Standards and Measurements for Clean Air

IPQ, 14 October, 2016

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

❑ Responsibilities of GAWG

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

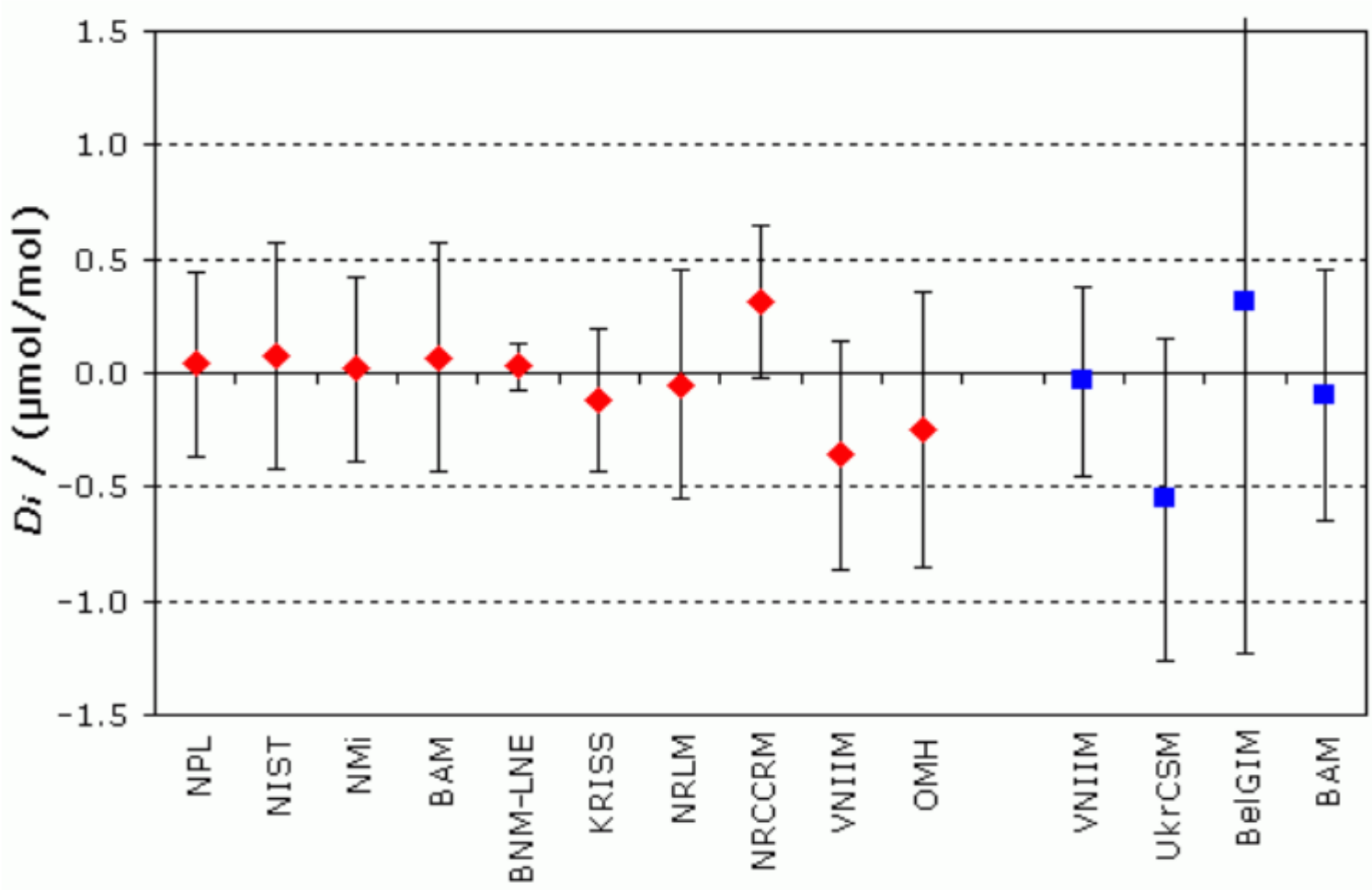
   Emission level: Automobile emission, VOCs, HCHO, H_2S, NH_3
2. Climate change monitoring (CO_2, CH_4, N_2O, CFCs, HFCs, SF_6)

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)

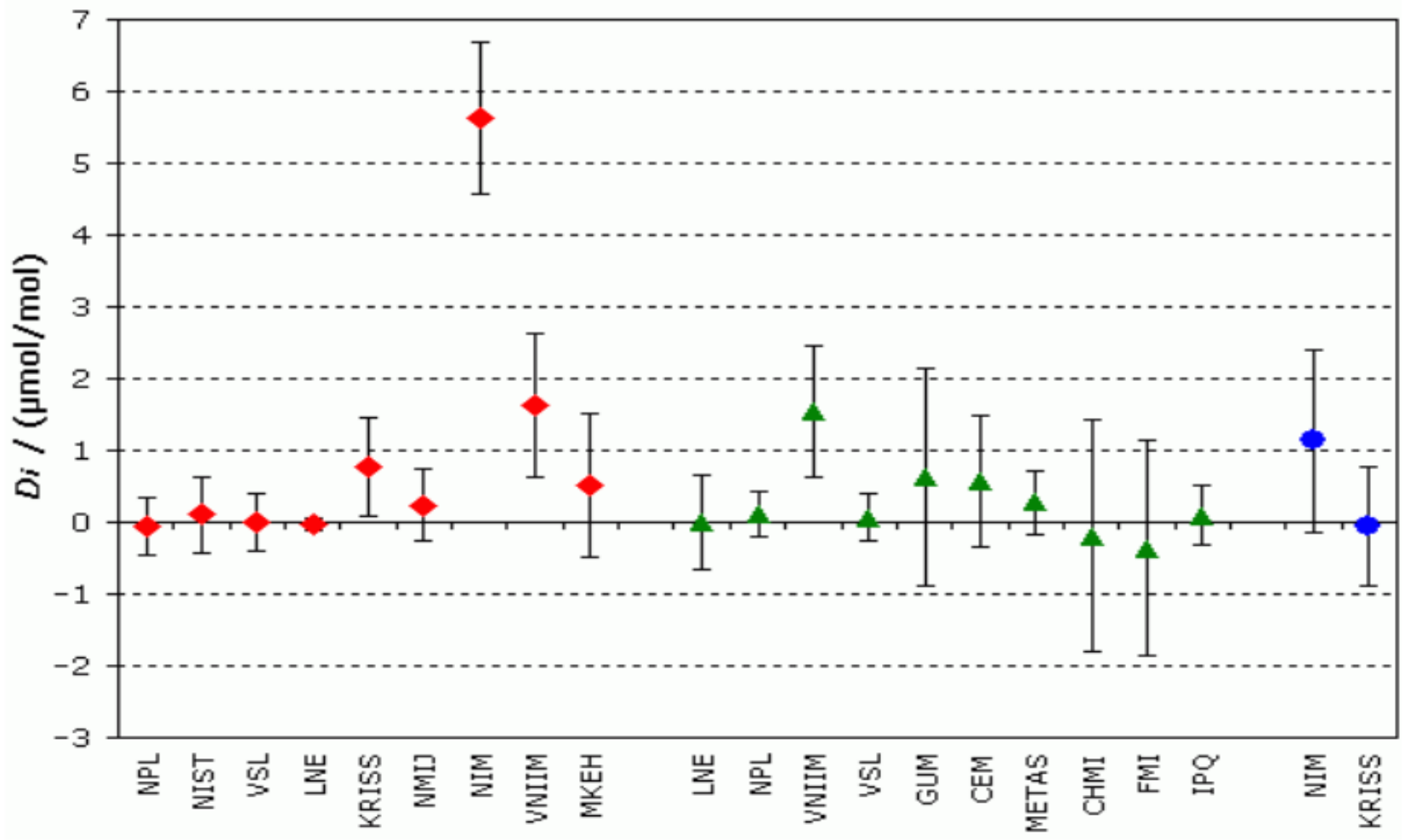
- Coordinating Lab: VSL
- Substance: **100 µmol/mol CO in Nitrogen**



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

CCQM-K1c (1996)

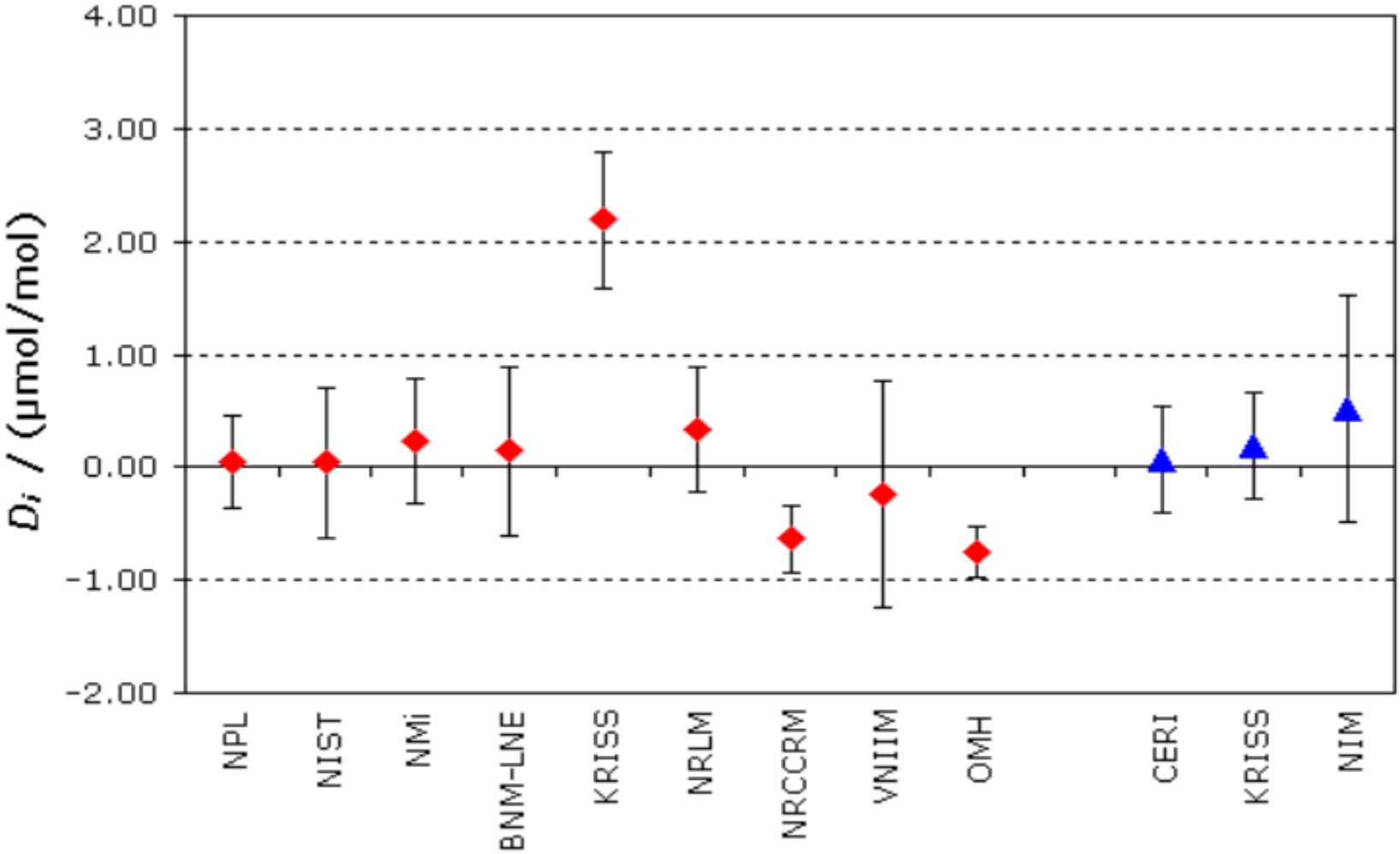
- Coordinating Lab: VSL
- Substance: **100 µmol/mol NO in Nitrogen**



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

CCQM-K1d (1997)

- Coordinating Lab: VSL
- Substance: **100 µmol/mol SO_2 in Nitrogen**



Red diamonds: participants in CCQM-K1.d
Blue triangles: participants in APMP.QM-K1.d

The first key comparison of primary standard gas mixtures

A. Alink (Metrologia, Volume 37, Number 1)

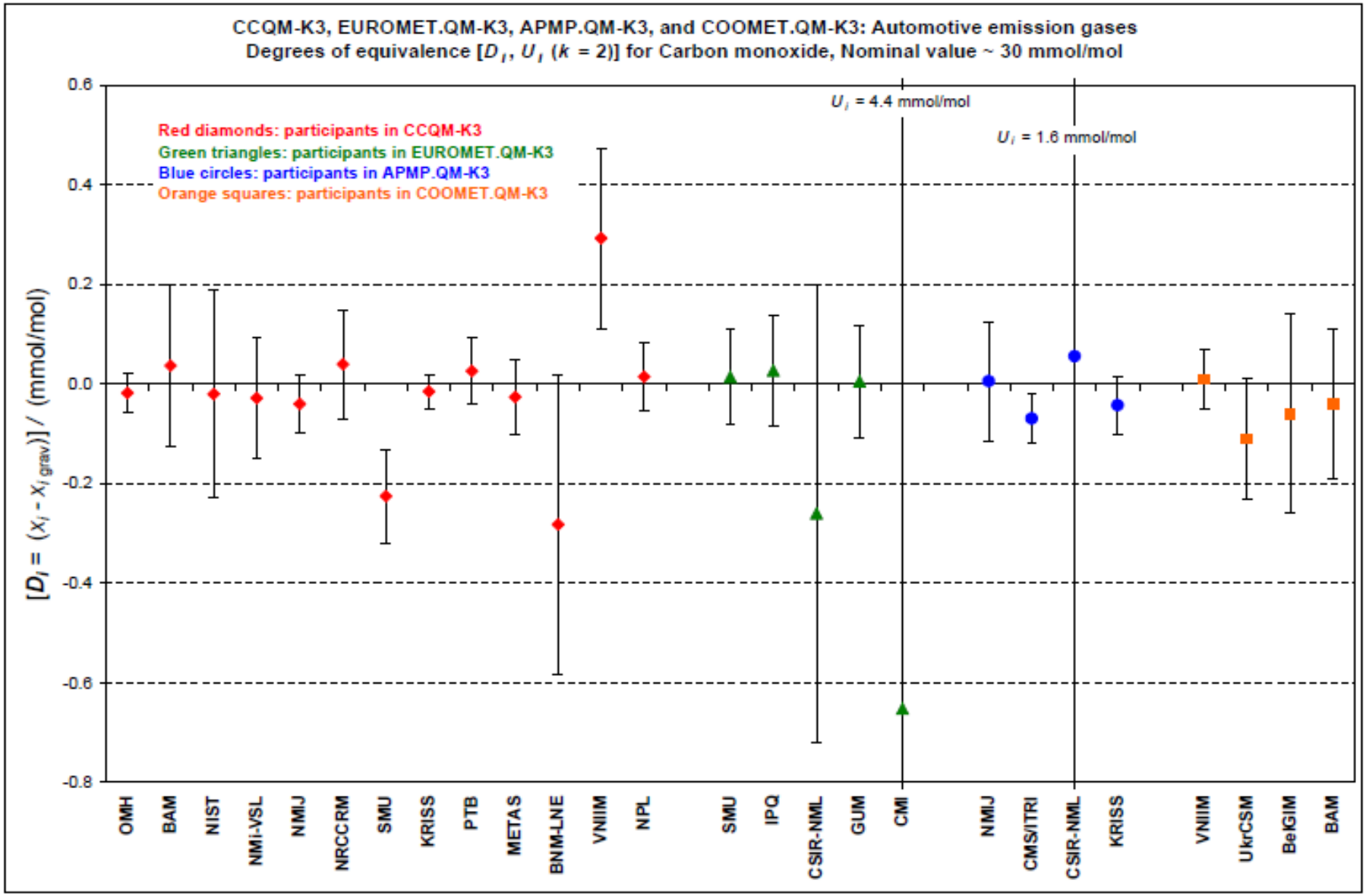
Abstract

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

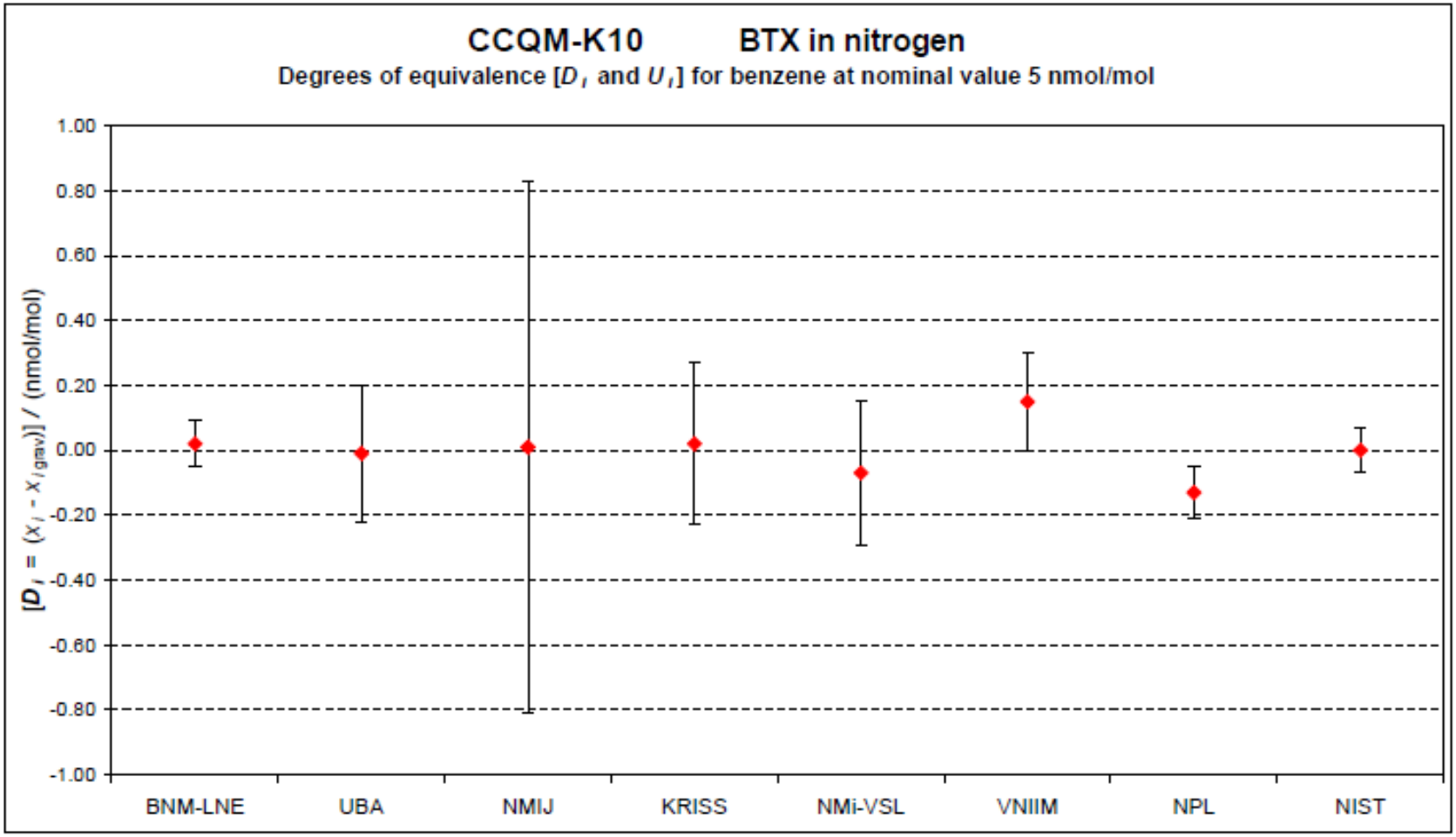
CCQM-K3 (2000) Automobile Emission Gases



CCQM-K10 (2001)

BTX in Nitrogen

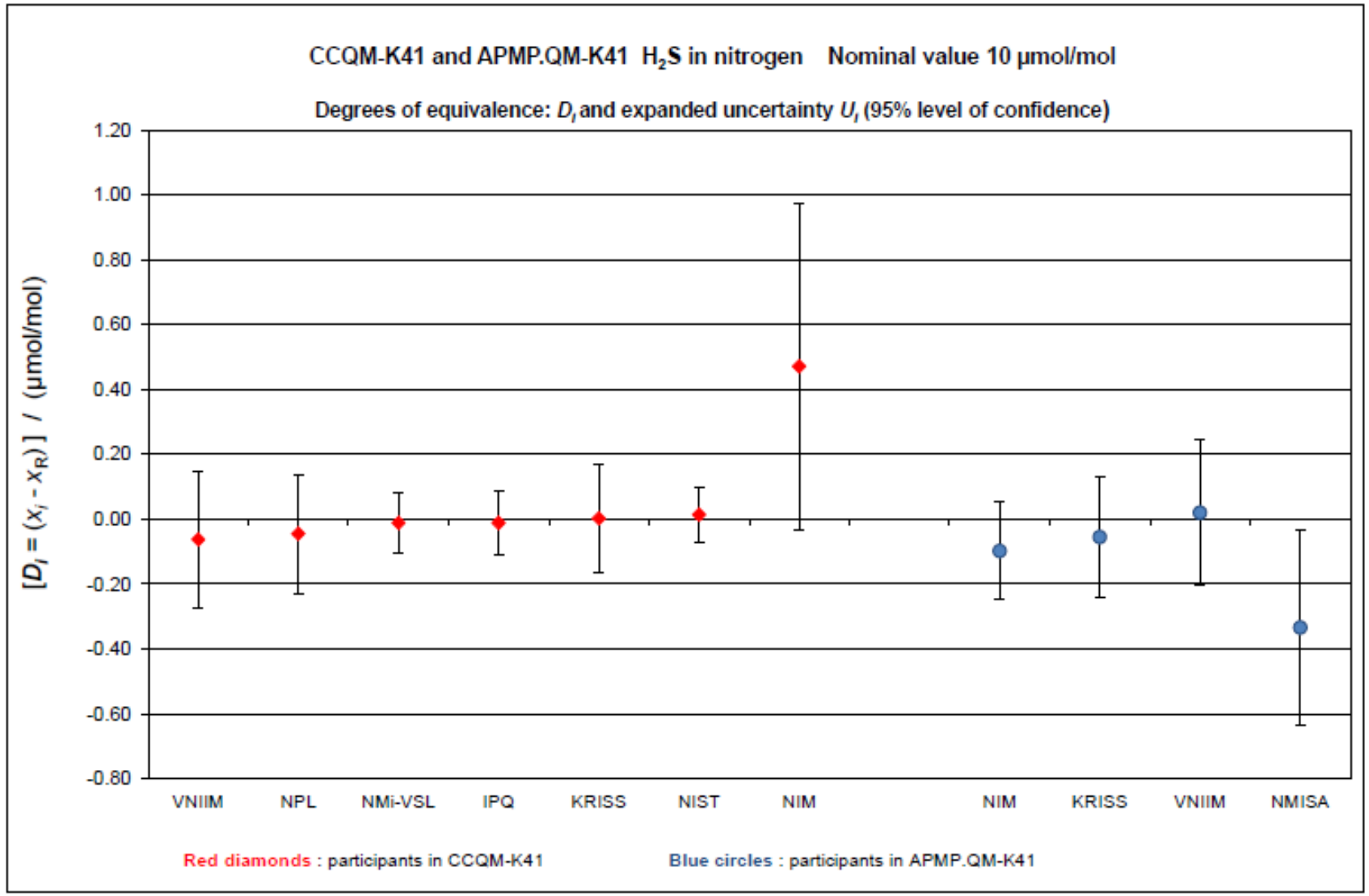
5 nmol/mol



CCQM-K41 (2005)

H_2S in Nitrogen

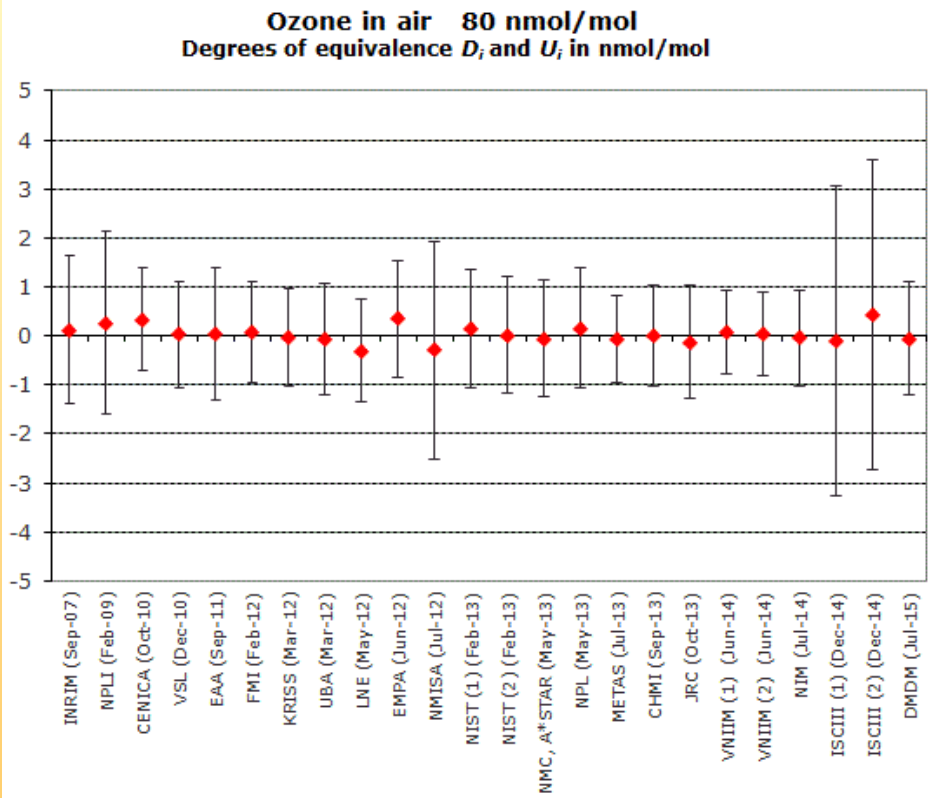
10 µmol/mol

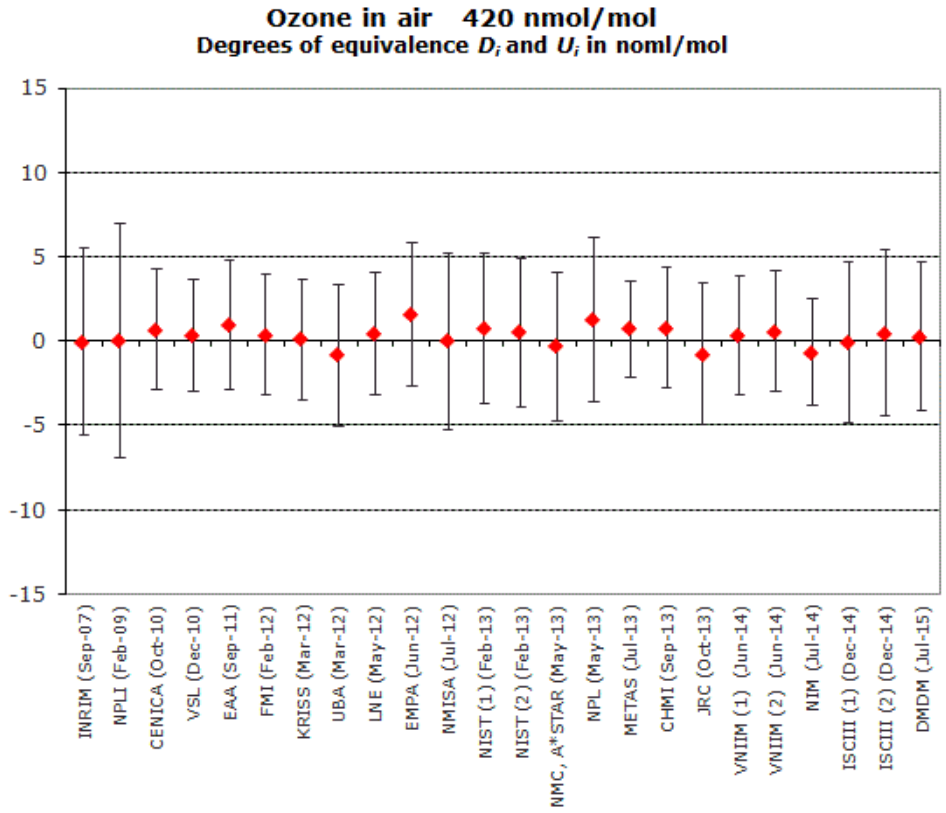


BIPM.QM-K1 Ozone, ambient level

24 degrees of equivalence between 2007 and 2015

(Keep in good agreement)

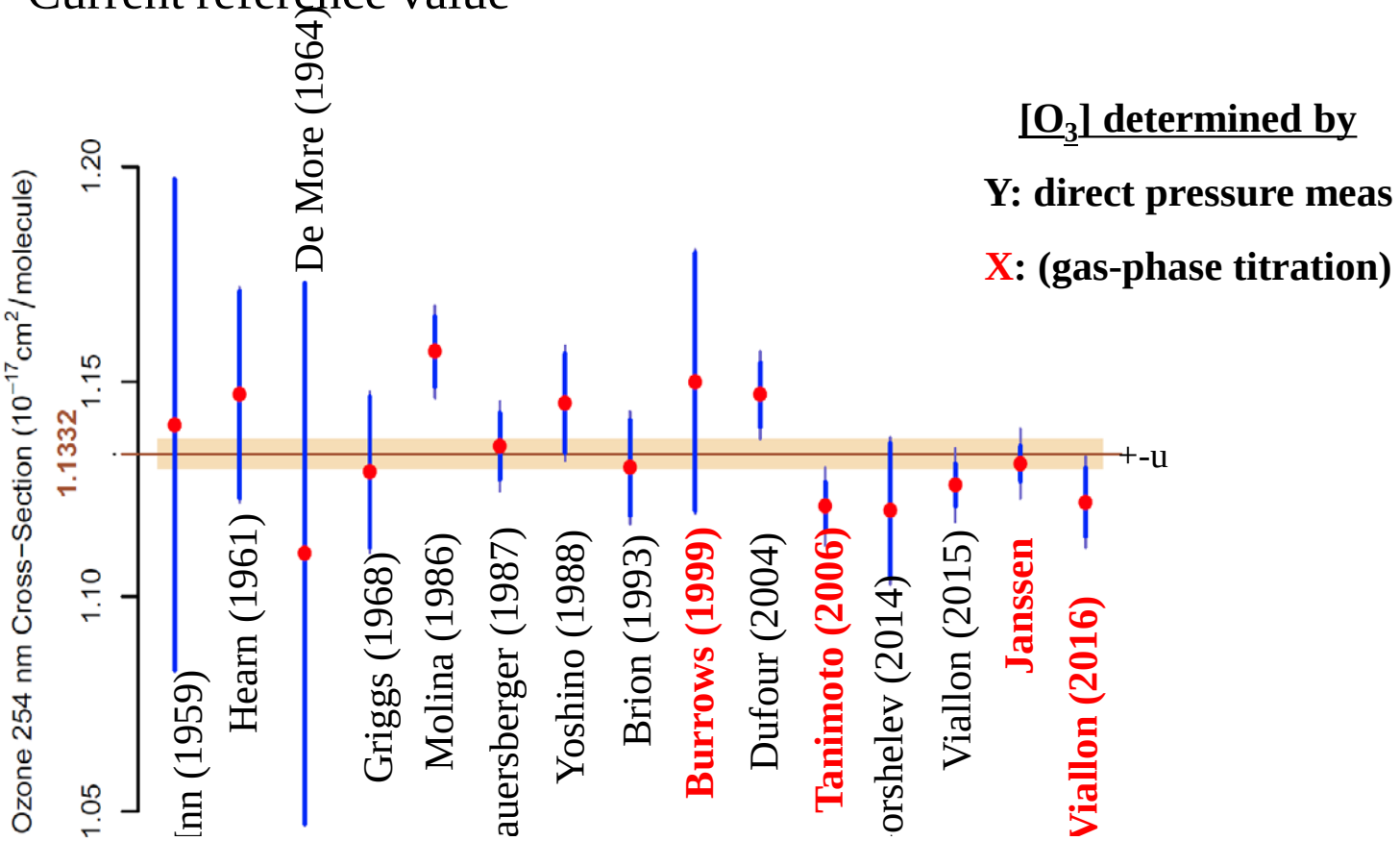




CCQM-GAWG Ozone Cross Section Task Group

Statistical analysis 253.65 nm O_3 cross section measurements

Current reference value



Task group on Particulate Comparison

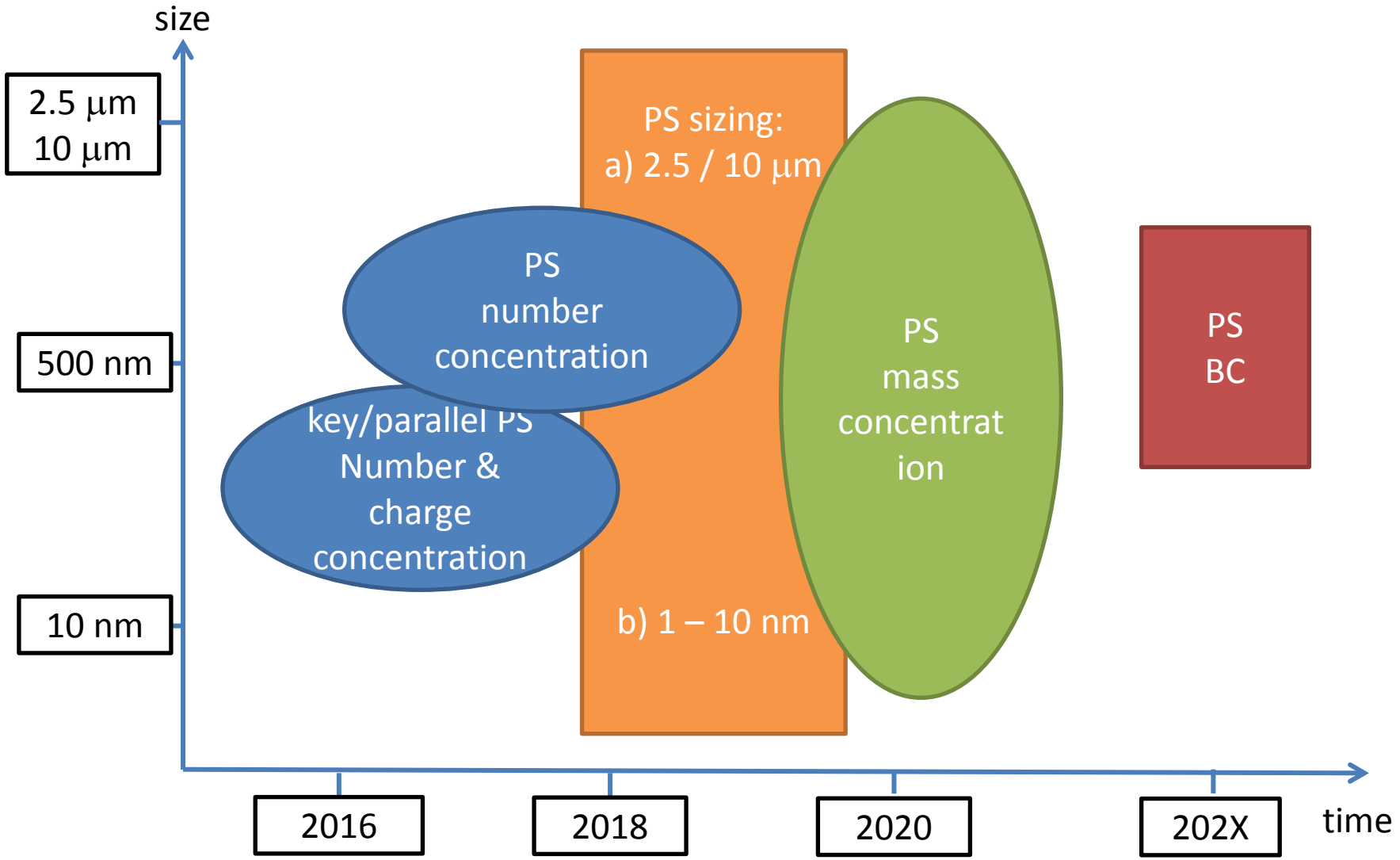
- Members:
  Liu Junji (NIM), Paul Quincy (NPL), Andreas Nowak (PTB), Hanspeter Andres (METAS), Shankar G. Aggarwal (NPLI) and Yuri Kustikov (VNIIM)

- 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)

Draft Roadmap

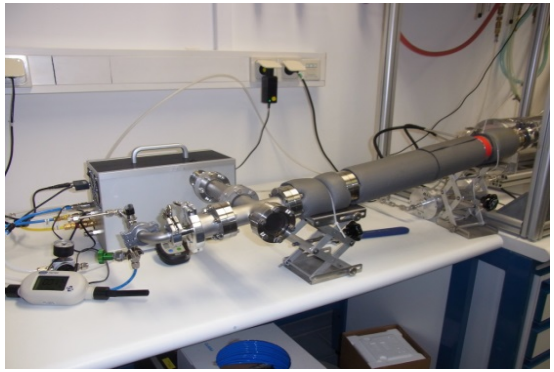
*PS = pilot study



Comparison on number / charge concentration

Repeat of EURAMET 1224 (charge conc.),1282 (number conc.)

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



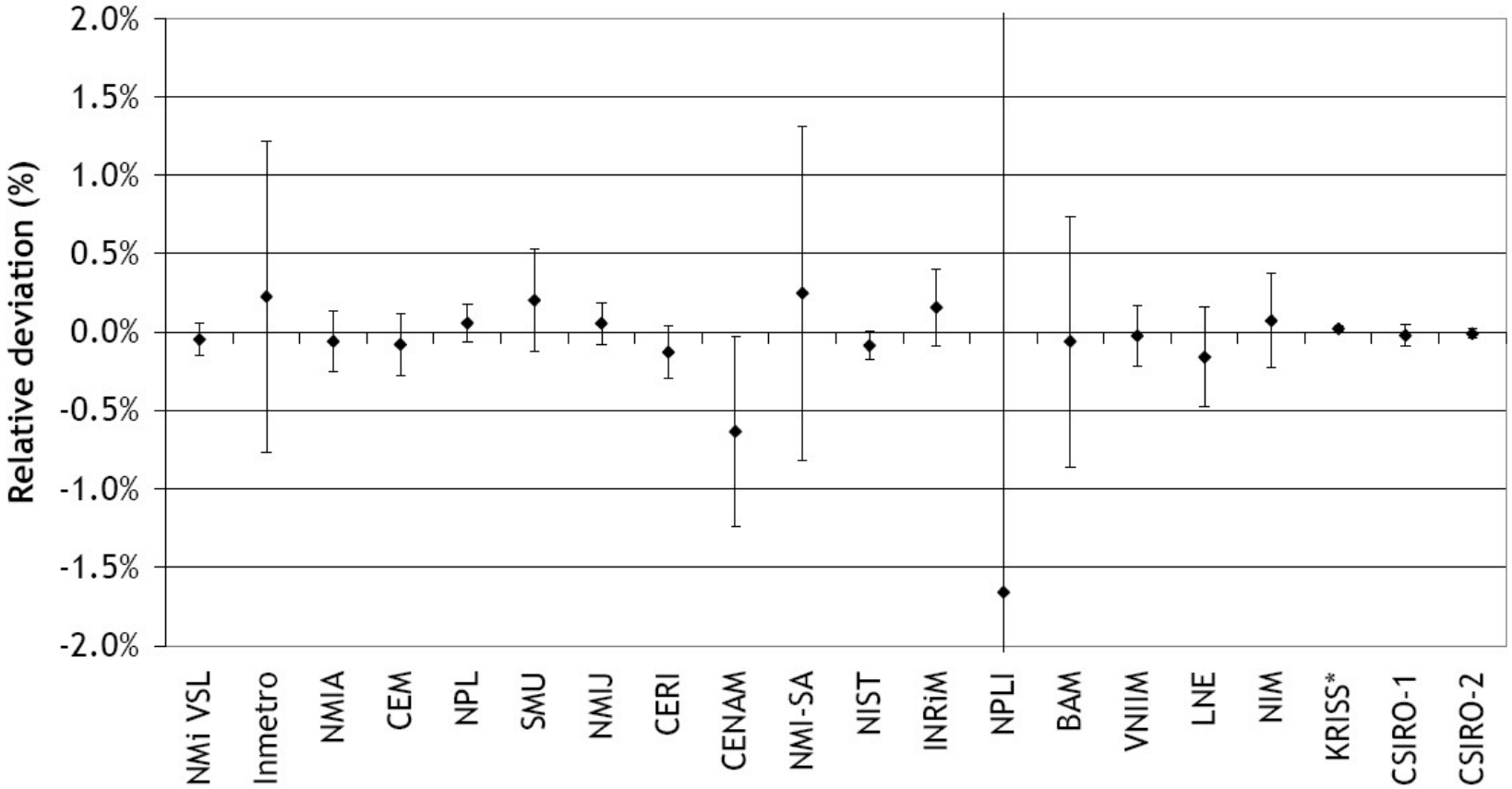
- Timescale: Protocol: December 2016
  comparison in second half of 2017
  Draft A: 2018

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

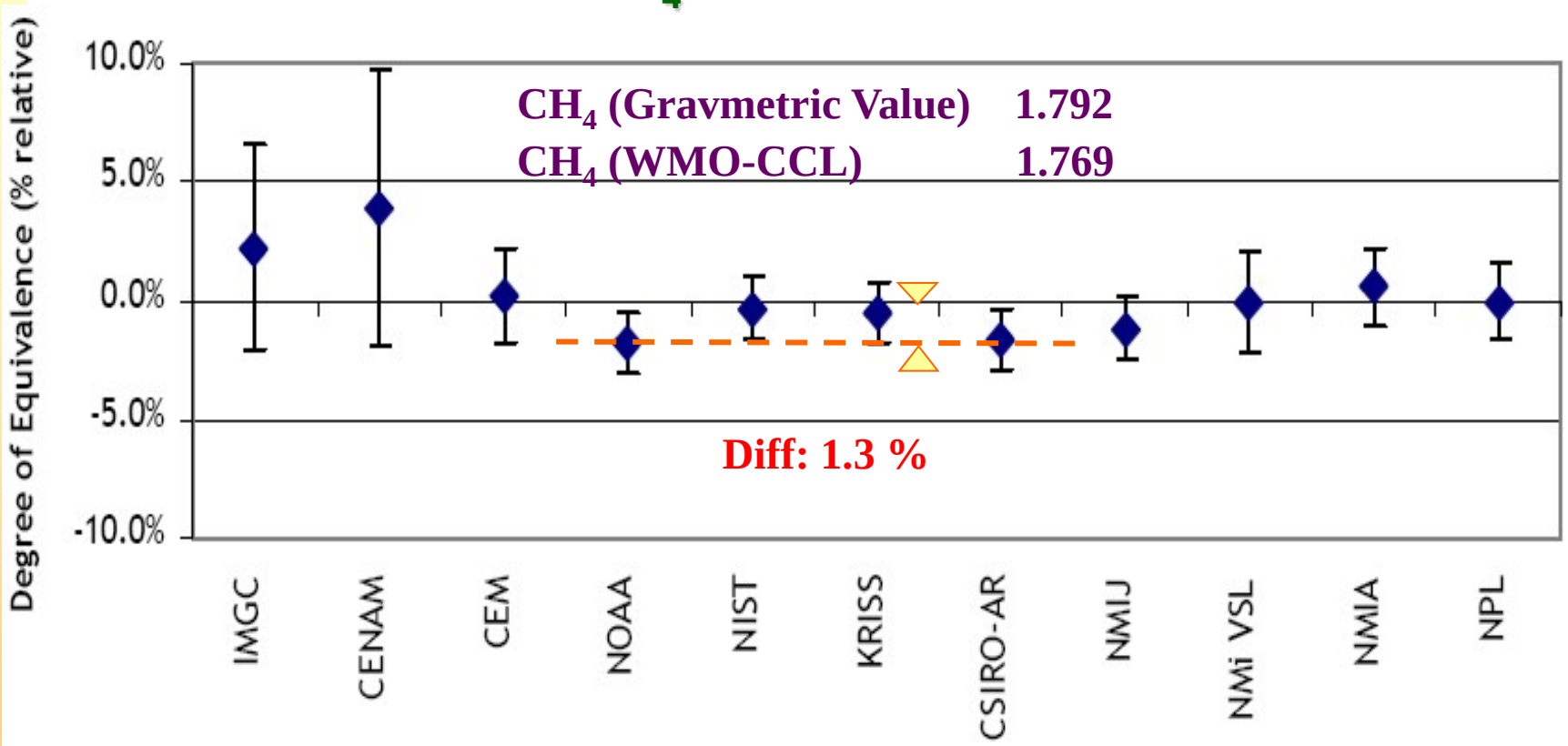
CCQM-K52 (2008)

- Coordinating Lab: VSL
- Substance: Carbon dioxide in Synthetic Air



CCQM-P41 (2003)

Ambient Level CH_4

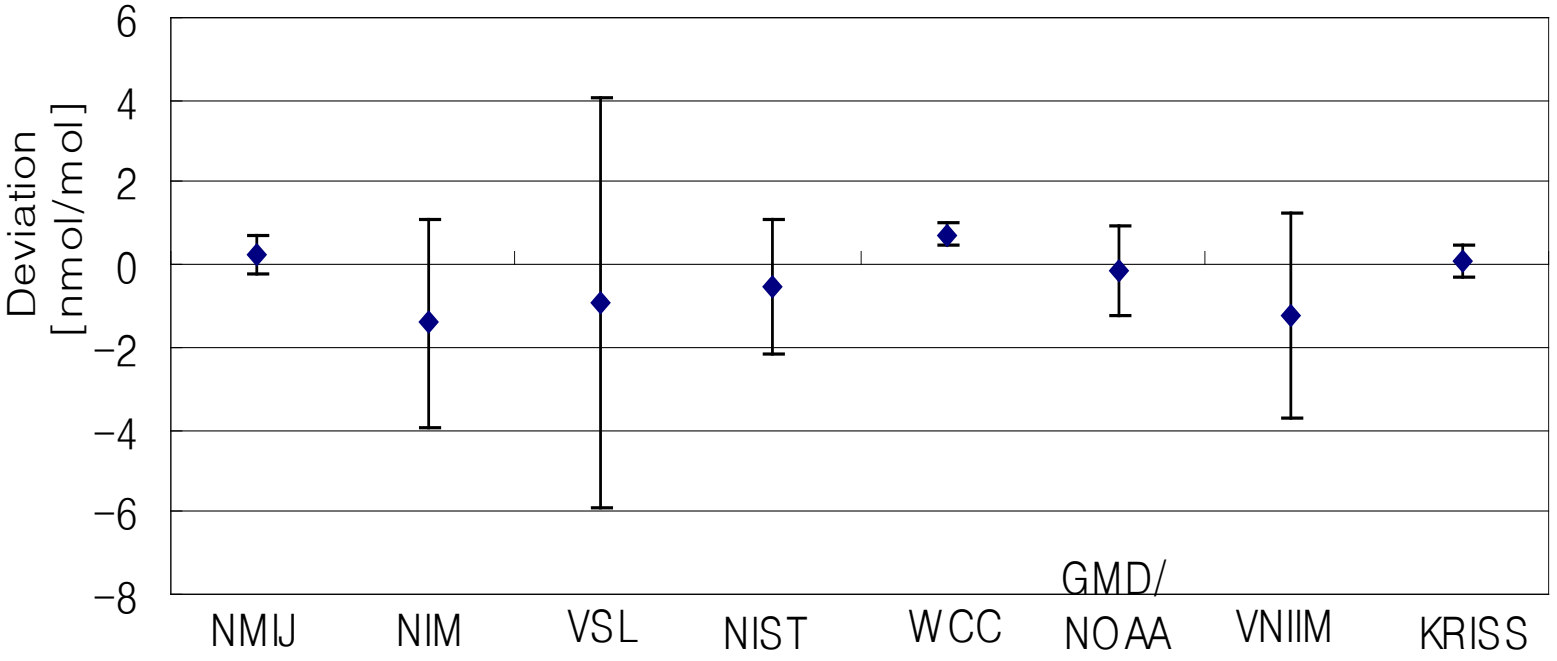


Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale (1.24 % higher than before)

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

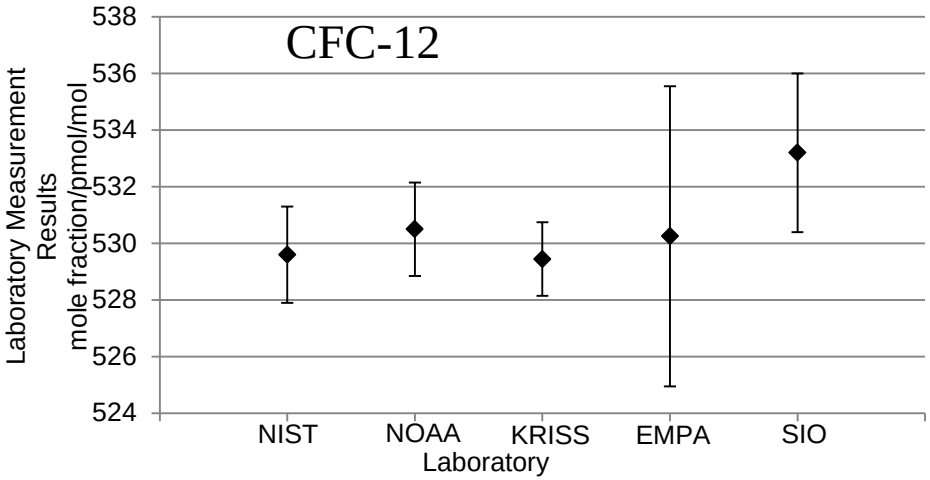
CCQM-K68 (2010)

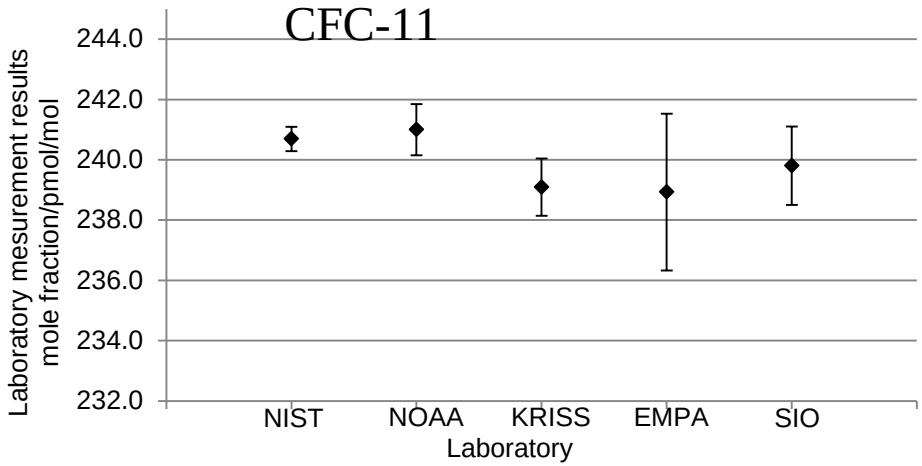
- Coordinating Lab: KRISS
- Subatance: Nitrous oxide 320 nmol/mol in Synthetic Air

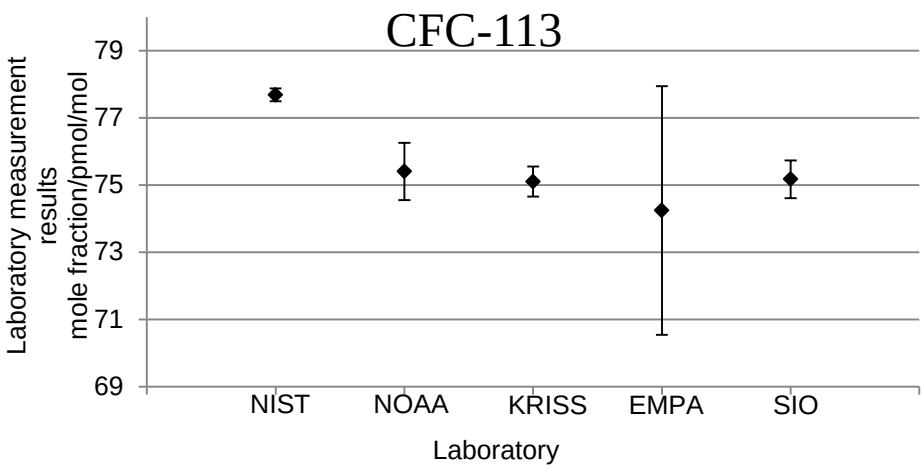


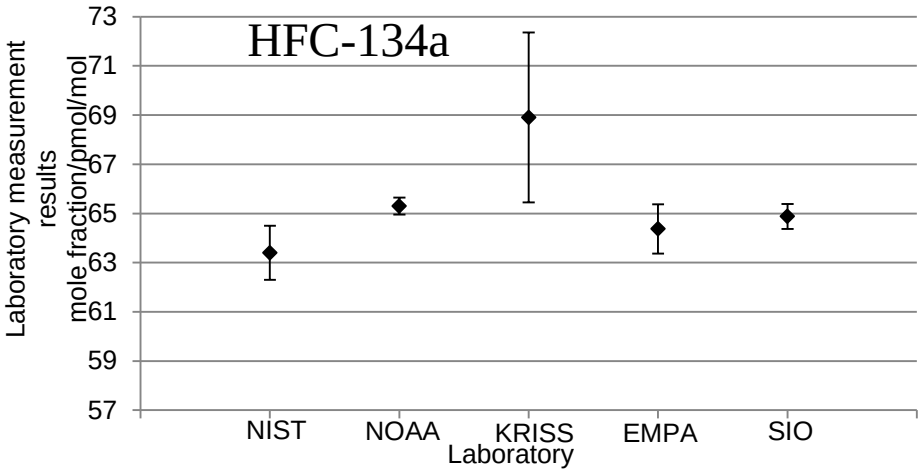
Draft A report

CCQM-K84 Halocarbons in real air by NIST

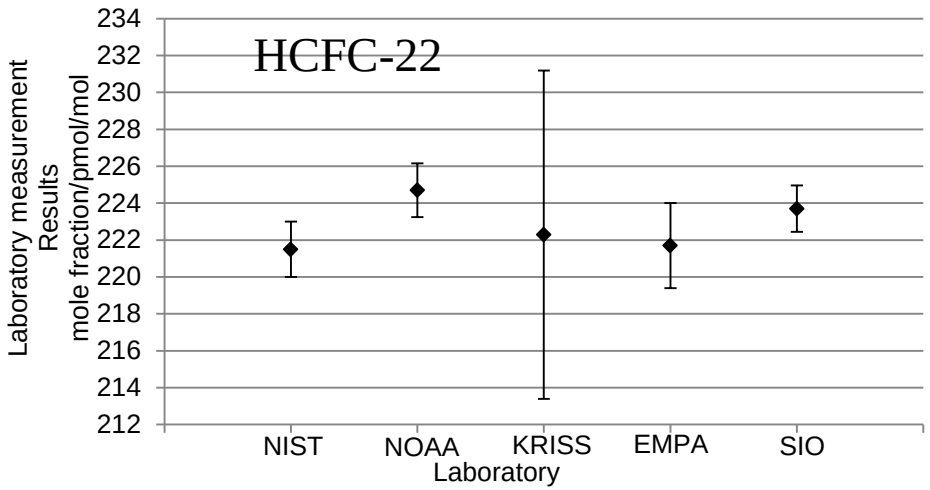


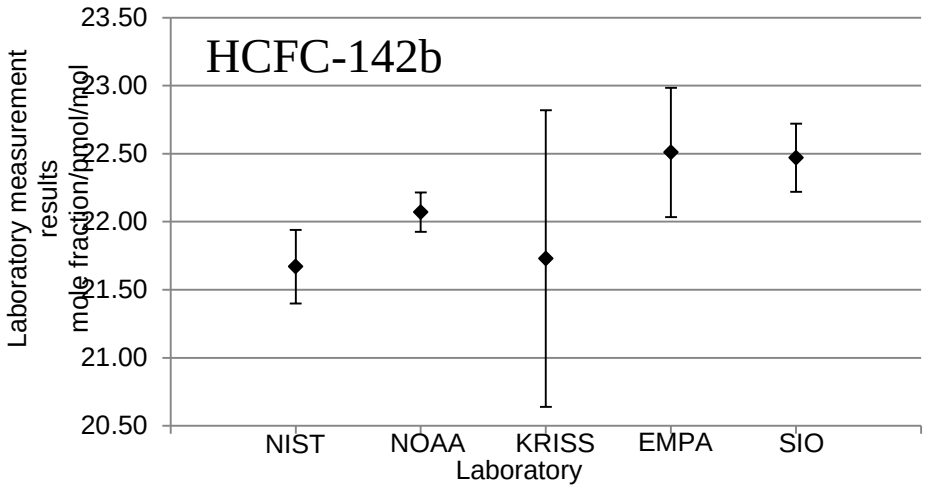






CCQM-K84 Halocarbons in real air by NIST



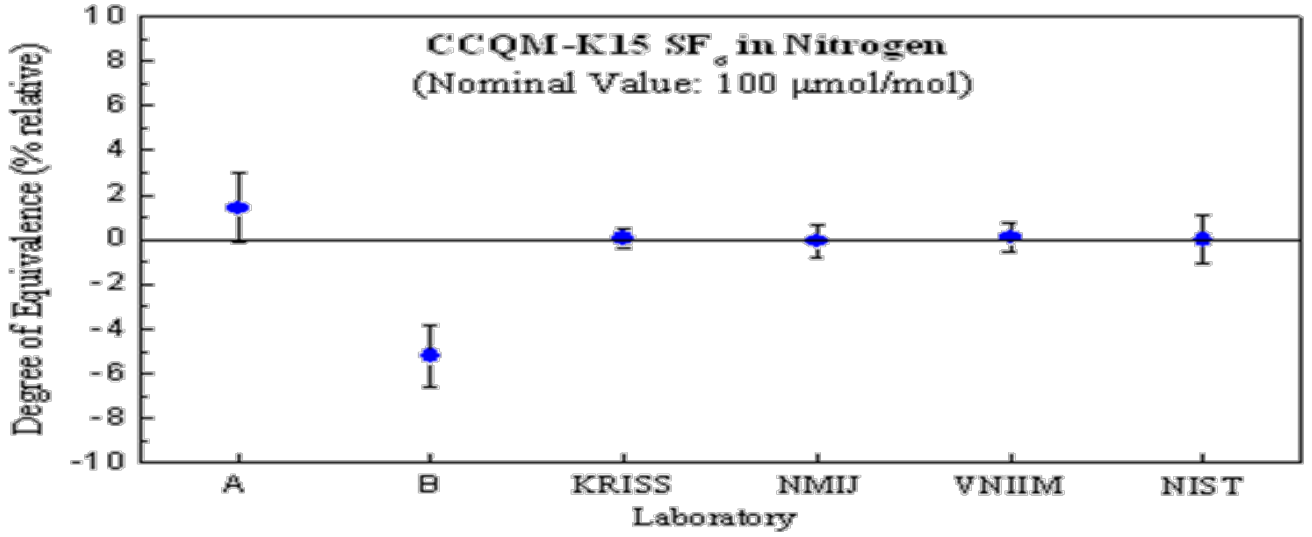


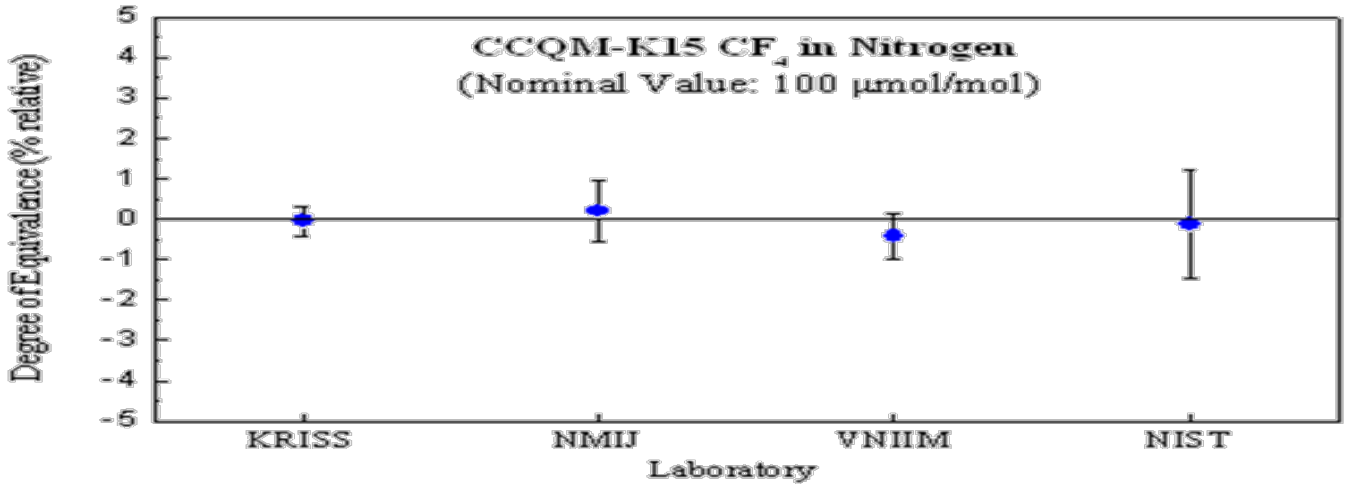
Results: The results indicate consistency within ± 2.0 %
except two points.

Action: KCRV from results of NMIs; NIST & KRISS
All participant's results will be Pilot Study

CCQM-K15 (2003)

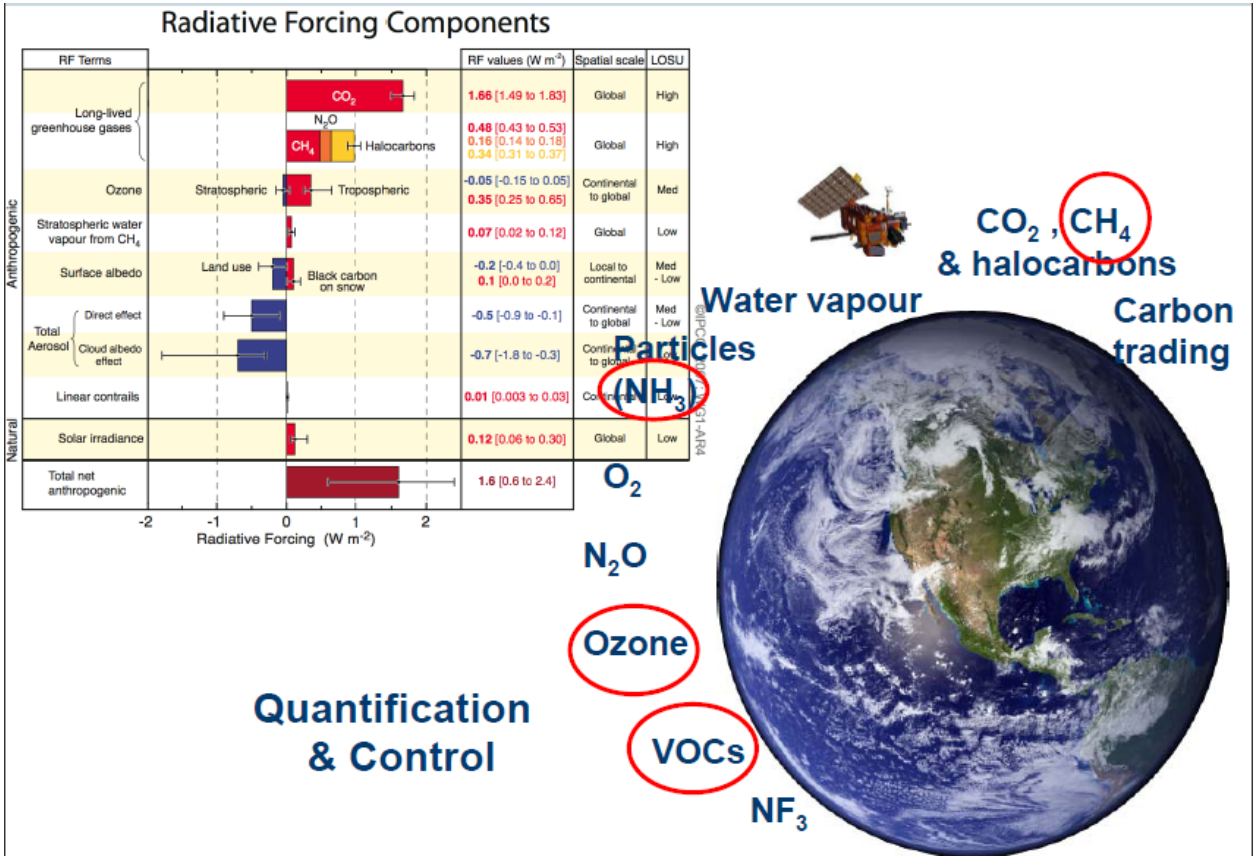
- Coordinating Lab: KRISS
- Subatance: SF_6 & CF_4 hundred μmol/mol level





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_2S by KRISS
2018	NO_2 by BIPM	2018	Automobile gases by VSL
2018	VOCs by NIST		



Planned KCs by GAWG

Reference No.	Description	Pilot (Coordinating) Laboratory	Expected Start date	Rational for Key Comparison
BIPM.QM-K1	KC (Ozone at ambient level)	BIPM / 20	2007 - ongoing	Atmospheric and air quality
CCQM-K117	KC (NH_3)	VSL&NIST	2016	Atmospheric and air quality
CCQM-K118	KC (Natural gas)	VSL & BAM	2016	Energy gases
CCQM-K120a	KC (Ambient CO_2, 380 to 480 µmol/mol)	BIPM with NIST	2016	Atmospheric and air quality CO_2 (380 to 480 µmol/mol) in a matrix of air
CCQM-K120b	KC (Ambient CO_2, 480 to 800 µmol/mol)	BIPM with NIST	2016	Atmospheric and air quality CO_2 (480 to 800 µmol/mol) in a matrix of air
CCQM-K137	Track A (NO in Nitrogen, 30-70 µmol/mol)	BIPM	2017	Atmospheric and air quality Repeat of CCQM-P73
CCQM-K41.2017	KC (H_2S in Nitrogen, 10 µmol/mol)	KRISS	2017	Atmospheric and air quality Repeat KC of CCQM-K41 in 2017
CCQM-KXX	KC(Micro-scale particles, number/charge conc	PTB/NPL	2017	Atmospheric and air quality
CCQM-K74.2018	KC (NO_2 in Nitrogen, 10 µmol/mol)	BIPM	2018	Atmospheric and air quality Repeat KC of CCQM-K74 in 2018
CCQM-P172	PS (Spectroscopic impurity study, NO_2 in Nitrogen, 10 µmol/mol)	BIPM	2018	Spectroscopic study of HNO3, NO, etc. as impurities in NO_2/Nitrogen
CCQM-K10.2018	BTEX 5 nmolo/mol in Nitrogen	NIST	2018	Air Quality/New emerging requirements
CCQM-K3.2019	Track A (Automotive gases)	VSL	2019	Atmospheric and air quality, Car Emission
CCQM-K68.2019	KC (Ambient N_2O)	BIPM with KRISS	2019	Atmospheric and air quality
CCQM-PXX	PS (Carbon/Oxygen isotope ratios in CO2)	BIPM with IAEA	2020	Atmospheric and air quality
CCQM-KXX	Hydrogen purity		2020	New emerging requirements
CCQM-KXX	DMS ambient level (5 nmol/mol in nitrogen)	KRISS	2020	Atmospheric and air quality
CCQM-KXX	KC (Nano & micro-scale particles)		2020	New emerging requirements
CCQM-KXX	Track A (SO_2)	NIST	2021	Atmospheric and air quality
CCQM-KXX	KC/PS (HCl emission level)	BIPM	2021	Atmospheric and air quality
BIPM.QM-K2	KC (Ambient CO_2)	BIPM	2022	PVT+Spectroscopy
CCQM-KXX	KC (Natural gas)		2022	Energy gases

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.