



Metrology for Climate Relevant VOCs

Preparation of static reference gas mixtures – traceability and uncertainty

Annarita Baldan



VSL
National
Metrology
Institute



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Relevant documentary standards



ISO/TC 158 is responsible for developing documentary standards in gas analysis, including:

- ❑ *ISO 14617* General quality aspects and metrological traceability of calibration gas mixtures
- ❑ *ISO 6142* Calibration gas mixture preparation by gravimetric method
- ❑ *ISO 6145* calibration gas mixture preparation by dynamic methods
- ❑ *ISO 6143* Comparison methods for determining and checking the composition of calibration gas mixtures
- ❑ *ISO 19229* Purity analysis and the treatment of purity data
- ❑ *ISO 14912* Conversion of gas mixture composition data (e.g., from amount fractions to concentrations)

ISO 6142 – Part 1

Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures

- ❑ Method for “Static Reference Gas Mixtures”
- ❑ Root of metrological traceability chain
- ❑ Class I type gas mixtures are individually verified
- ❑ Rigorous and comprehensive QA/QC for preparation and verification (e.g. accreditation ISO 17034)
- ❑ Uncertainties in general substantially smaller than by any other preparation method.
- ❑ ‘Stable’ components



Preparation: the route to traceability



- 1- Purity analysis of the gases (or liquids) that will be used for the gas mixture
- 2- Selection of the high-pressure gas cylinder and cleaning process
- 3- Evacuated cylinder is filled with the first gas by pressure difference
- 4- Cylinders are weighed using calibrated mass comparator (by difference against a reference cylinder)
- 5- Steps 3 and 4 are repeated for multi-component gas mixtures
- 5- As last the matrix gas (e.g. nitrogen) is introduced to ca. 100-130 bar to achieve the target mole fraction
- 6- Calculation of the gas mixture purity table (mass fractions are converted into mole fractions)

Preparation: the route to traceability (cont.)

In case of liquid (e.g. VOCs), these are inserted in the gas cylinder as a single component or a liquid mixture by loop or syringe injection (gravimetrically)



Verification & Stability

By comparison against traceable standards (ISO 6143) with proven accuracy and stability

Static reference gas mixtures

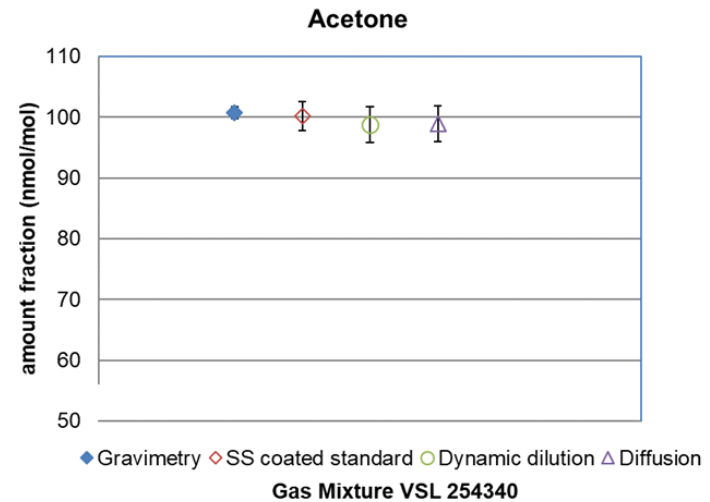


By cross-check against an independent reference method (dynamic)

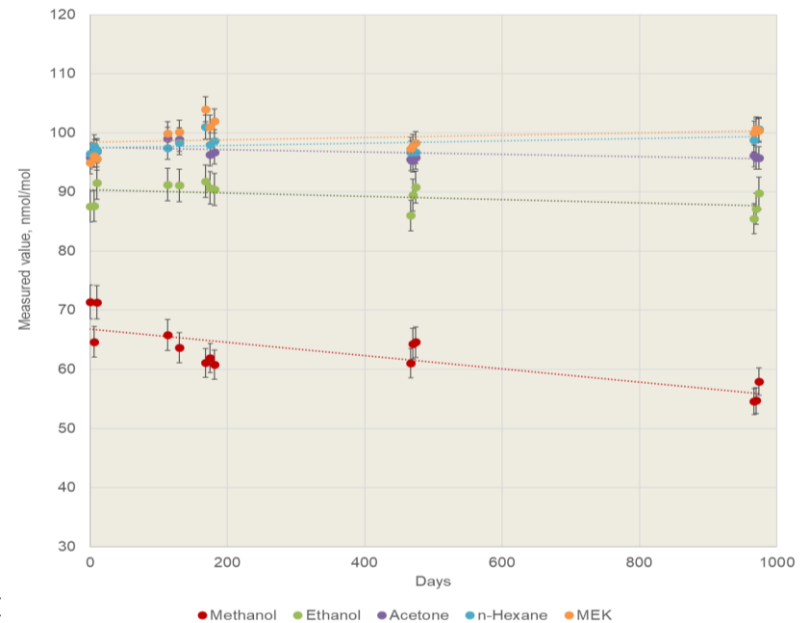


MetClimVOC

Meeting M1C



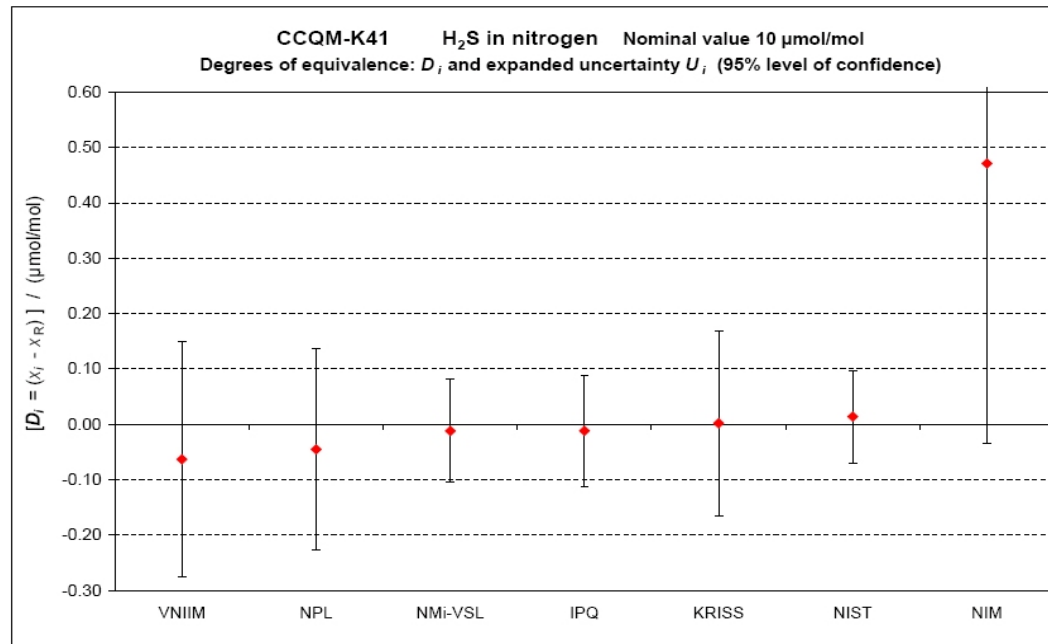
Stability testing



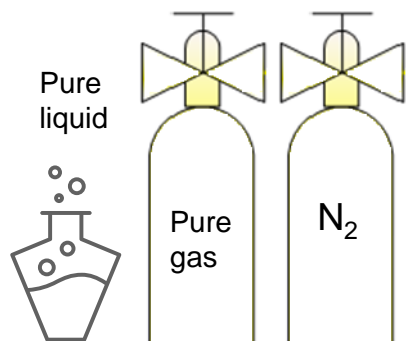
Mutual Recognition of measurement standards

CIPM Mutual Recognition Arrangement (MRA)

- ❑ Demonstrated equivalence between National Metrology Institutes (<https://www.bipm.org/kcdb/>)
- ❑ Mutual recognition of certificates



Primary realisation of gas mixtures in mole fractions



Uncertainty sources

Purity analysis
ISO 19229:2015

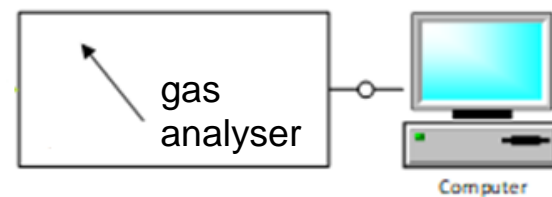
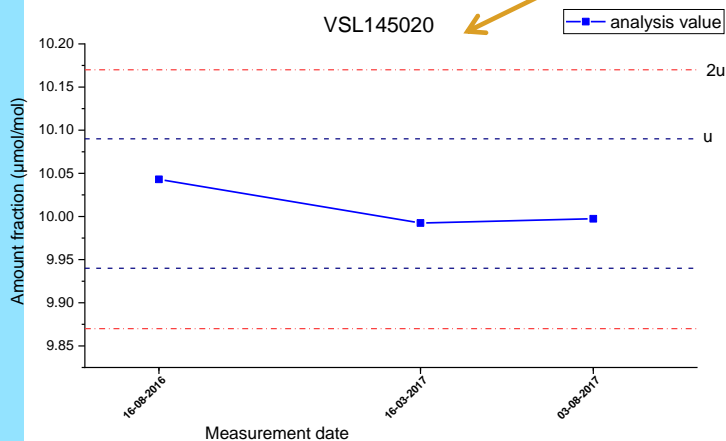
Preparation
ISO 6142-1:2015

($u_p \approx 0.01-0.1\%$)

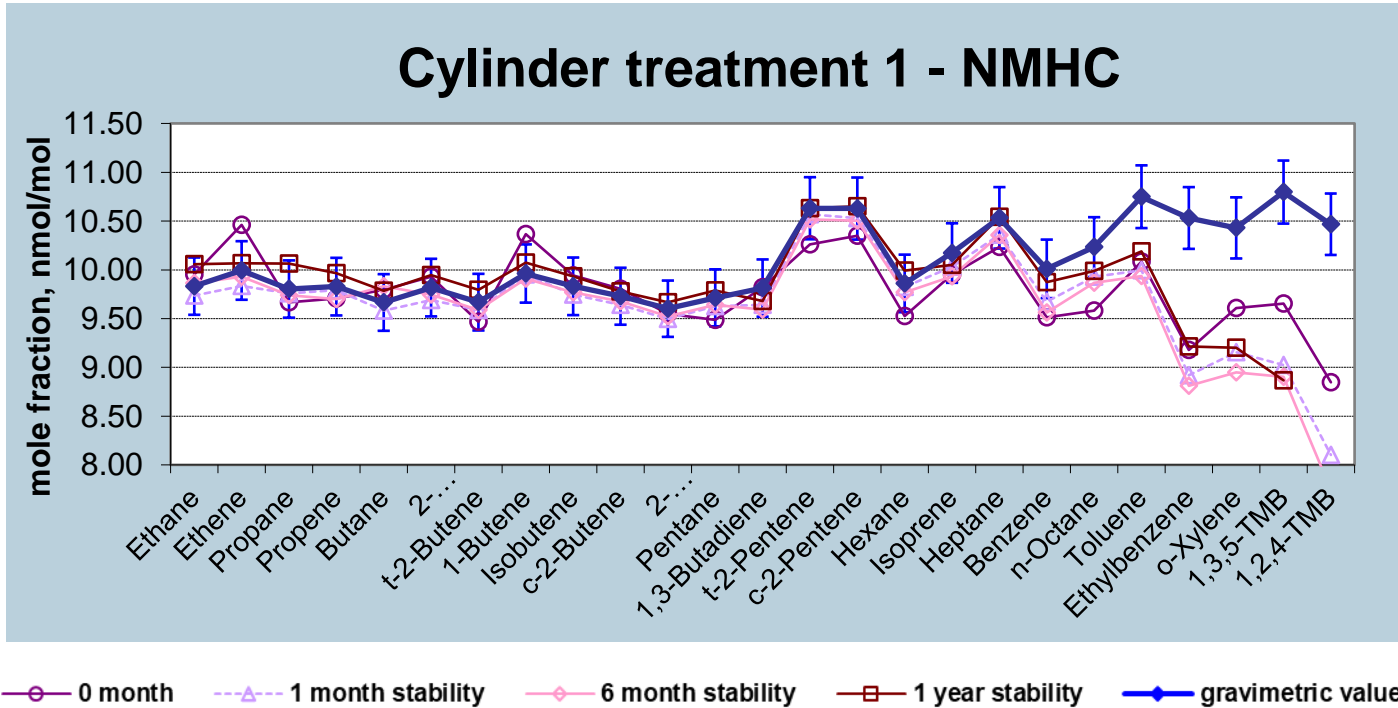
Stability

Verification
ISO 6143:2001

($u_{an} \approx 0.05 - 1\%$)



Challenges for trace levels NMHC



What goes in the cylinder it does not per se come out!
Interaction with the cylinder surfaces and side reactions may occur, affecting the accuracy of preparation and stability

→ There is no universal cylinder to fit all gases or fractions !



Metrology for Climate Relevant VOCs

Thank you for your attention!

Abaldan@vsl.nl

For more information, visit

www.metclimvoc.eu



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States