METROLOGY for HYDROGEN VEHICLES

The challenges with developing Primary Reference Materials for Hydrogen Purity

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Overview

- Purpose of Primary Reference Materials
- Why are there yet no PRMs for all impurities in Hydrogen
- Availability of PRMs
- Progress made in MetroHyve
- Remaining challenges

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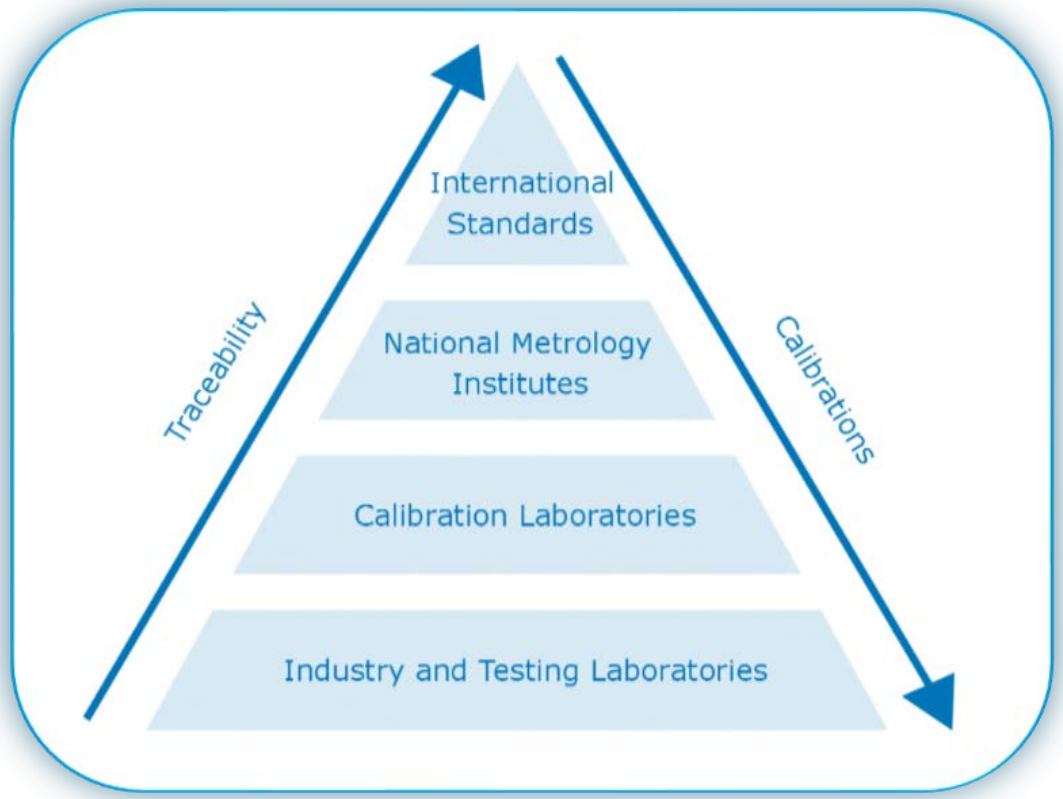
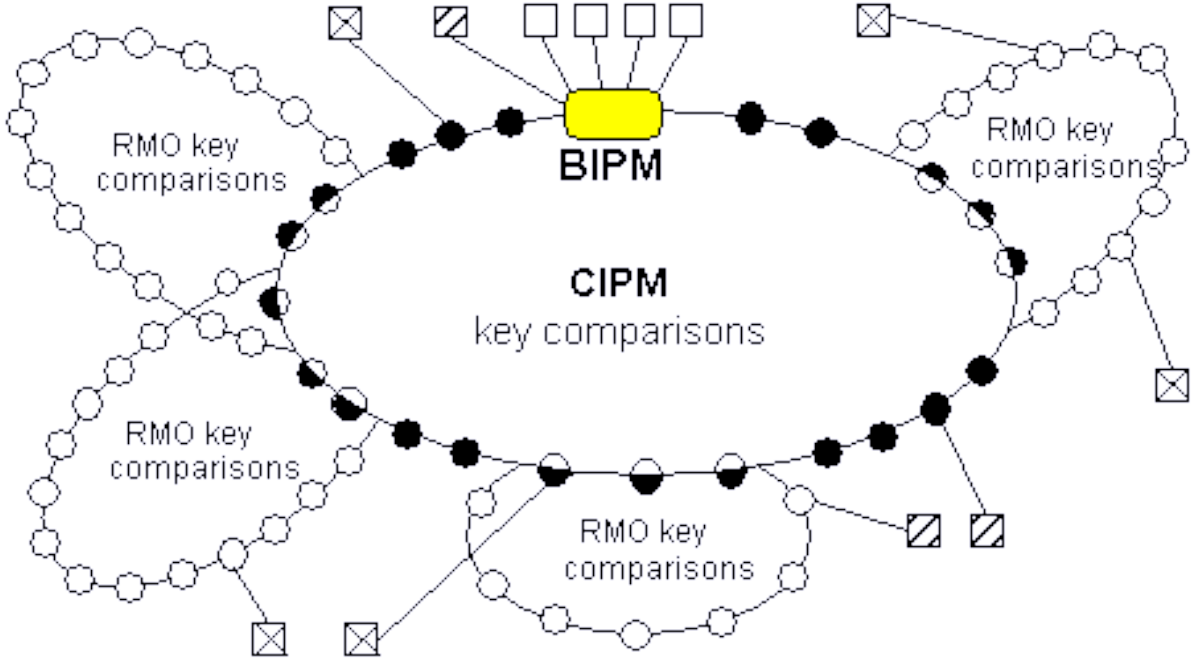
Measurement challenge

- Some of the impurities to be measured are at low concentration
- Some of the impurities are very reactive
- Classes of ‘total concentration’ like total halogenates are impossible for gravimetric preparation of gasmixtures

Metrological infrastructure





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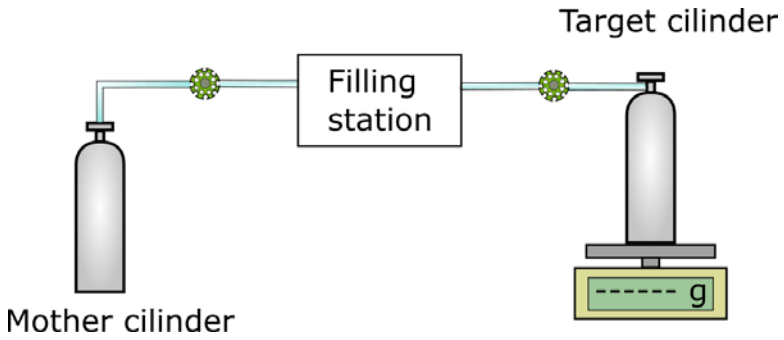
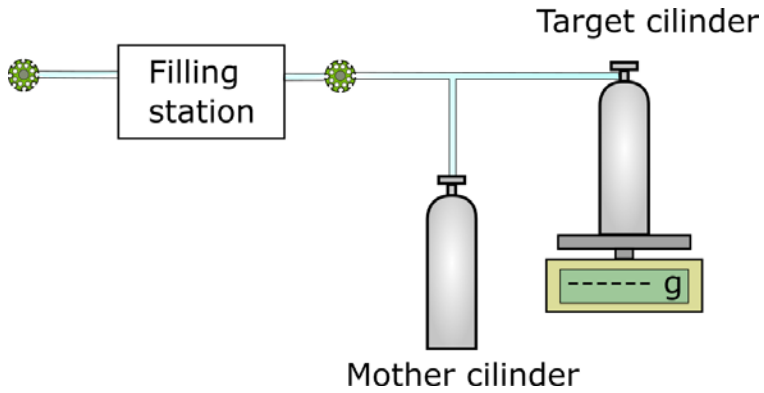
Preparation of Primary Reference Materials (1)

- Gravimetric preparation according to ISO6142
  - Thorough purity analysis of parent gases
  - Suitability of cylinders used
    - material compatibility, coatings, adsorption, stability
  - Verification of the prepared standards by accurate analytical methods





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Preparation of Primary Reference Materials (2) MetroHyve report A2.3.1

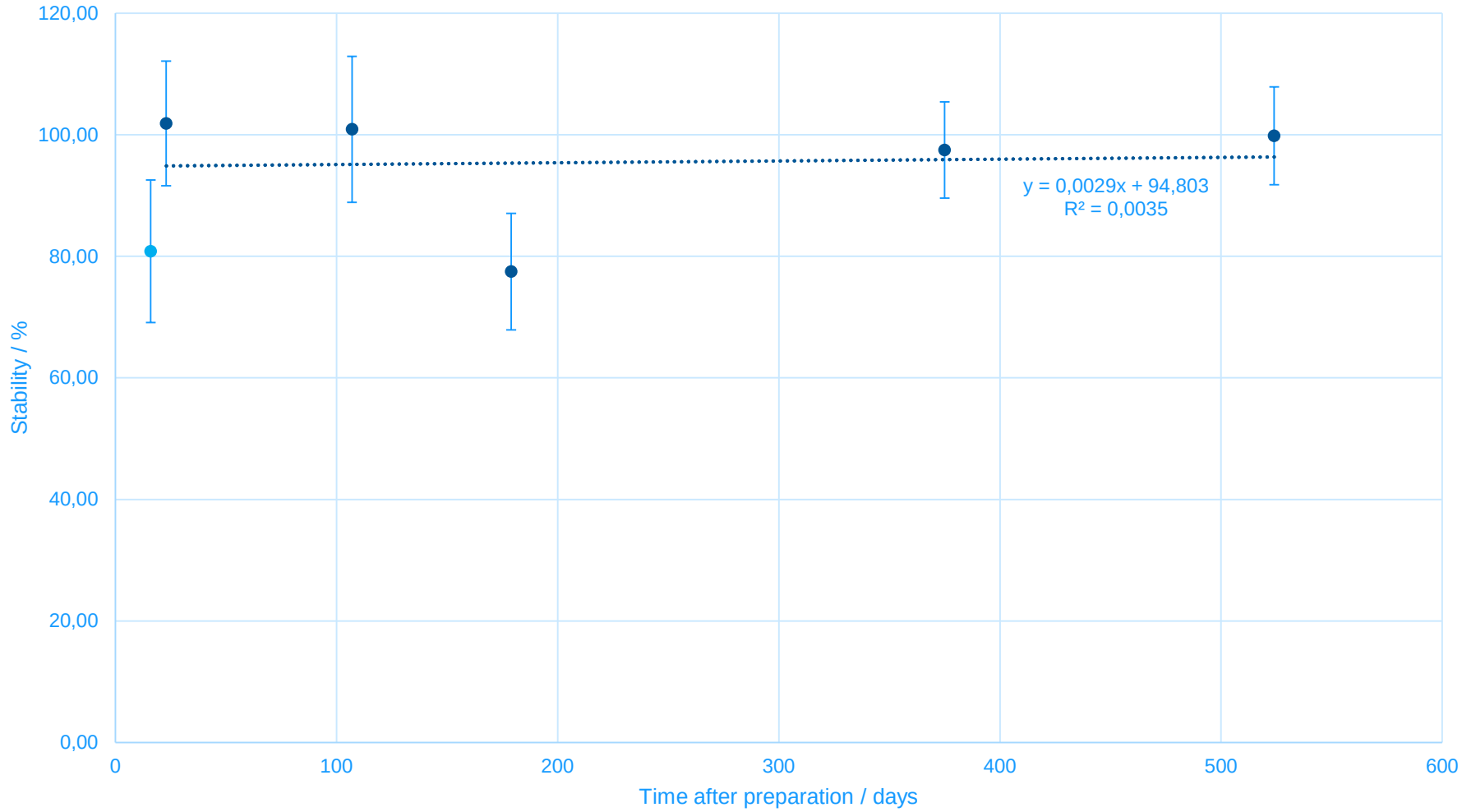
- Stability in Nitrogen does not mean stability in Hydrogen
  - 1 µmol/mol CO in Nitrogen is stable in coated aluminium cylinders but 1 µmol/mol CO in air has shown signs of instability
- Stability and concentration are closely linked
  - In Euramet 1220 a 1 µmol/mol mixture of H_2S in H_2 showed 2 years stability, a test on 10 nmol of H_2S showed a large loss the day after preparation
- Even cylinders with the same treatment can behave very differently

Accreditation: ISO17025 (calibration) ISO17034 (reference materials)

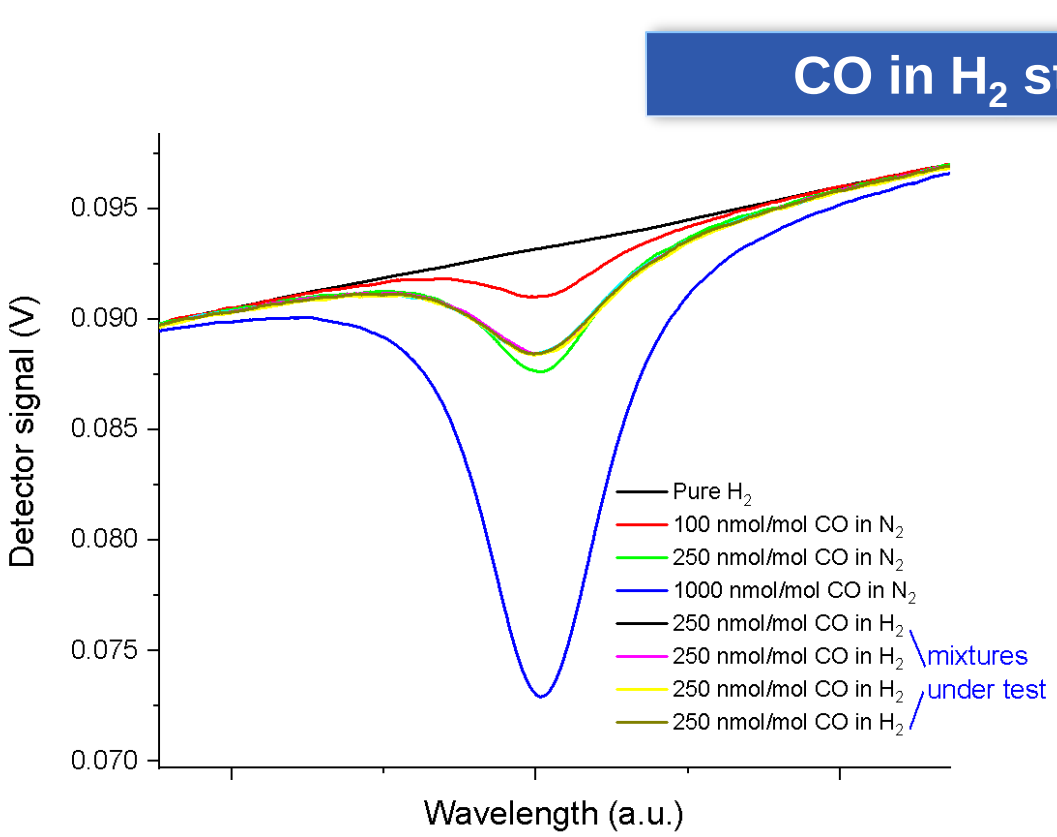
- Measurement capabilities in the BIPM KCDB
- Calibration entries by KRISS, NPL, VSL and VNIIM for hydrogen purity
- No entries for reference materials
- NPL has ISO17034 accreditation for stable components in Hydrogen

ISO 14687	
Water	Carbon monoxide
Total hydrocarbons	Total sulfur
Methane	Formaldehyde
Oxygen	Formic acid
Helium	Ammonia
Nitrogen	Halogenated compounds
Argon	
Carbon dioxide	

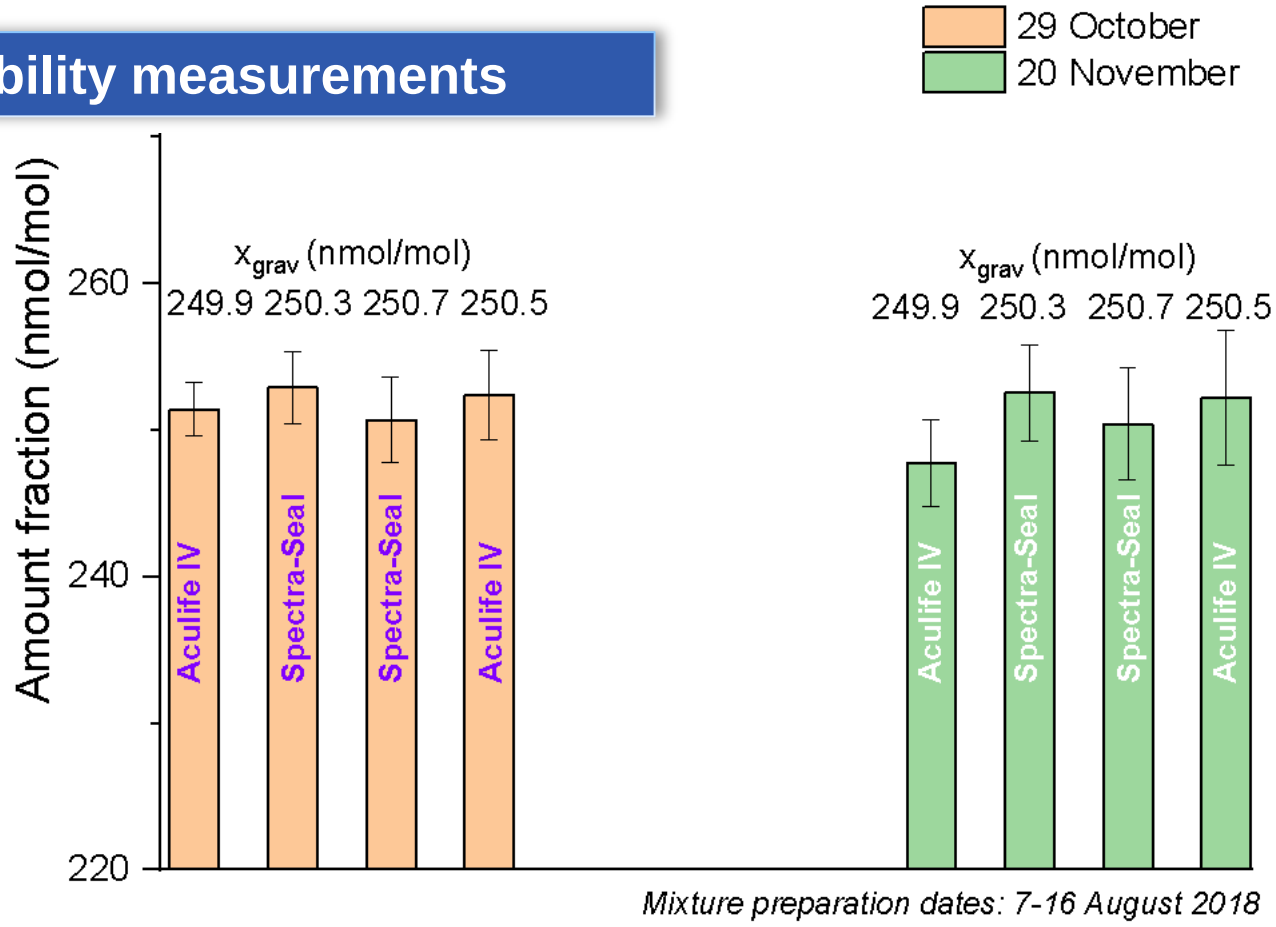
Stability for 40 ppb H_2S in H_2 mixtures at NPL



Short term stability for CO mixtures



CO in H_2 stability measurements



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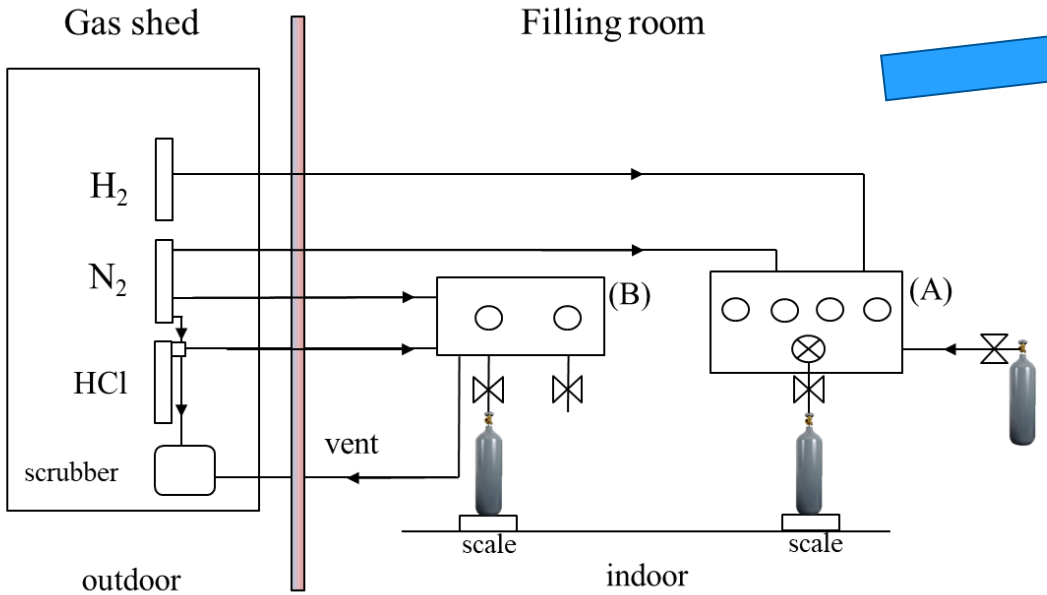
HCl in H_2 standards preparation by CEM

- By static gravimetric method (ISO 6142-1)
- 26 gas mixtures prepared in total
- Ranging from 10 µmol/mol to 4% mol/mol using dilution steps
- 5L Aluminium alloy cylinders



Key modifications of existing facilities at CEM

- HCl pure bottle placed outdoor ---- safety
- New filling station for HCl only, (B)
- New facilities allow purging with dry N_2 before HCl filling ---- removing water inside lines
- Vented HCl is conducted to a water scrubber

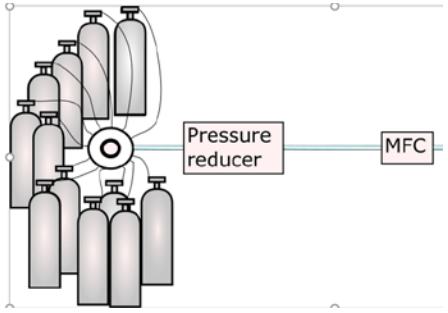
Analysis of the mixtures

- Technique: Micro-GC-TCD
- Lowest concentration mixture analysed: 350 µmol/mol
- Still far away from ISO 14687-2 value: 0.05 µmol/mol

Short term stability test static HCl mixtures

- Prepared in Aculife IV:
  -10 and 30 µmol/mol HCl in H_2
  -10 µmol/mol HCl in N_2

- Followed short term stability using CRDS (3 measurements in 9 days)
- Combined with MSB measurements
- Afterwards additional measurement using TDLS with spider (⇨ HCl mixtures in H_2 now empty 😟)



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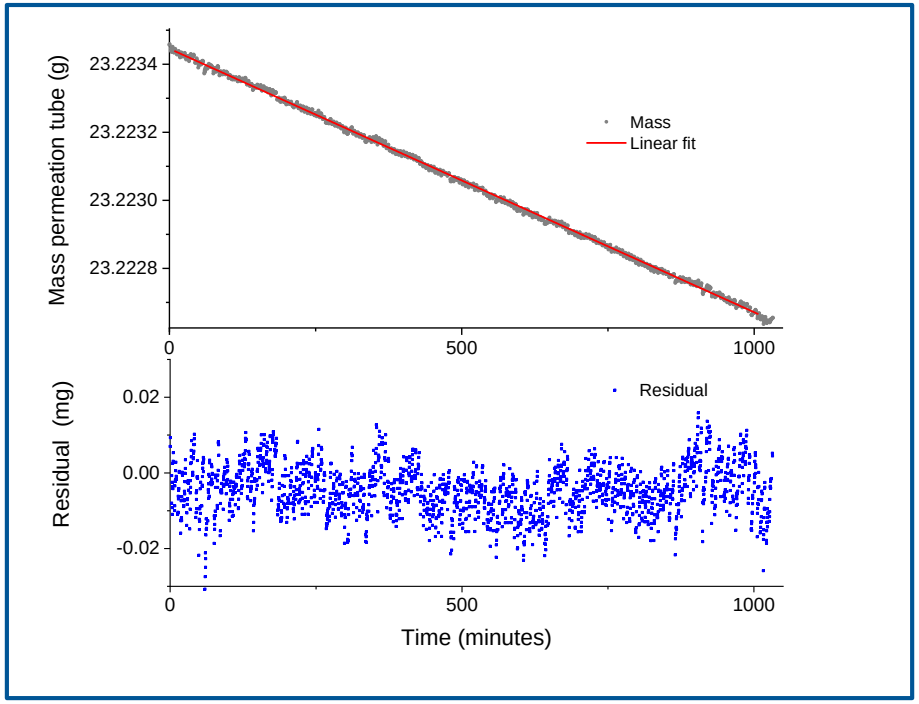
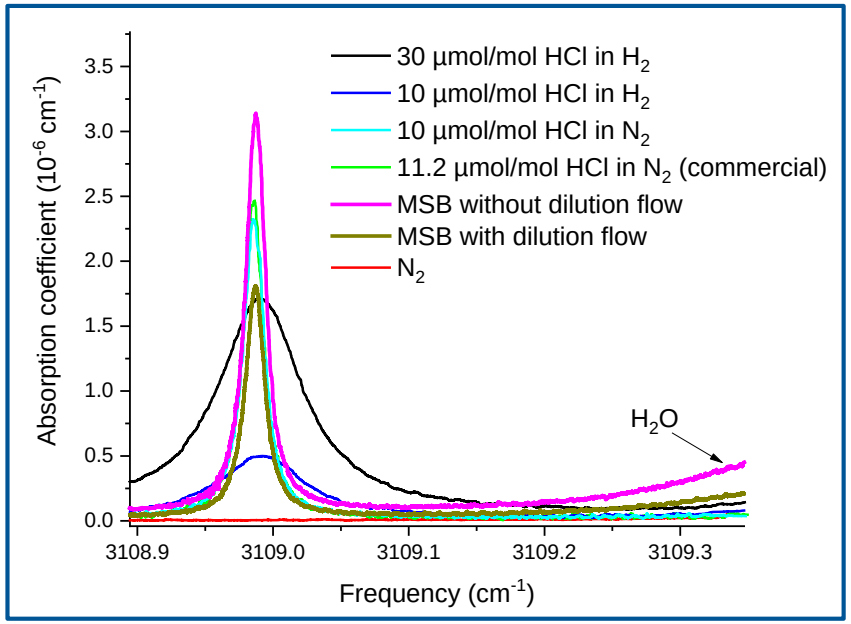
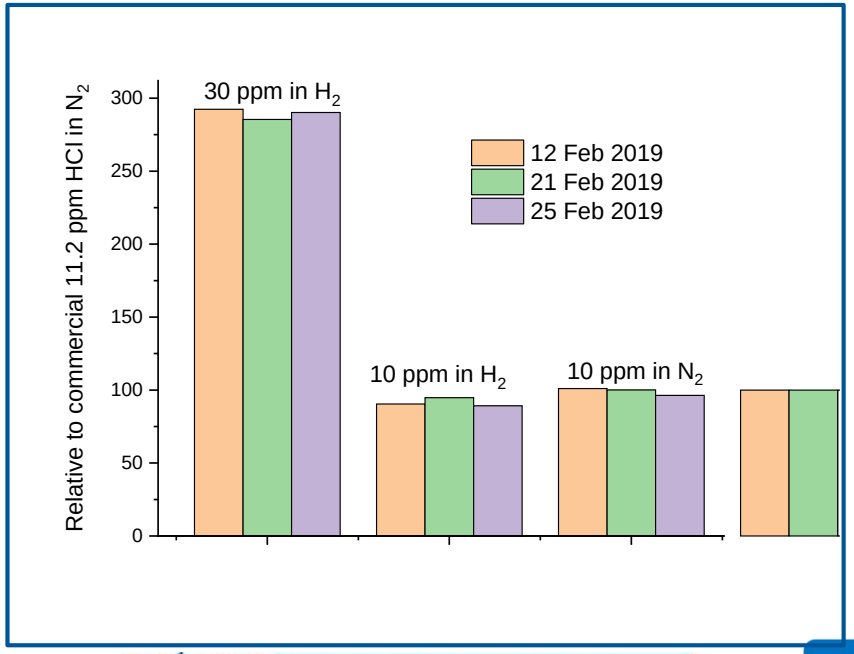
Static gas mixtures HCl in H_2 at VSL



Analysis MSB data in progress to assign HCl amount fraction





Challenges

- Perform long term stability for CO and HCl in H_2 gas mixtures
- Development of PRMs for impurities like ammonia, formic acid and formaldehyde; the analytical methods developed are sensitive enough to be able to assess stability for those components
- What is the minimum shelf life acceptable to industry
- For NMIs: to perform comparisons to underpin the measurement infrastructure

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THANK YOU

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