background and urban level). [Metrologia](https://iopscience.iop.org/journal/0026-1394), [V 56](https://iopscience.iop.org/volume/0026-1394/56), [N 1A](https://iopscience.iop.org/issue/0026-1394/56/1A).

[2] Brewer PJ, van der Veen AMH. GAWG strategy for comparisons and CMC claims, CCQM Gas Analysis Working Group, (2016).

[3] Nara, H.; H. Tanimoto; Y. Tohjima; H. Mukai; Y. Nojiri; K. Katsumata; C. W. Rella. Atmos. Meas. Tech.2012, 5(11): 2689‐2701.

**Report form COOMET.QM‐K120.b**

**A1. General information**

|  |  |
| --- | --- |
| Institute |  |
| Address |  |
| Contact person |  |
| Telephone |  |
| Email\* |  |

**A2. NMI submitted values. Carbon dioxide mole fraction**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Cylinder Identification number | Carbon dioxide mole fraction  x CO2,cert  μmol/mol | Expanded uncertainty  U (x CO2,cert)  μmol/mol | Coverage factor |
| 1 |  |  |  |  |
| 2 |  |  |  |  |

**A3. NMI submitted values**

**Matrix compositions (for each standard submitted):**

(Standard 1) Cylinder Identification Number:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Component | Mole fraction Value | Unit | Expanded  Uncertainty | Unit | Coverage  Factor |
| N2 |  | mol/mol |  | mol/mol |  |
| O2 |  | mol/mol |  | mol/mol |  |
| Ar |  | mol/mol |  | mol/mol |  |
| CH4 |  | nmol/mol |  | nmol/mol |  |
| N2O |  | nmol/mol |  | nmol/mol |  |
|  |  |  |  |  |  |
|  |  |  |  |  |  |
|  |  |  |  |  |  |

(Standard 2) Cylinder Identification Number:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Component | Mole fraction Value | Unit | Expanded  Uncertainty | Unit | Coverage  Factor |
| N2 |  | mol/mol |  | mol/mol |  |
| O2 |  | mol/mol |  | mol/mol |  |
| Ar |  | mol/mol |  | mol/mol |  |
| CH4 |  | nmol/mol |  | nmol/mol |  |
| N2O |  | nmol/mol |  | nmol/mol |  |
|  |  |  |  |  |  |
|  |  |  |  |  |  |
|  |  |  |  |  |  |

**CO2 isotope ratio (vs. VPDB) for each standard submitted (Optional):**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Cylinder  Identification Number | δ13C | *U*(δ13C) | Coverage Factor | δ18O | *U*(δ18O) | Coverage Factor |
| 1 |  |  |  |  |  |  |  |
| 2 |  |  |  |  |  |  |  |
| 3 |  |  |  |  |  |  |  |

### A4. Uncertainty Budget

Please provide a complete uncertainty budgets for the CO2 mole fraction values reported

### A5. Additional information

Please include in this section in the case of standards produced with synthetic air:

1. a purity table with uncertainties for the nominally pure CO2 parent gas;
2. a purity table with uncertainties for the nominally pure N2, O2, Ar, NO2 and CH4 parent gas;
3. a brief outline of the dilution series undertaken to produce the final mixtures;
4. a brief outline of the verification procedure applied to the final mixtures;
5. a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to VNIIM; and
6. cylinder pressure before shipment to VNIIM

or, with real air:

1. a purity table with uncertainties for the nominally pure CO2 parent gas;
2. results of the analysis and mole fractions and uncertainties of CO2, N2,O2,Ar, N2O and CH4 in the scrubbed real air (if performed);
3. a brief outline of the preparation procedure of the final mixtures;
4. a composition table for each of the final mixtures, including gravimetric uncertainties when relevant;
5. a brief outline of the verification procedure applied to the final mixtures;
6. a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to VNIIM; and
7. cylinder pressure before shipment to VNIIM