Global Activities in Gas Metrology
- For Clean Air -

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KRISS
Gas Analysis Working Group (GAWG)

Terms of Reference

1. To establish global comparability of measurements through promoting traceability to the SI
2. To contribute to the implementation and maintenance of the CIPM MRA in gas measurements
1. To carry out **Key Comparisons** to evaluate claimed competences for standards and capabilities for;
   - gas composition
   - nanoparticle and aerosol concentration
   - isotope ratio measurement
   - concentration of dissolved gases in liquid or solid

2. To assist in identifying and establishing inter-laboratory work, pilot studies and research activities to improve the SI traceability of new measurement technologies in gas analysis
Stakeholders of GAWG

- Government
- Health and Energy Sector
- Specialty Gas Manufacturers
- Calibration Laboratories
- Industries in need of the service covered by GAWG
- International body; WMO, IAEA, IUPAC

1. Environmental monitoring: CO, NOx, SOx, Ozone, Particulates
   Emission level: Automobile emission, VOCs, HCHO, H₂S, NH₃
2. Climate change monitoring (CO₂, CH₄, N₂O, CFCs, HFCs, SF₆)
1. GAWG Activity on Environmental Monitoring

- At early stage, GAWG conducted KCs related to Environmental Monitoring gas mixtures such as CO, NO, SO$_2$.
- Comparability of Gravimetric preparation
- Cylinder selection and treatment
- Purity and Zero gas assessment
CCQM-K1a (1995)

- Coordinating Lab: VSL
- Substance: 100 µmol/mol CO in Nitrogen

Red diamonds: participants in CCQM-K1.a
Blue squares: participants in COOMET.QM-K1.a
International comparison

CCQM-K1c (1996)

- Coordinating Lab: VSL
- Substance: 100 µmol/mol NO in Nitrogen

Red diamonds: participants in CCQM-K1.c
Green triangles: participants in EUROMET.QM-K1.c
Blue circles: participants in APMP.QM-K1.c
International comparison

CCQM-K1d (1997)

- Coordinating Lab: VSL
- Substance: 100 µmol/mol SO₂, in Nitrogen

![Graph showing comparison results for various labs. Red diamonds represent participants in CCQM-K1.d, and blue triangles represent participants in APMP.QM-K1.d.](image)
The first key comparison of primary standard gas mixtures
A. Alink  (Metrologia, Volume 37, Number 1)

Abstract
This paper reports the results of the first key comparison of primary standard gas mixtures (PSMs), held under the auspices of the Consultative Committee for Amount of Substance (CCQM). PSMs are (national) measurement standards for the realization of specific gas mixture compositions. This key comparison, registered at the Bureau International des Poids et Mesures (BIPM) as CCQM-K1.a-g, encompasses thirteen different gas mixture compositions. In total, 125 transfer standards were prepared and distributed among ten participating institutes. The results show that joint activities in the development and maintenance of PSMs lead to a relative agreement within $10^{-2}$ of the reference values for the results of the international comparison.
Emission Reduction by Industries
- Regulation: Automobile emission, Stack emission
- VOCs, Toxic gases, Particles
CCQM-K10 (2001)  
BTX in Nitrogen  
5 nmol/mol
CCQM-K41 (2005)  

**H$_2$S in Nitrogen**  

10 µmol/mol
BIPM.QM-K1  Ozone, ambient level

24 degrees of equivalence between 2007 and 2015

( Keep in good agreement)
CCQM-GAWG Ozone Cross Section Task Group
Statistical analysis 253.65 nm O₃ cross section measurements

Current reference value

[O₃] determined by
Y: direct pressure meas
X: (gas-phase titration)
Task group on Particulate Comparison

• Members:
  Liu Junji (NIM), Paul Quincy (NPL), Andreas Nowak (PTB), Hanspeter Andres (METAS), Shankar G. Aggarwal (NPLI) and Yuri Kustikov (VNIIM)

• Strategy development:
  June 2015: kick-off at ETHZ particle conference
  Sep. 2015: first draft available to circulate

• Comparison protocols:
  Presented at GAWG meeting (April 2016)
PS sizing:
a) 2.5 / 10 µm

b) 1 – 10 nm

Draft Roadmap

size

2.5 µm
10 µm

500 nm

10 nm

2016
2018
2020
202X

PS number concentration
key/parallel PS Number & charge concentration

PS mass concentration

*PS = pilot study
CCQM.Kxxx  Particle Comparison in 2017

Comparison on number / charge concentration
Repeat of EURAMET 1224 (charge conc.); 1282 (number conc.)

- Coordination: PTB/NPL
- Host: TROPOS (WMO WCC physical aerosol measurements)

  comparison in second half of 2017
  Draft A: 2018
2. Cooperation between WMO & GAWG

- WMO designates Central Calibration Lab (CCL) for developing accurate and precise references

- NMIs establish Primary methods for accurate measurement and support CCLs
CCQM-K52 (2008)

- Coordinating Lab: VSL
- Substance: Carbon dioxide in Synthetic Air
Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale \((1.24 \% \text{ higher than before})\)

Dlugokencky, E. J. et. al., (2005), *JGR-Atmospheres*, 110
CCQM-K68 (2010)

- Coordinating Lab: KRISS
- Substance: Nitrous oxide 320 nmol/mol in Synthetic Air
CCQM-K84 Halocarbons in real air by NIST

**CFC-12**

Laboratory measurement results

- NIST
- NOAA
- KRISS
- EMPA
- SIO

**CFC-11**

Laboratory measurement results

- NIST
- NOAA
- KRISS
- EMPA
- SIO

**CFC-113**

Laboratory measurement results

- NIST
- NOAA
- KRISS
- EMPA
- SIO

**HFC-134a**

Laboratory measurement results

- NIST
- NOAA
- KRISS
- EMPA
- SIO
Results: The results indicate consistency within ± 2.0 % except two points.
Action: KCRV from results of NMIs; NIST & KRISS
All participant’s results will be Pilot Study

- Coordinating Lab: KRISS
- Substance: SF₆ & CF₄ hundred μmol/mol level
GAWG Program for Clean Air Monitoring

2012  CO by KRISS             2015  Terpenes by NIST
2016  CO$_2$ by BIPM/NIST      2016  NH$_3$ by VSL
2017  NO by BIPM               2017  H$_2$S by KRISS
2018  NO$_2$ by BIPM           2018  Automobile gases by VSL
2018  VOCs by NIST
<table>
<thead>
<tr>
<th>Reference No.</th>
<th>Description</th>
<th>Pilot (Coordinating) Laboratory</th>
<th>Expected Start date</th>
<th>Rational for Key Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIPM.QM-K1</td>
<td>KC (Ozone at ambient level)</td>
<td>BIPM / 20</td>
<td>2007 - ongoing</td>
<td>Atmospheric and air quality</td>
</tr>
<tr>
<td>CCQM-K117</td>
<td>KC (NH₃)</td>
<td>VSL&amp;NIST</td>
<td>2016</td>
<td>Atmospheric and air quality</td>
</tr>
<tr>
<td>CCQM-K118</td>
<td>KC (Natural gas)</td>
<td>VSL &amp; BAM</td>
<td>2016</td>
<td>Energy gases</td>
</tr>
<tr>
<td>CCQM-K120a</td>
<td>KC (Ambient CO₂, 380 to 480 μmol/mol)</td>
<td>BIPM with NIST</td>
<td>2016</td>
<td>Atmospheric and air quality CO₂ (380 to 480 μmol/mol) in a matrix of air</td>
</tr>
<tr>
<td>CCQM-K120b</td>
<td>KC (Ambient CO₂, 480 to 800 μmol/mol)</td>
<td>BIPM with NIST</td>
<td>2016</td>
<td>Atmospheric and air quality CO₂ (480 to 800 μmol/mol) in a matrix of air</td>
</tr>
<tr>
<td>CCQM-K137</td>
<td>Track A (NO in Nitrogen, 30-70 μmol/mol)</td>
<td>BIPM</td>
<td>2017</td>
<td>Atmospheric and air quality Repeat of CCQM-P73</td>
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<tr>
<td>CCQM-K41.2017</td>
<td>KC (H₂S in Nitrogen, 10 μmol/mol)</td>
<td>KRISS</td>
<td>2017</td>
<td>Atmospheric and air quality Repeat KC of CCQM-K41 in 2017</td>
</tr>
<tr>
<td>CCQM-KXX</td>
<td>KC(Micro-scale particles, number/charge conc)</td>
<td>PTB/NPL</td>
<td>2017</td>
<td>Atmospheric and air quality</td>
</tr>
<tr>
<td>CCQM-K74.2018</td>
<td>KC (NO₂ in Nitrogen, 10 μmol/mol)</td>
<td>BIPM</td>
<td>2018</td>
<td>Atmospheric and air quality Repeat KC of CCQM-K74 in 2018</td>
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<tr>
<td>CCQM-P172</td>
<td>PS (Spectroscopic impurity study, NO₂ in Nitrogen, 10 μmol/mol)</td>
<td>BIPM</td>
<td>2018</td>
<td>Spectroscopic study of HNO₃, NO, etc. as impurities in NO₂/Nitrogen</td>
</tr>
<tr>
<td>CCQM-K10.2018</td>
<td>BTEX 5 nmol/mol in Nitrogen</td>
<td>NIST</td>
<td>2018</td>
<td>Air Quality/New emerging requirements</td>
</tr>
<tr>
<td>CCQM-K3.2019</td>
<td>Track A (Automotive gases)</td>
<td>VSL</td>
<td>2019</td>
<td>Atmospheric and air quality, Car Emission</td>
</tr>
<tr>
<td>CCQM-K68.2019</td>
<td>KC (Ambient N₂O)</td>
<td>BIPM with KRISS</td>
<td>2019</td>
<td>Atmospheric and air quality</td>
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<tr>
<td>CCQM-PXX</td>
<td>PS (Carbon/Oxygen isotope ratios in CO₂)</td>
<td>BIPM with IAEA</td>
<td>2020</td>
<td>Atmospheric and air quality</td>
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<td>CCQM-KXX</td>
<td>Hydrogen purity</td>
<td></td>
<td>2020</td>
<td>New emerging requirements</td>
</tr>
<tr>
<td>CCQM-KXX</td>
<td>DMS ambient level (5 nmol/mol in nitrogen)</td>
<td>KRISS</td>
<td>2020</td>
<td>Atmospheric and air quality</td>
</tr>
<tr>
<td>CCQM-KXX</td>
<td>KC (Nano &amp; micro-scale particles)</td>
<td></td>
<td>2020</td>
<td>New emerging requirements</td>
</tr>
<tr>
<td>CCQM-KXX</td>
<td>Track A (SO₂)</td>
<td>NIST</td>
<td>2021</td>
<td>Atmospheric and air quality</td>
</tr>
<tr>
<td>CCQM-KXX</td>
<td>KC/PS (HCl emission level)</td>
<td>BIPM</td>
<td>2021</td>
<td>Atmospheric and air quality</td>
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<td>BIPM.QM-K2</td>
<td>KC (Ambient CO₂)</td>
<td>BIPM</td>
<td>2022</td>
<td>PVT+Spectroscopy</td>
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<tr>
<td>CCQM-KXX</td>
<td>KC (Natural gas)</td>
<td></td>
<td>2022</td>
<td>Energy gases</td>
</tr>
</tbody>
</table>
Conclusions

- Significant contributions have been made by GAWG
  - to improve **Air Quality for the Clean Air**
  - to provide **global comparability of measurements**
  - to harmonize with **international bodies**

- **International collaboration is central** to these activities and will greatly increase leverage in the future

- **Future challenges** will be focus on new emerging area
  - **reactive gases**
  - **nanoparticle and aerosol**
  - **isotope ratio measurement**
Thank you.