



ENV52 HIGHGAS workpackage 1 High Accuracy Primary Reference gas mixtures

Gerard Nieuwenkamp (VSL)
Paris, 13th November 2014



Contents of the presentation



- Background information (drivers / needs)
- Objectives
- Deliverables (summary)
- Scientific challenges / beyond the state of the art

Background (1)



Background:

The measurement of greenhouse gases is pivotal to understanding the changes in the Earth's climate

Consequently there is an urgent requirement for a validated and traceable measurement infrastructure to provide the basis for stable and comparable measurements of the highest impact GHG's

Standards with challengingly low uncertainties and long term stability are of paramount importance

Background (2)



Current situation:

Requirements for long term observations are represented by Data Quality Objectives (DQO) set by the WMO

The current approach, adopted by the atmospheric monitoring community, is that all measurements are traceable to a “scale” / a collection of artefacts

The required uncertainties of the DQO’s are not realized (at the start of the project)

Objective HIGHGAS



Develop a metrological infrastructure to underpin measurement of the highest impact greenhouse gases

(combine the qualities of the meteorological and metrological community!)

Objectives WP1 (1)

High accuracy primary reference gas mixtures



Develop static reference standards for CO₂, CH₄, CO and N₂O with challengingly low uncertainties

Component	Ambient Amount Fraction	Target Uncertainty (DQO/WMO)	% Target Uncertainty (DQO/WMO)
CO ₂ (northern hemisphere)	400 µmol/mol	100 nmol/mol	0.025%
CH ₄	1.8 µmol/mol	2 nmol/mol	0.11%
CO	300 nmol/mol	2 nmol/mol	0.67%
N ₂ O	325 nmol/mol	0.1 nmol/mol	0.03%

DQO uncertainties are ≈ 5 - 20 times lower than current NMI CMC claims

Objectives WP1 (2)

High accuracy primary reference gas mixtures



Investigation of analytical bias caused by variation in isotopic composition

Assessment of the comparability of the new developed traceable reference standards to the existing standards and scales

Deliverables WP1



High accuracy reference standards in cylinders

- Full uncertainty budget
- Quantification of impurities in balance gases
- Stability studies long-term and short-term for different cylinder passivation chemistries

Reference standards with variation in isotopic composition

- Varying $^{13}\text{CH}_4$ or CH_3D
- Varying CO_2 isotopic composition
- Improved isotope ratio mass spectrometry (IRMS)
- Analytical bias assessment as function of isotopic composition

Comparison of the “new” standards to mixtures from the NOAA/AGAGE scale

Scientific challenges (1)



High accuracy reference standards in cylinders

Total uncertainty has to go down by a factor of $\approx 5 - 20$

-Uncertainty sources in gas mixture preparation and analyses that used to be negligible become significant!

Impurity quantification of e.g. N_2O in nitrogen or air has to improve by a factor of 10 or more

-Current detection limit of ≈ 0.5 nmol/mol is much higher than required uncertainty of 0.1 nmol/mol for the reference material

Initial and long-term adsorption effects at the internal cylinder surface should be investigated, understood and quantified.

-Adsorption of a monolayer CO_2 to the internal cylinder surface causes a loss of $\approx 0,5$ $\mu\text{mol/mol}$

Scientific challenges (2)

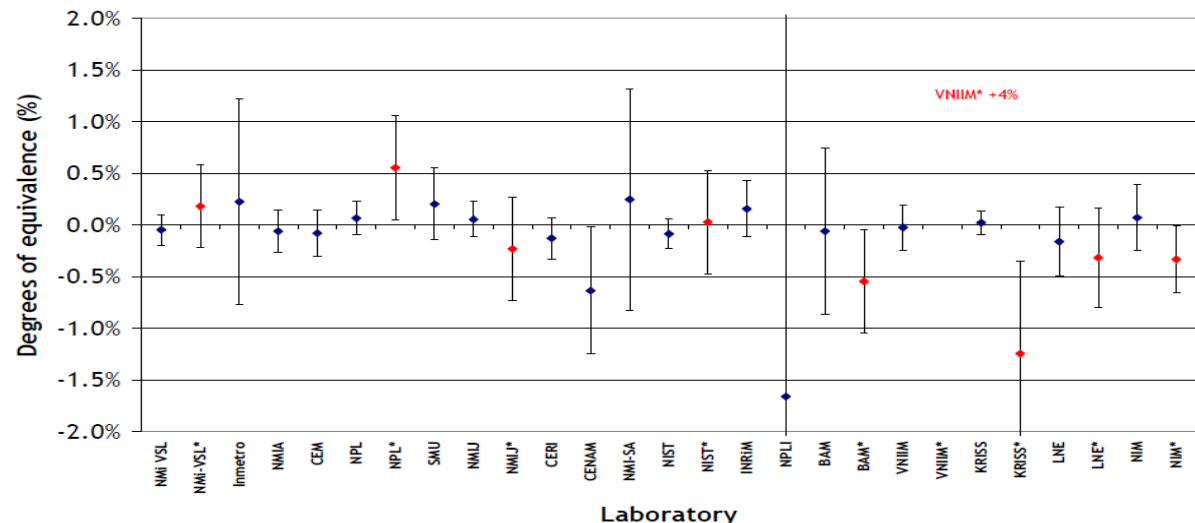


Reference mixtures with varying isotopic composition.

- Improved analytical repeatability and reproducibility for IRMS
- Quantification of analytical bias: method dependent and/or instrument dependent

Comparison to current scales
challenging targets

CCQM-K52 vs CCQM-K1b Carbon dioxide in Synthetic air



Thanks for the attention



Input from stakeholders:

- requirements
- involvement
- collaboration