METROLOGY for HYDROGEN VEHICLES

Online Gas & Particle Analysers

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Workshop on hydrogen quality and flow metering for hydrogen fuel cell vehicles,
VSL, Delft, The Netherlands

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EMPIR EURAMET FCH

Overview

- State-of-the-art commercially available gas analysers
- MetroHyVe developments
- Inter-comparison validation methodology
  - Preliminary results
- MetroHyVe hygrometer response study
  - Significance of error or drift
- Points of consideration when purchasing commercial hygrometers for HRSs
- *Particle analysers*
- Available resources

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Measurement challenges

- To implement H_2 quality control methods specified in **ISO 19880-8**, development and trialling of online purity analysers must be performed

- HRS's will typically need to install instruments that can **continuously monitor key impurities** online to ensure harmful impurities never reach the FCEV's

- Measurement of **canary species** to guarantee global quality of the hydrogen provided

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Currently available gas analysers

Protea
technology leadership
in measurement solutions

Tigeroptics
High-Performance Gas Analyzers

MEECO

AquaVolt / AquaVolt +

M-i

Power+Energy
Fueling the Hydrogen Economy

V&F Analyse- und Messtechnik GmbH

MICHELL Instruments

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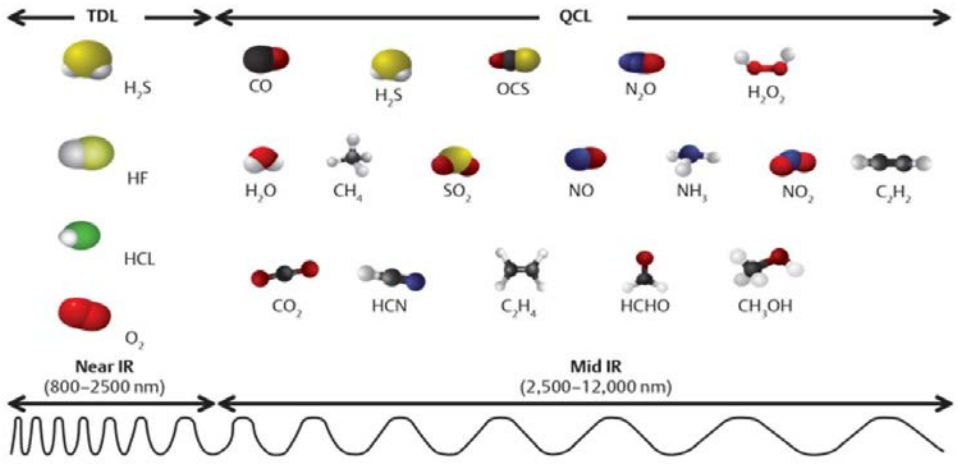
Under development within MetroHyVe

- Quantum cascade laser technology
- Measures up to 12 gases simultaneously
- Rosemount CT5800 certified for Class I, Division 2 hazardous areas
- Capability to measure H_2O and CO at ISO 14687 threshold levels



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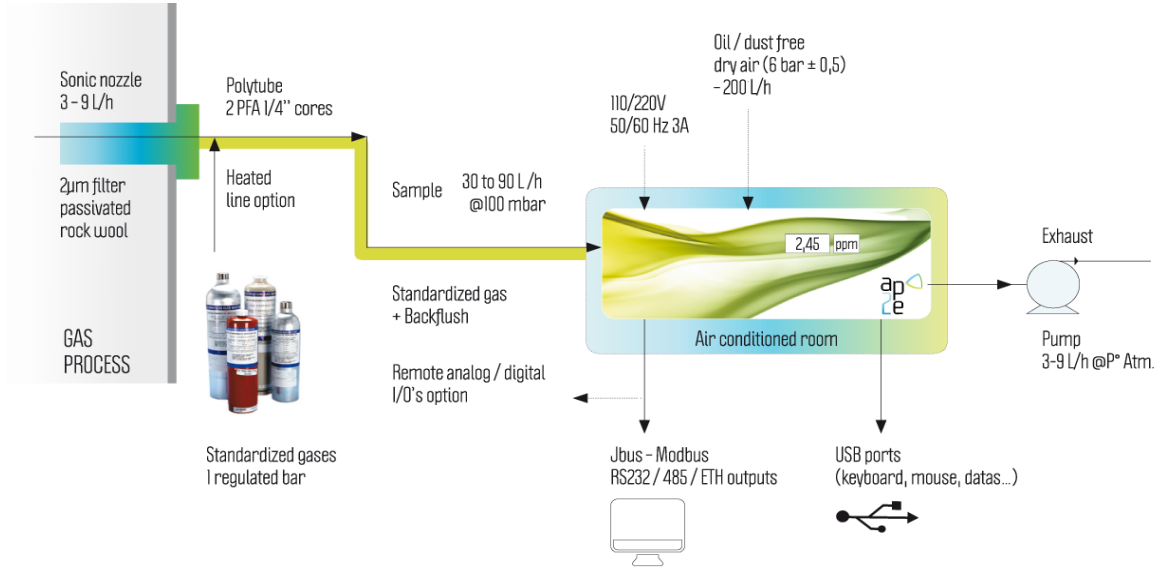
- OFCEAS IR laser technology
- Low pressure sampling enables direct measurement
- ATEX compliant configuration available
- Capability to measure H_2O, CO, O_2 and H_2S at ISO 14687 threshold levels



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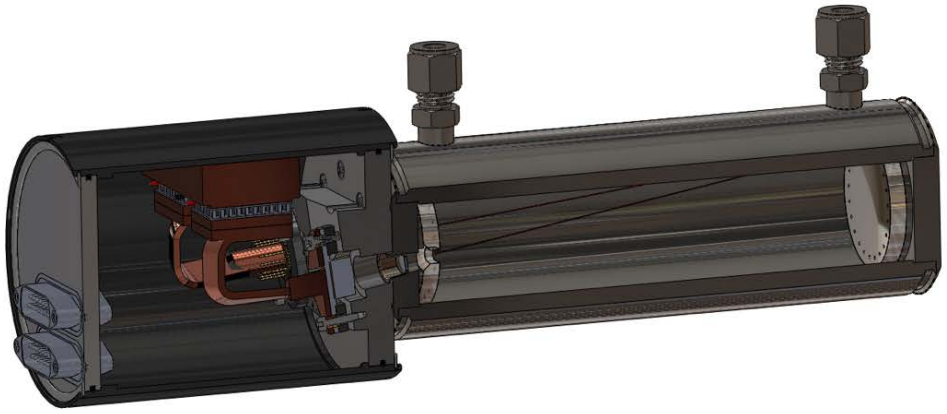
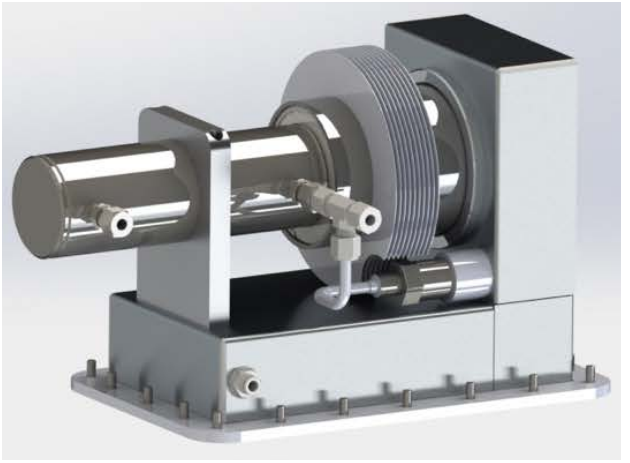
Under development within MetroHyVe

- IR spectroscopy
- 8 metre path length
- Absorbance spectrum produced according to Beer-Lambert law
- Capability to measure several species, including H_2O, CO, O_2 and H_2S at ISO 14687 threshold levels





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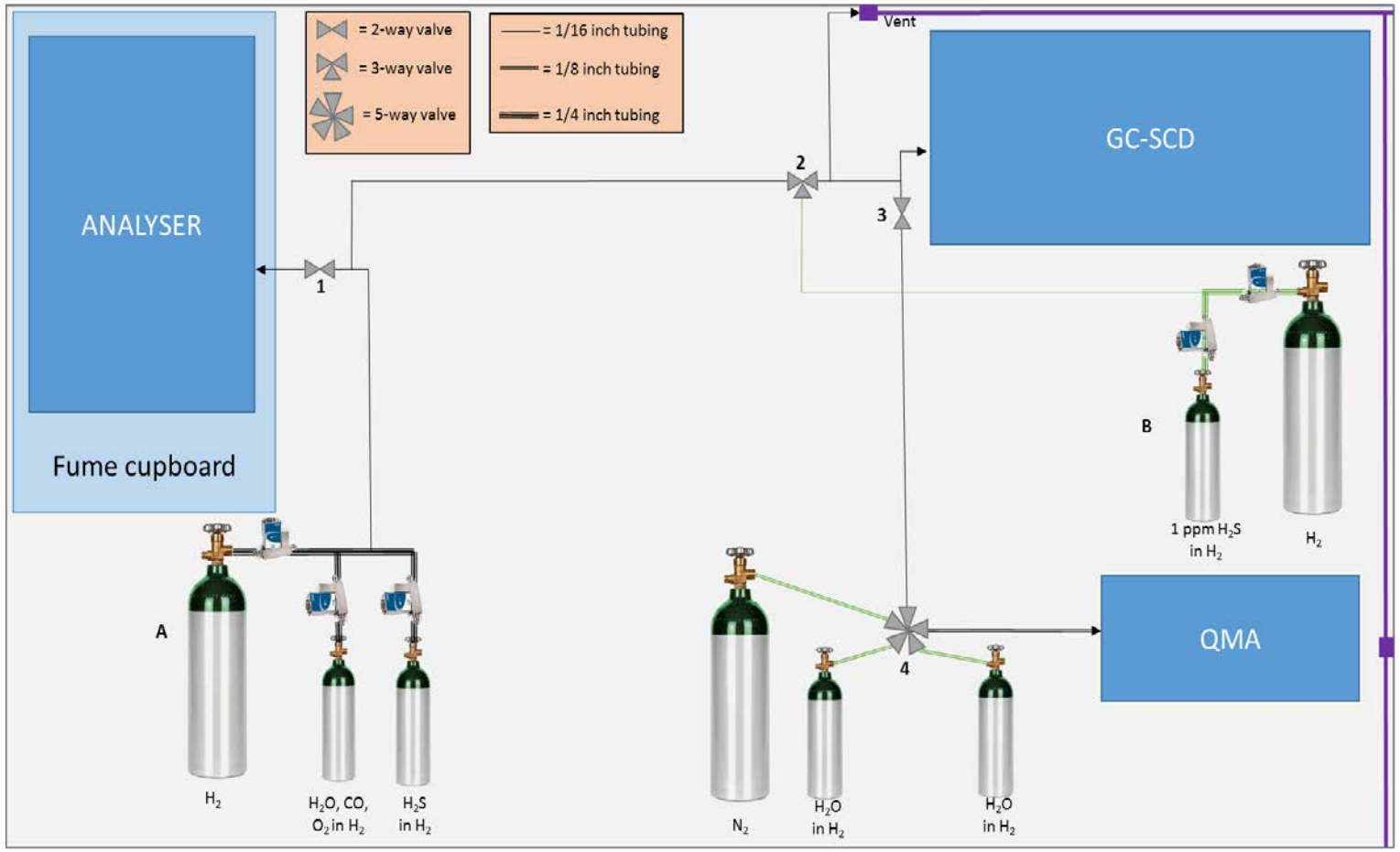
Importance of validating

- Latest spectroscopic developments = many options for online hydrogen purity analysers available
  - claim to be able to measure a number of / all impurities
  - evidence???
- Development of methods for validating H_2 quality control instruments as detailed in ISO 19880-8
- Instruments require testing or validating using traceable standards

Analyser Inter-comparison



- Traceable standards
- MFC dilution system
- Verification using PRMs + calibrated analysers
- H_2O, CO, O_2 and H_2S in H_2
- Conc. above & below ISO 14687 threshold levels

- Assessment of response time and accuracy

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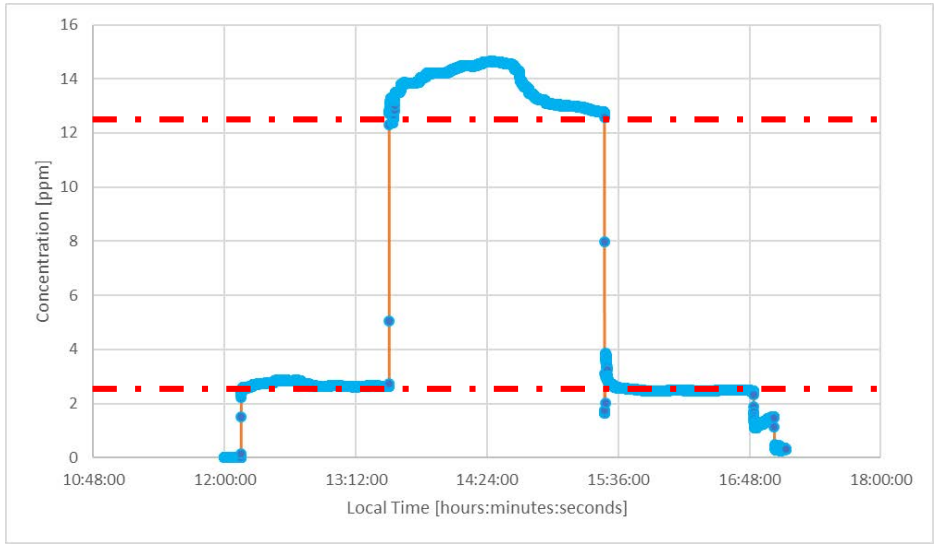
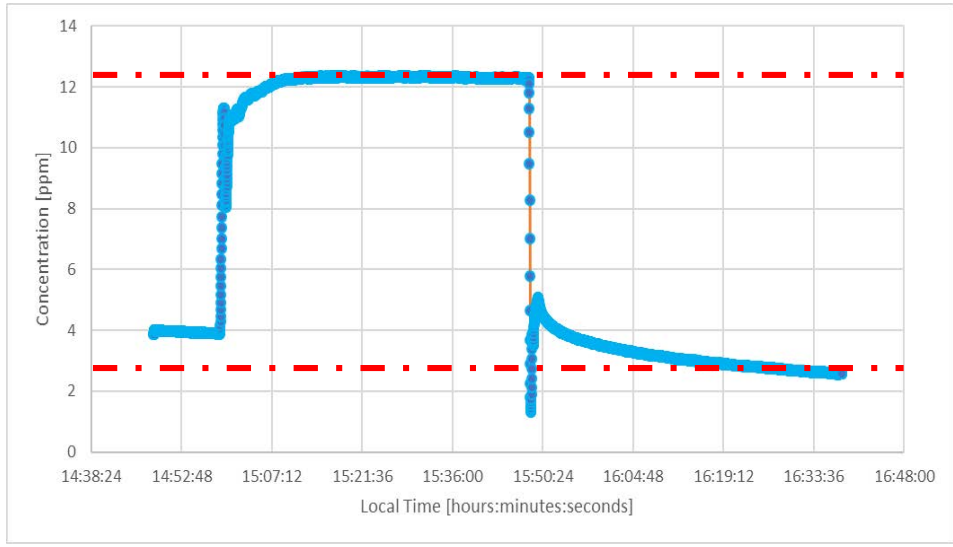
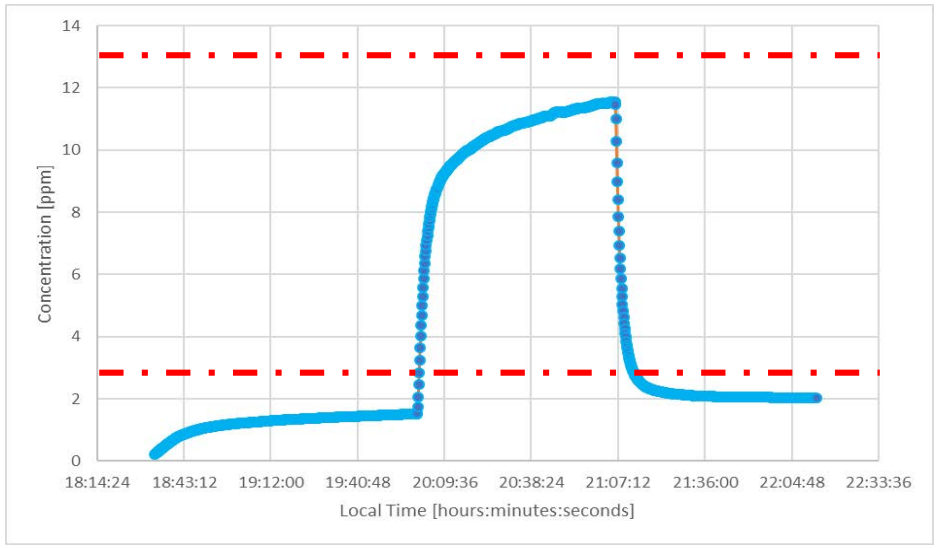
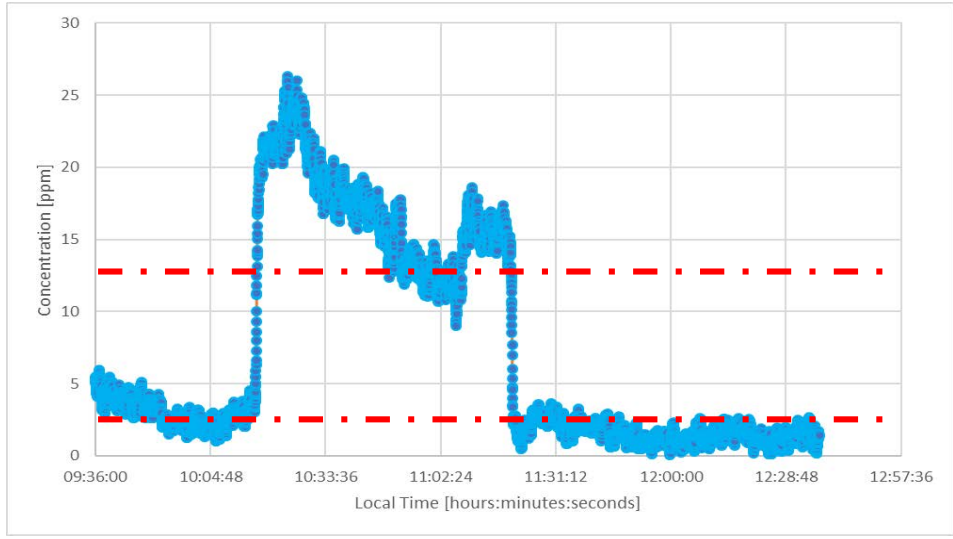
Inter-comparison results - preliminary





H_2O





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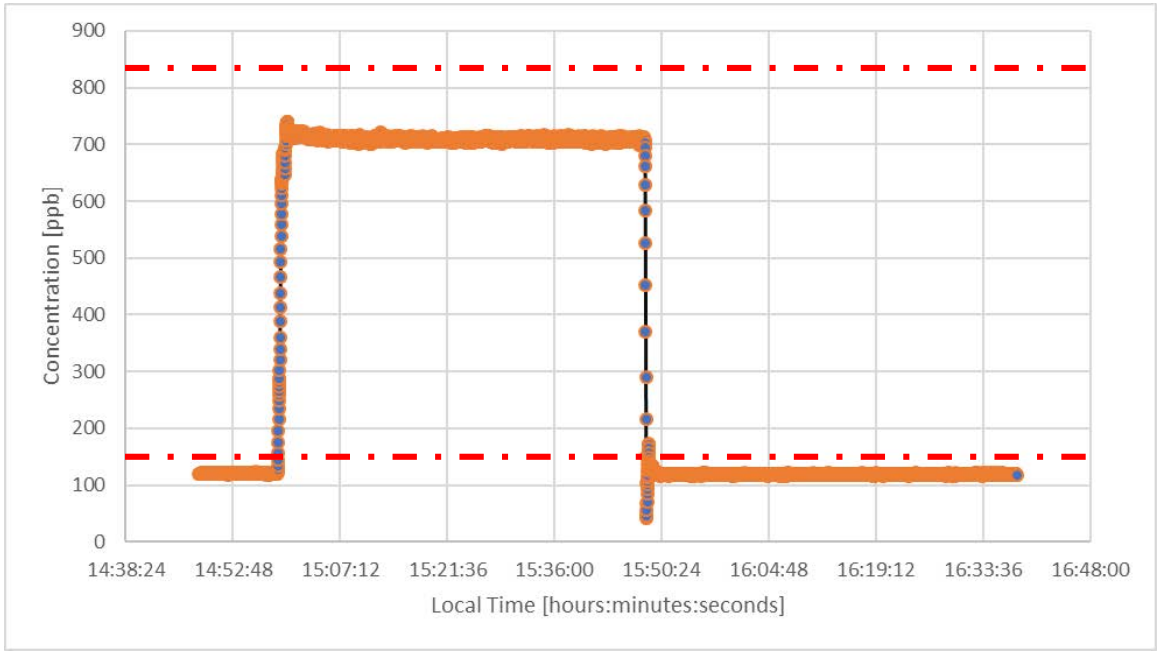
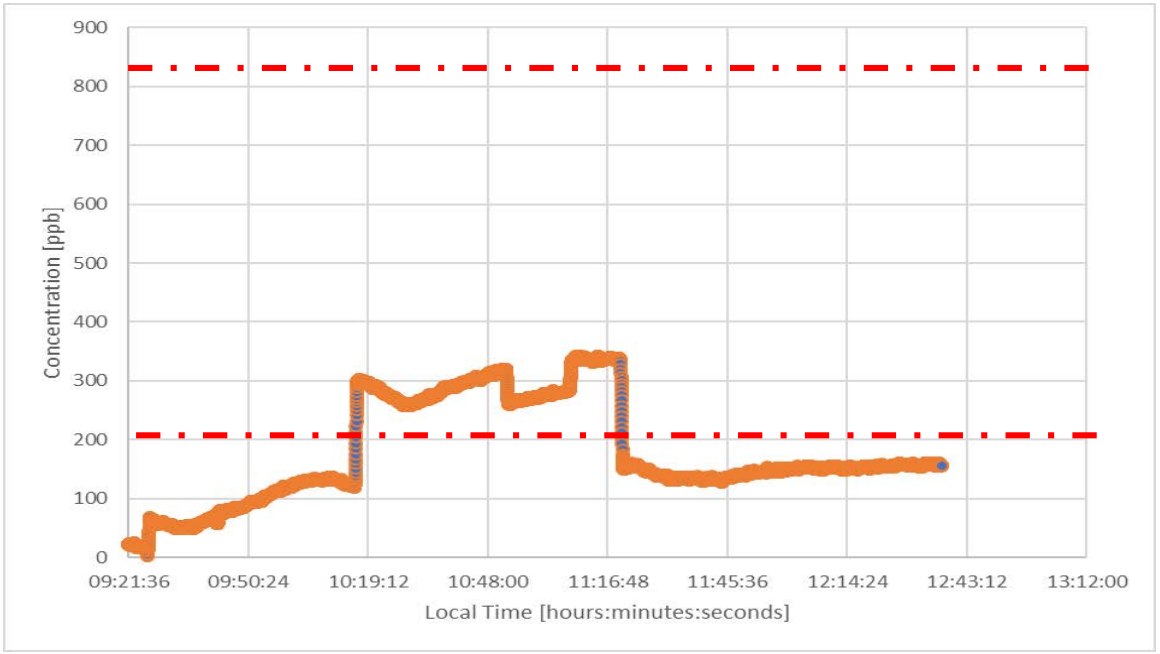
Inter-comparison results - preliminary

CO





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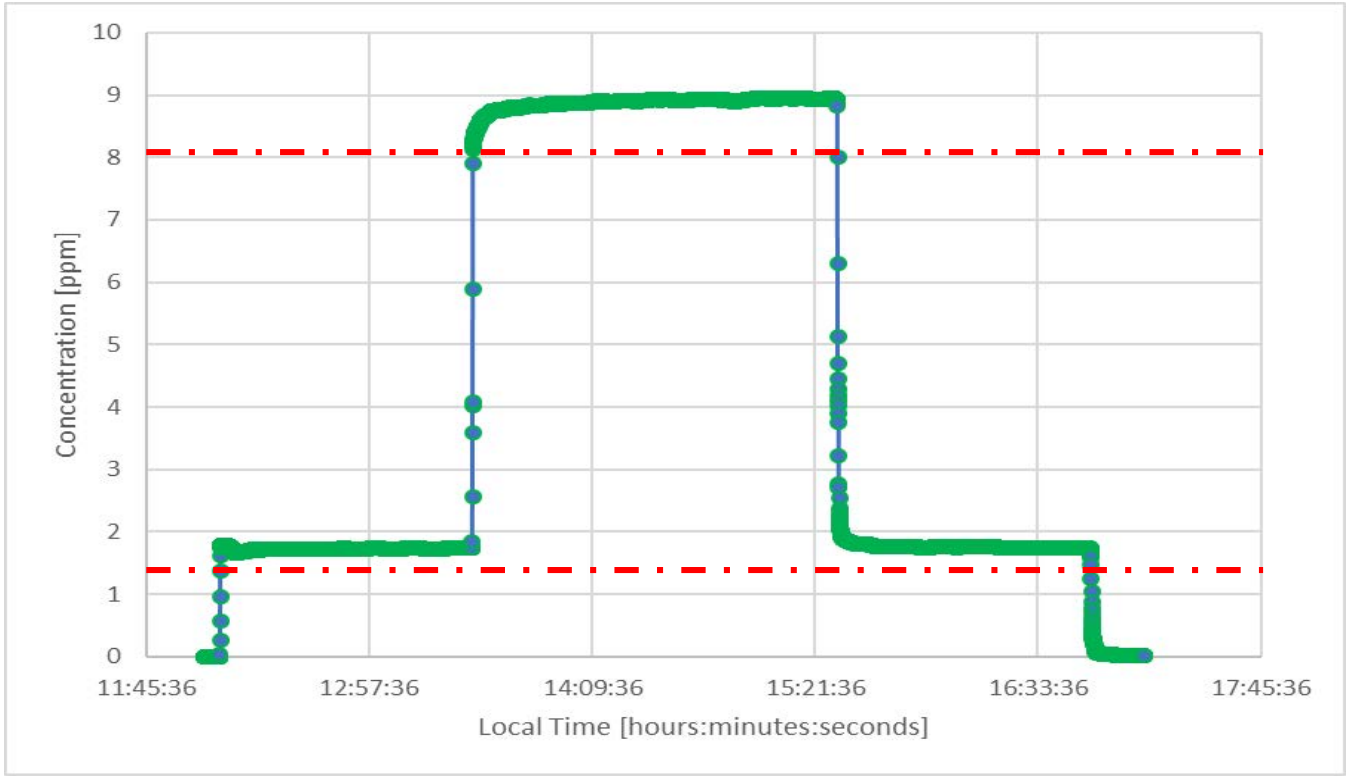
Inter-comparison results - preliminary

O_2



Hygrometers - moisture analysers for HRSs

- In HRS any water must remain in gas phase at -40 °C delivery temperature and at pressures exceeding 70 MPa (700 bar).
- ISO 14687-2 contaminant limit : 5 µmol mol^{-1} for water vapour.
- Although HRS hydrogen sampled periodically and analysed offline for quality -
- ISO 19880-8 hydrogen quality control, continuous online monitoring of water vapour using hygrometers – usually at lower pressure stage in HRS prior to compression to 70 MPa.

Source : Michell Instruments

- Metal-oxide dew-point probes typically used for continuous online monitoring of humidity

Source : GE Sensing

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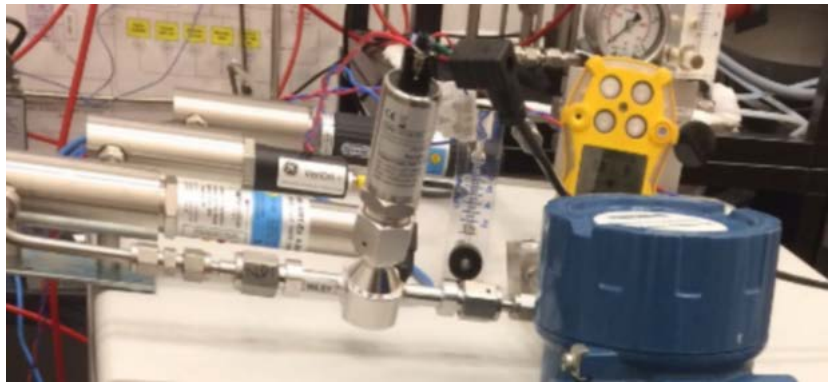
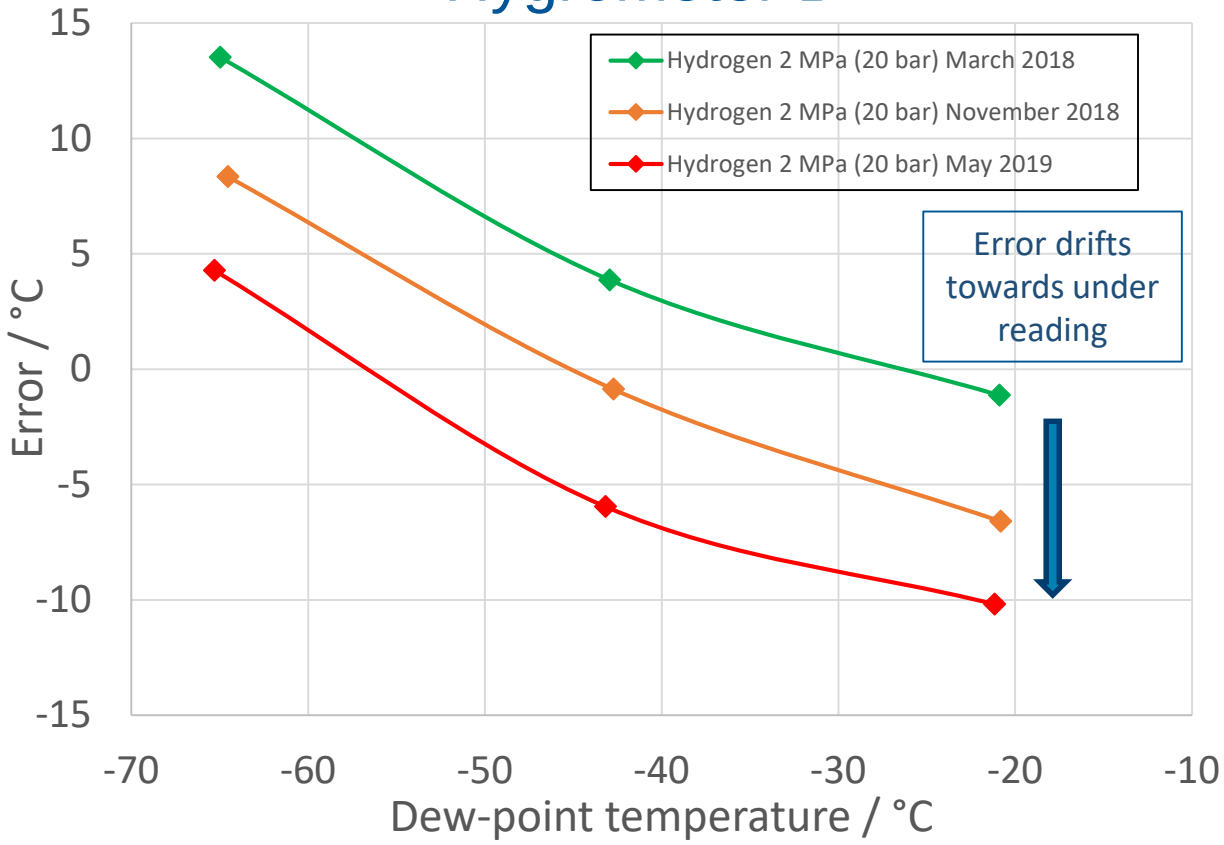
MetroHyVe Study of hygrometer response

- Six commercially available metal-oxide hygrometers loaned by collaborators.
- Including one in service in the ITM Power refuelling station at NPL used in H_2 at 2 MPa.
- Tests performed in nitrogen and hydrogen against the NPL multi-gas, multi-pressure humidity generator:
  - dew-point temperatures from -65 °C to -20 °C at pressures of 0.17 MPa and 2 MPa (20 bar)
  - corresponding to amount fractions of water vapour from 0.5 to 50 µmol mol^{-1} at 2 MPa.
- Evaluation of drift - full measurement set repeated after ~6 and ~12 months.

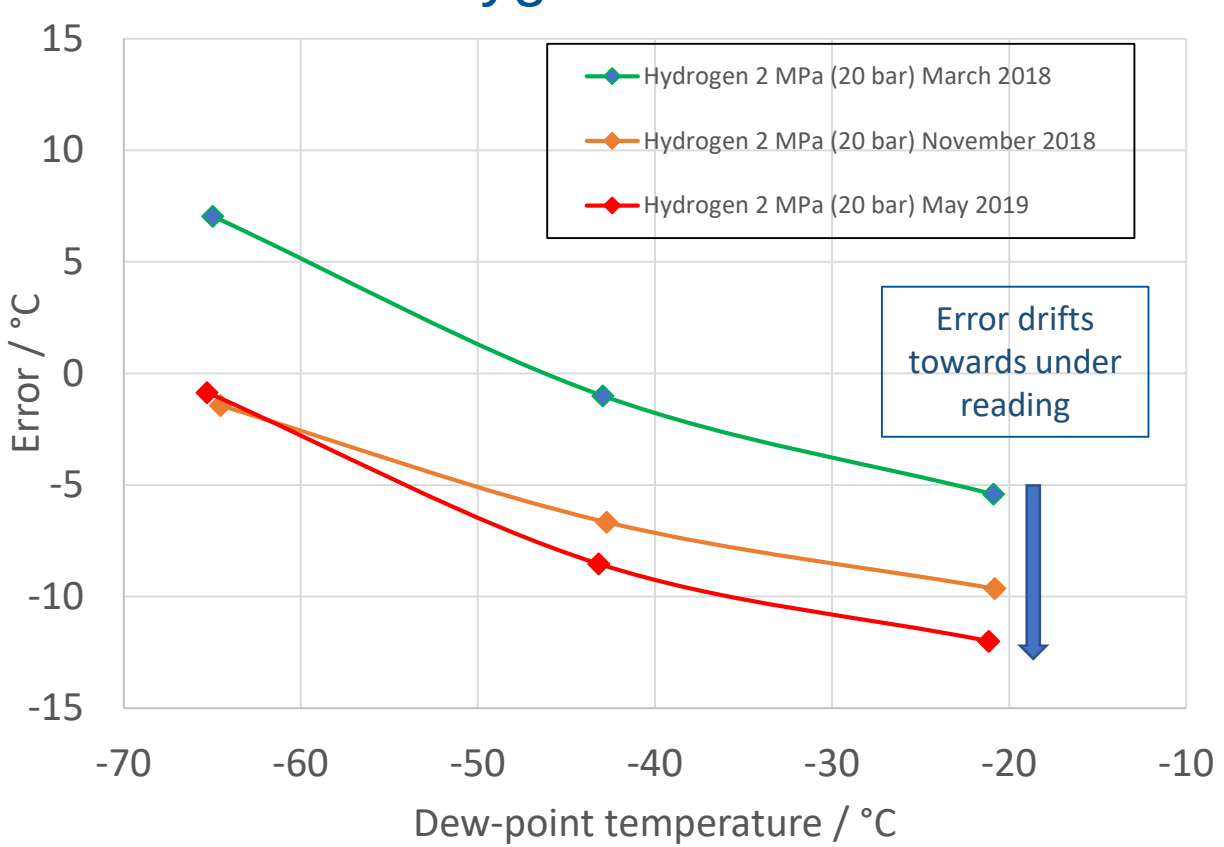


MetroHyVe Study of hygrometer response

Hygrometer D



Hygrometer E



- Note the significant initial error (green series), with or without any temporal drift
- Long-term drift between -7.5 ºC and -12.5 ºC after 12 months for majority of probes

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Significance of hygrometer error or drift of 5 °C to 10 °C

- Background gas change from nitrogen to hydrogen caused shift in reading of up to 4 ºC
- Pressure change from 0.17 MPa to 2 MPa caused shift in reading of up to 4 ºC

	Dew (frost) point (°C)	Amount fraction at 2 MPa (μmol mol^{-1})	
	-33	15	±10 °C
	-38	9	±5 °C
Limit →	**-43**	**5**	
	-48	3	
	-53	1.5	

- Errors and drift observed are both significant relative to requirement of <5 μmol mol^{-1}
- If sensors initially over-read, extra work will be done to dry H_2 – unnecessarily
- If sensors drift to under-read, risk that H_2 will be wetter than expected

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Humidity sensors good practice guide

- Measurement uncertainty factors applicable to corrected humidity values should be carefully considered including:
  - The calibration uncertainty of the hygrometer
  - Long-term hygrometer drift
  - Pressure sensitivity of the hygrometer
  - Sensitivity of hygrometer to background gas
  - Equilibration (settling time, response time)

- Where possible ensure hygrometer is calibrated using **hydrogen** at the anticipated **pressure of use** (to replicate operating conditions) and **temporal drift** is estimated and included in the measurement uncertainty.

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Online Particle Analysis - Measurement Need

ISO 14687 includes a specification for particles which must have less than 1 mg kg^{-1} for hydrogen provided to full cell vehicles. In order for laboratories to provide a suitable service for measuring particles, there must be a traceability chain established (which currently does not exist). The current method used for measuring particles in hydrogen is by placing particulate filters in the stream of supplied hydrogen and weighing the filters before and after mass is collected. However, the approach used by industry is not proven to be traceable to National Standards which would be required to guarantee that the measurements are correct. There are commercially available techniques that could be employed to perform online measurement of particulates directly at the station allowing for an immediate result to be provided to the customer, however these techniques need to be developed and validated for hydrogen at high pressures.

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EMPIR Project: MetroHyVe

- Online measurement of particulate mass concentration and sizing
  - Particle size and concentration measurements using an Optical Particle Counter (OPC)
  - Possibility of an online mass measurement using a Tapered Element Oscillating Microbalance (TEOM)

'The EMPIR Metrology for Hydrogen Vehicles will be the first large scale project of its kind that will tackle the four measurement challenges that currently prevent the industry from meeting requirements set by International Standards such as flow metering, quality control, quality assurance and sampling.'

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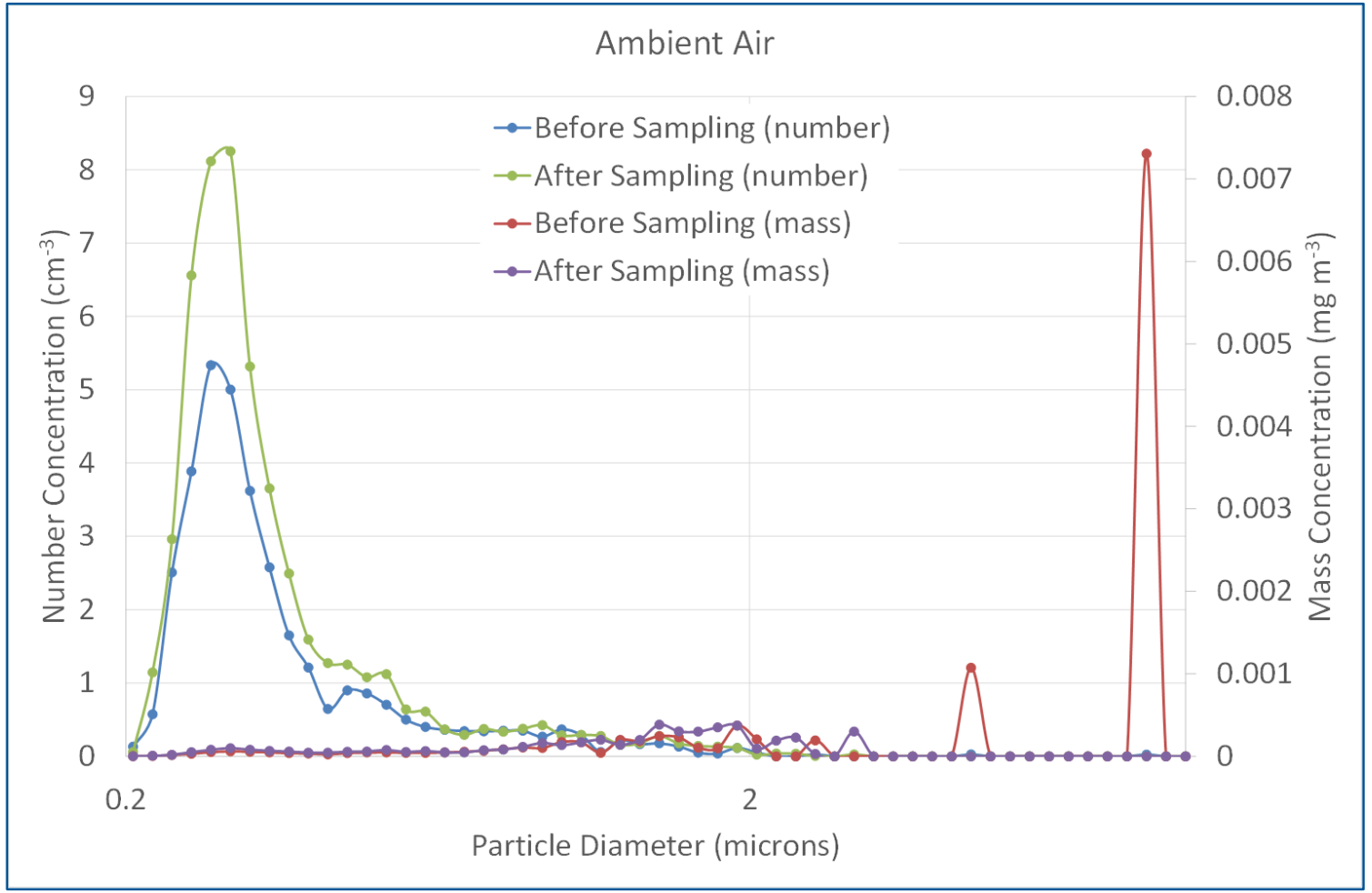
Online measurement of particulate mass concentration and sizing

- Real time size and number concentration measurements in a range of 0.2 Microns - 10 Microns
- Particle number concentrations from 0 - 80K P/cm^3
- Samples at 5 l/min
- Separate sampling head and body
- 30 meter fibre optic cables

Online measurement of particulate mass concentration and sizing



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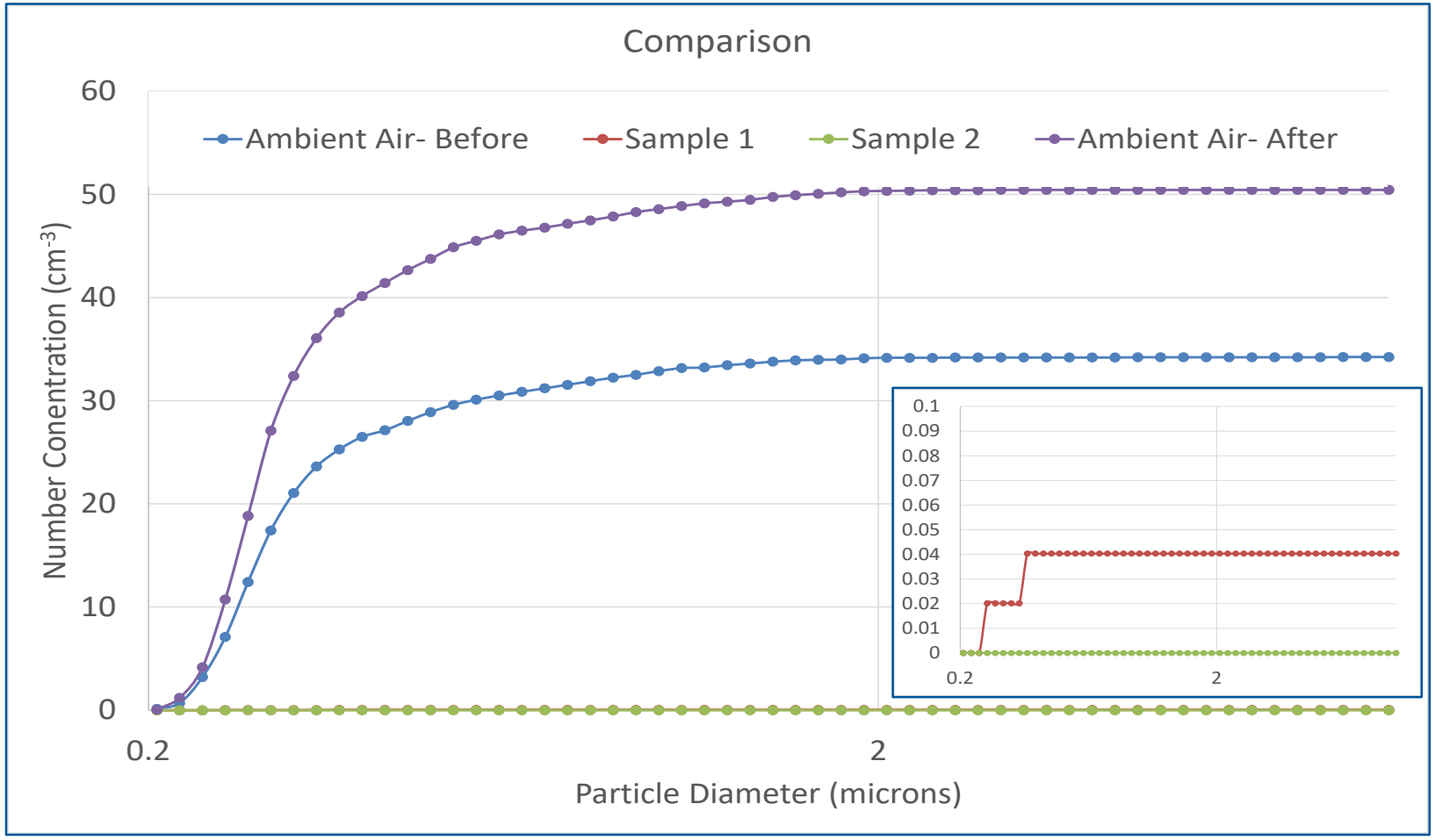

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Online measurement of particulate mass concentration and sizing

- A thin glass tube with a filter is oscillated at a measured frequency
- Carrier gas enters the TEOM and passes through the oscillating filter trapping any particles
- The mass of the particles on the filter changes the frequency of oscillation
- This change in oscillating frequency can be linked to the mass of particles on the filter

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Online measurement of particulate mass concentration and sizing

- Leak testing of the TEOM
  - Air
  - Helium (increased penetration)
- Hydrogen use with TEOM
  - Controlled laboratory environment
- Real time mass measurement at HRS

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Conclusions

- Online measurement of particulate mass concentration and sizing
  - Particle size and concentration measurements using an Optical Particle Counter (OPC)
  - Possibility of an online mass measurement using a Tapered Element Oscillating Microbalance (TEOM)

- The OPC has been used at the HRS at NPL
- Safety issues were overcome
- Negligible particle concentrations detected in the hydrogen fuel
- TEOM has been purchased and will be modified and tested for use in an explosive environment

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Available resources

Reports are available on the project website www.metrohyve.eu

- A3.2.2/3: Good practice guide on calibrating commercial humidity sensors for use at HRSs

- A3.4.2/3: Report recommending the best strategies for developing and implementing low cost sensors for performing online measurement of impurities in hydrogen at refuelling stations

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THANK YOU

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