HyCoRA

Recent development on hydrogen impurity analysis

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2nd OEM Workshop – 9th October 2015

- **New developments on hydrogen impurities**
- New capability at NPL
- Perspective for the NPL enrichment device

Hydrogen Analysis at NPL

cavity ringdown spectroscopy

Quartz crystal microbalance

Water

Validation ongoing

Gas chromatography with thermal conductivity detector

Helium

Under development…

Formaldehyde

Formic acid

Ammonia

Gas chromatography with mass spectrometer detector (or cavity ringdown spectroscopy)

Formaldehyde under validation

Hydrocarbons

Carbon dioxide

Methane

Carbon monoxide

Gas chromatography with methaniser and flame ionisation detector

Oxygen

Nitrogen

Argon

Gas chromatography with helium discharge ionisation detector

Sulphur Compounds

Gas chromatography with sulphur chemiluminescence detector

UKAS accredited ISO 17025

New development on hydrogen impurities

NPL National Physical Laboratory

Reactive gases

• **Water**	**(5 µmol/mol)**
• Total hydrocarbons	(2 µmol/mol)
• Oxygen	(5 µmol/mol)
• Carbon dioxide	(2 µmol/mol)
• Formic acid	(0.2 µmol/mol)
• Carbon monoxide	(0.2 µmol/mol)
• Ammonia	(0.1 µmol/mol)
• **Total halogenated compounds**	**(0.05 µmol/mol)**
• **Formaldehyde**	**(0.01 µmol/mol)**
• Total sulphur compounds	(0.004 µmol/mol)

Inert gases

• Helium	(300 µmol/mol)
• Nitrogen	(100 µmol/mol)
• Argon	(100 µmol/mol)

Non-gases

• Particulates	(1 mg/kg)

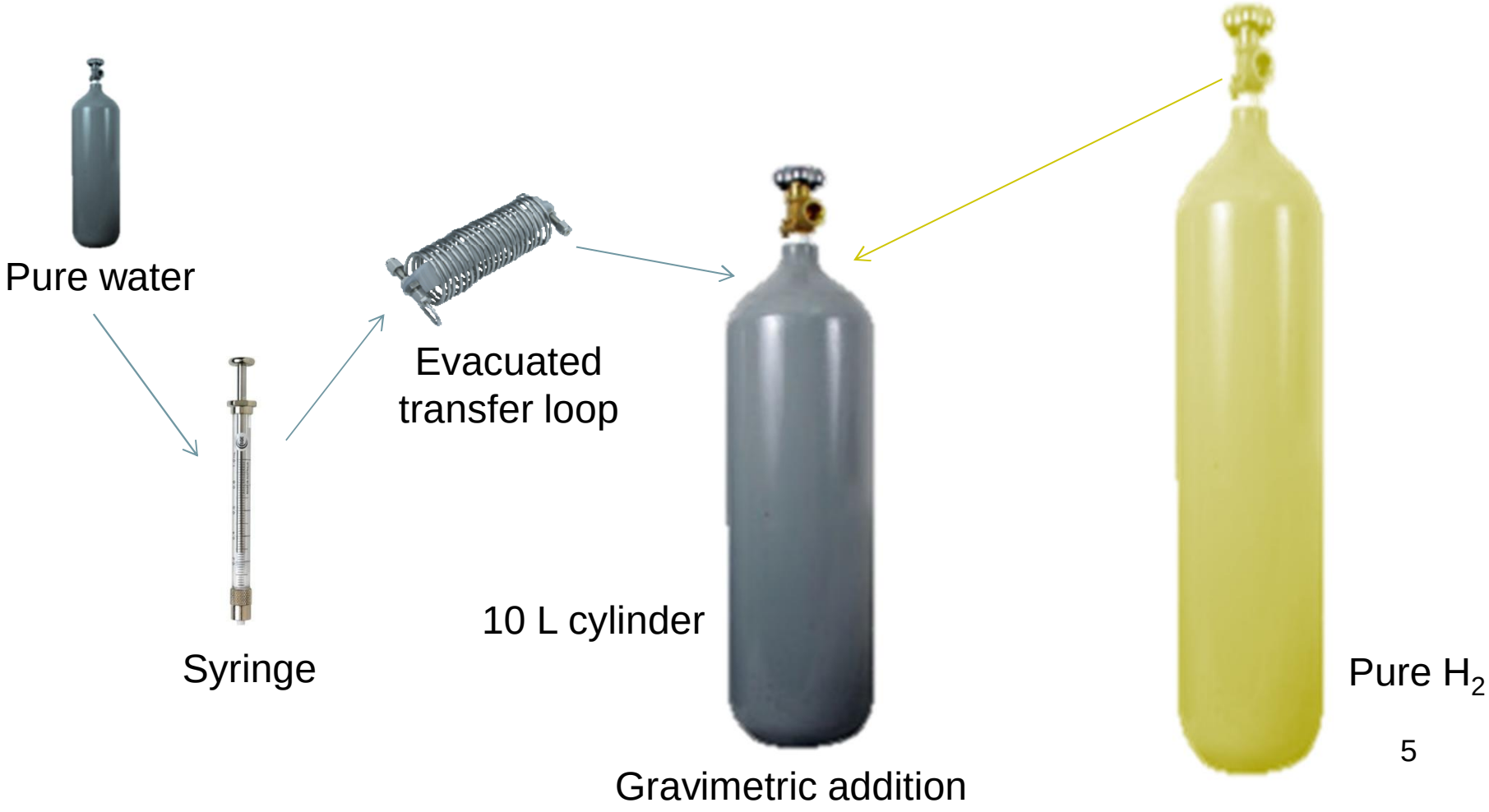
ISO International Organization for Standardization

ISO 14687-2:2012

Hydrogen fuel – Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles

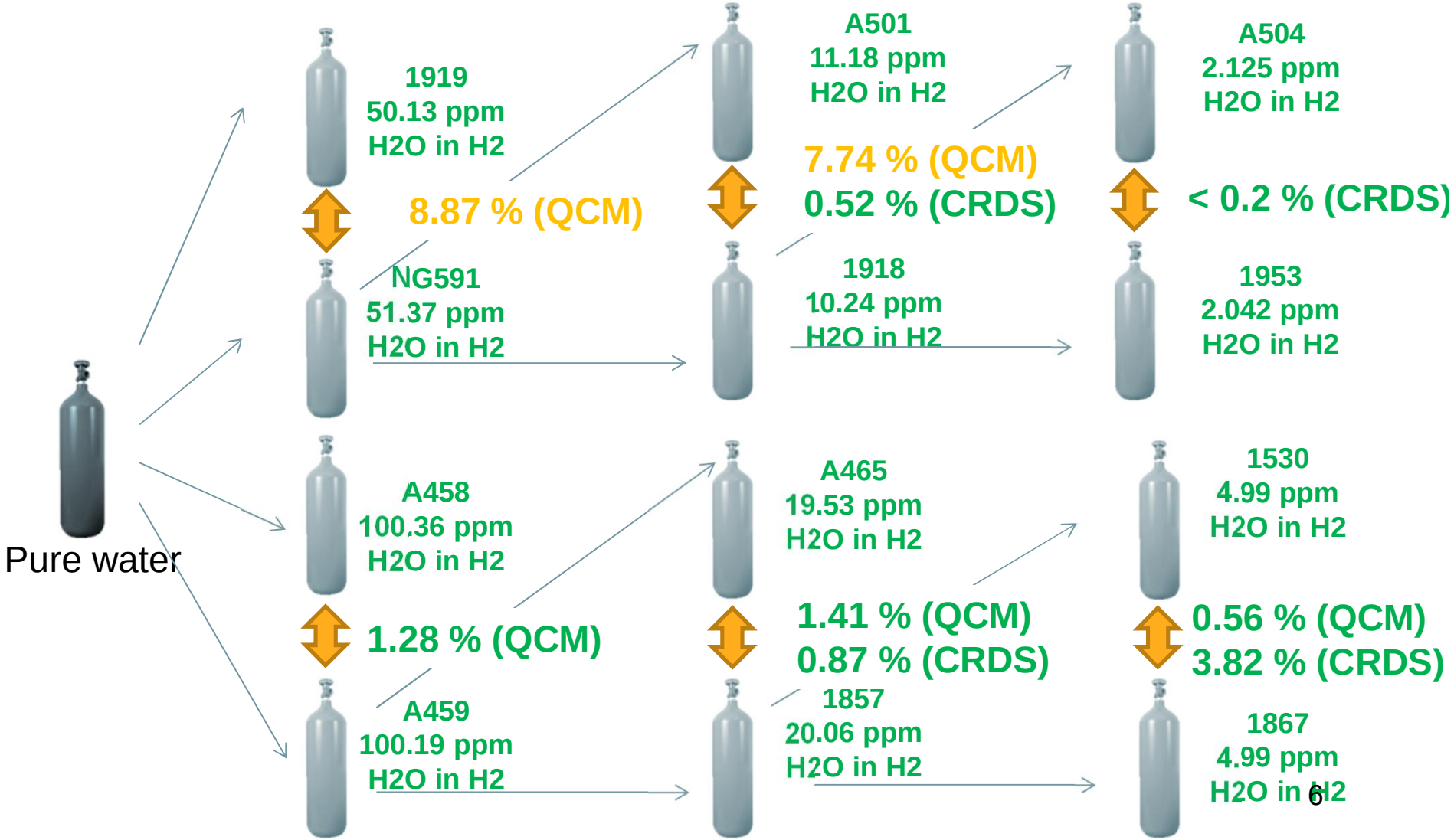
Water analysis

Water is added to the gas cylinder using a syringe and loop

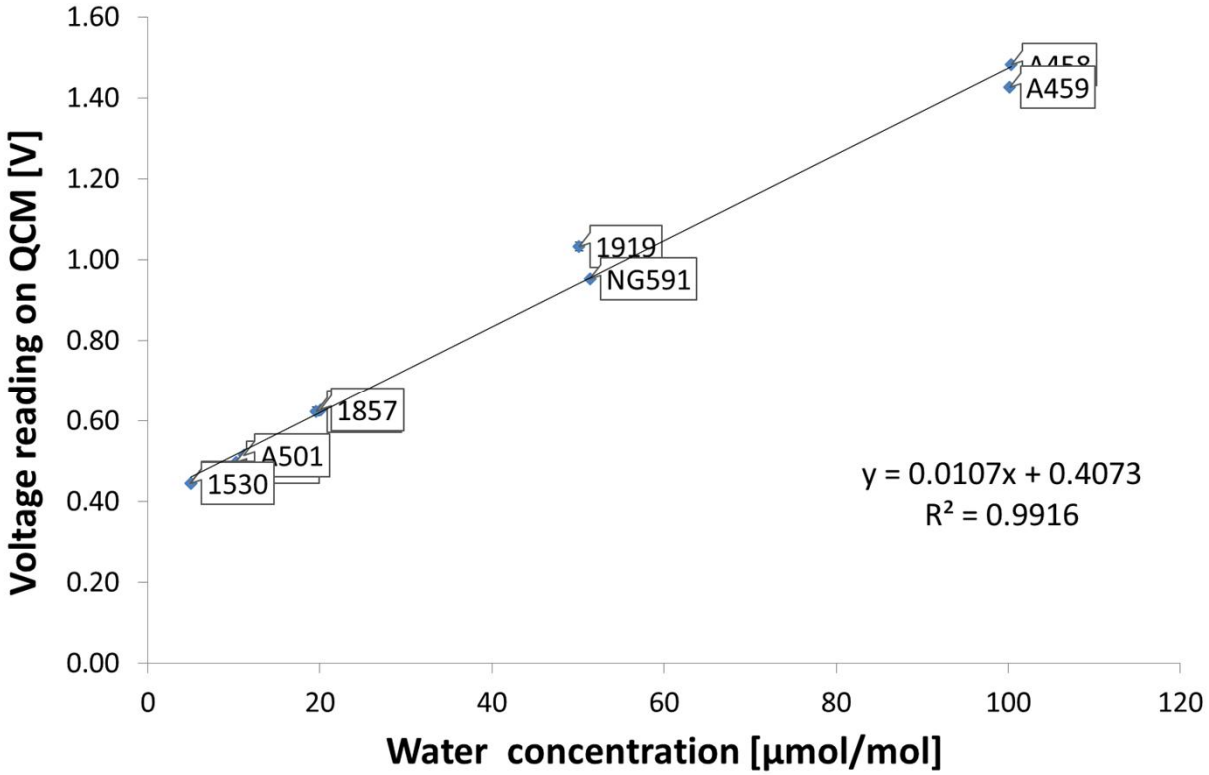


Water analysis

Primary reference materials for water content in hydrogen

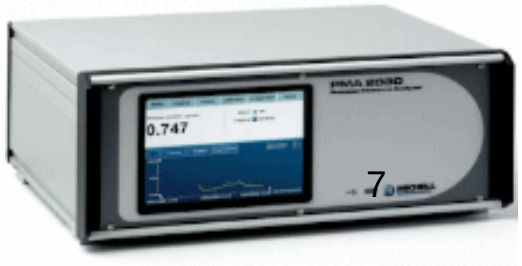


Water analysis – Linearity – QCM

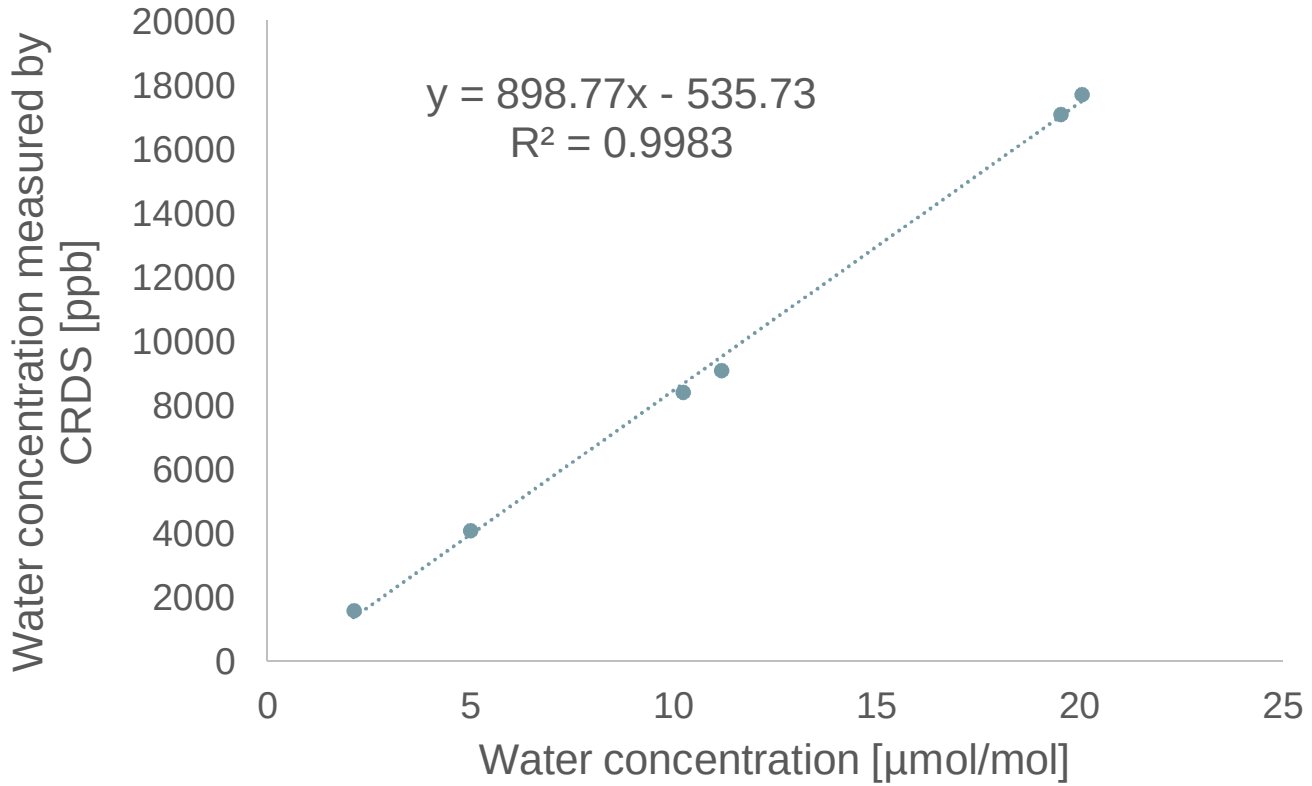


Acceptable linearity from 5-100 ppm water in H_2
Repeatability of slope: ± 30 % (day to day effect on instrument sensitivity)
Repeatability of analysis: < 1 %

Intermediate precision: study ongoing
Trueness: comparison with primary method (Dew point)



Water analysis – Linearity – CRDS



Good linearity from 2-20 ppm water in H_2
Repeatability of slope: ± 5 %
Repeatability of analysis: < 2 %

Intermediate precision: study ongoing
Trueness: comparison with primary method (Dew point)

Water analysis – Trueness assessment
Comparability of matrix N_2 and H_2

Compare our mixtures against dynamic standards and instruments against primary standard method:

Dew point analysis (primary method)

Certify

H_2 controlled atmosphere

N_2 controlled atmosphere

Comparability of matrix N_2 and H_2
(correction factor between the matrix)

Trueness calibration

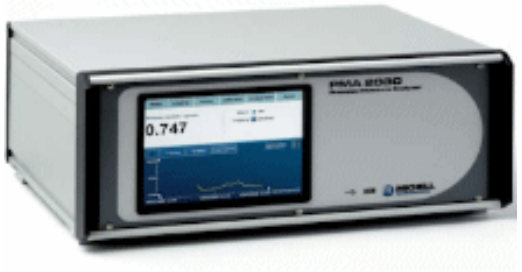
Certification

Standard H2O in N_2

5 - 20 ppm H2O in H_2

Water analysis - Summary

- CRDS
  - Linear 2-20 ppm
  - Repeatable
  - Low day-to-day effect
  - Trueness ongoing
  - Not accredited ISO17025 at NPL



- QCM
  - Linear: 5-100 ppm
  - Repeatable
  - Significant day-to-day effect
  - Trueness ongoing
  - Method accredited ISO17025 at NPL

Method extensively validated by end of October 2015

Formaldehyde analysis

NPL capability:

GC-PDHID: under development

Methaniser GC-FID: method not fully validated (theoretical LOD ~ 10 ppb)

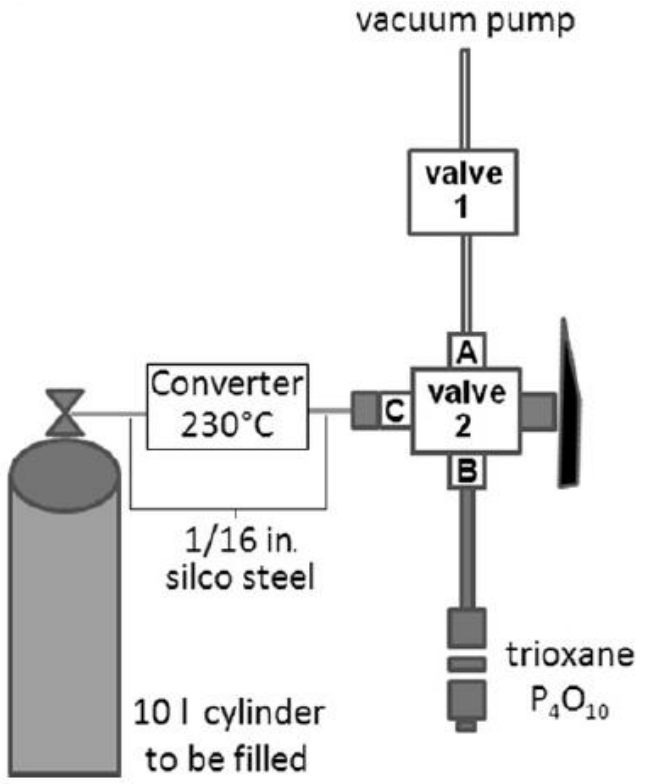
GC-MS with pre-concentration: validated by another NPL team (LOD < 10 ppb)

FTIR: only qualitative, identification

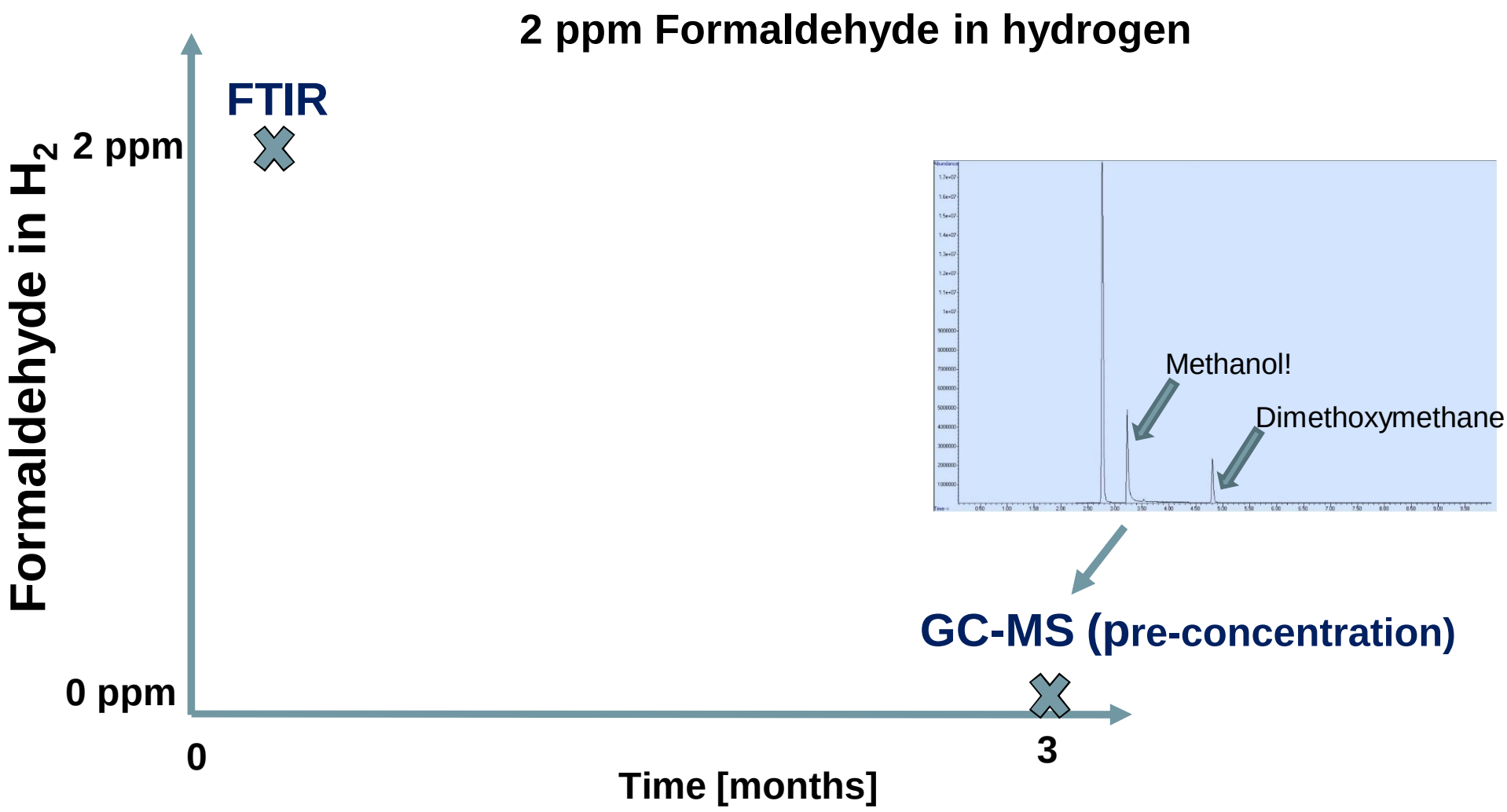
Formaldehyde analysis

Produce and validate formaldehyde standards at 2 ppm and 10 ppm in hydrogen matrix

- Pure formaldehyde is not stable
  (100% formaldehyde cannot be purchased easily)
- Formaldehyde gas standards can be derived from trioxane
- System is built for producing standards in nitrogen
- **Two gas mixtures containing 2 ppm and 10 ppm of formaldehyde in hydrogen have been prepared**



Formaldehyde analysis - 1st observation



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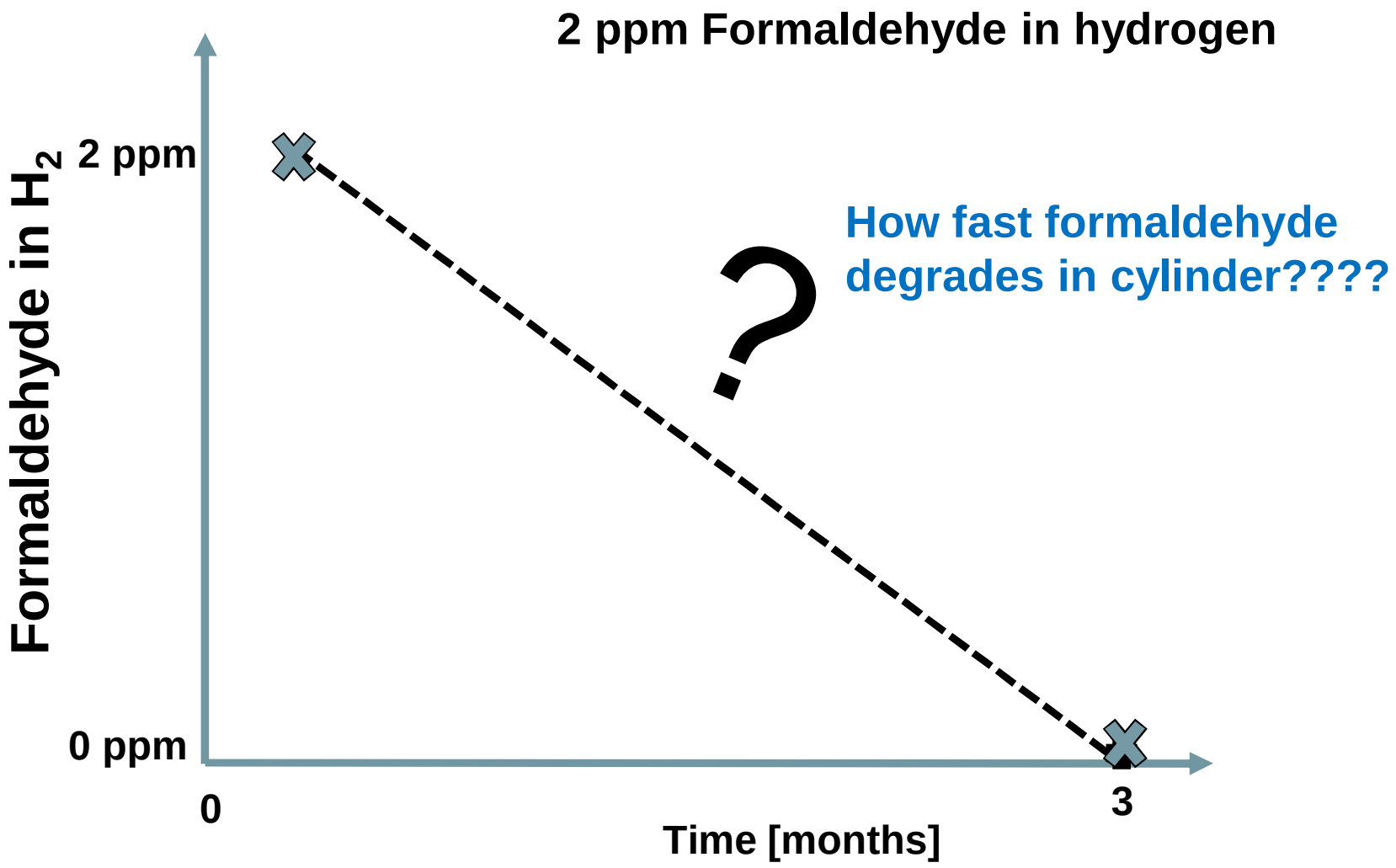
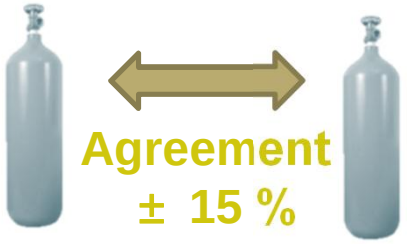


Formaldehyde analysis – Stability study

National Physical Laboratory

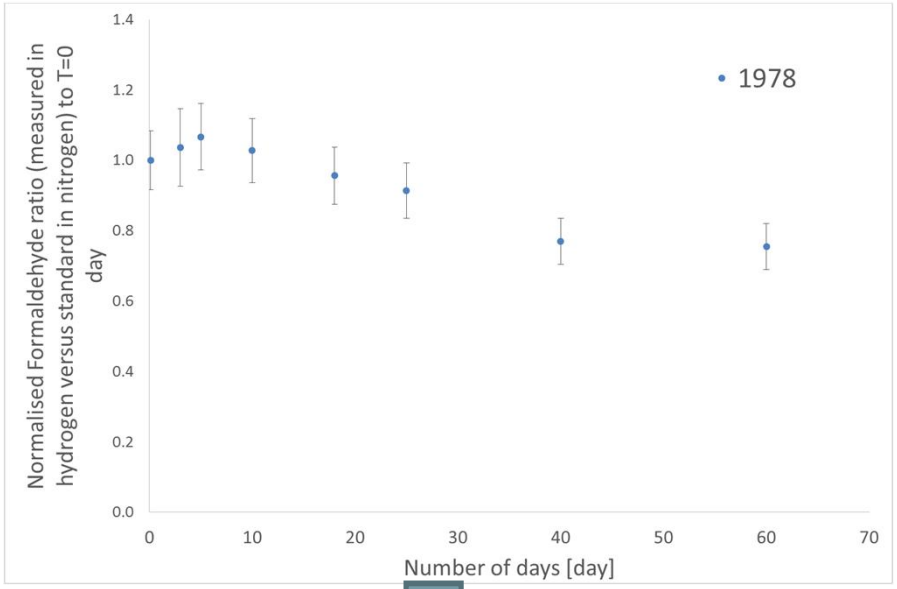
New standards:

10 ppm formaldehyde in H_2



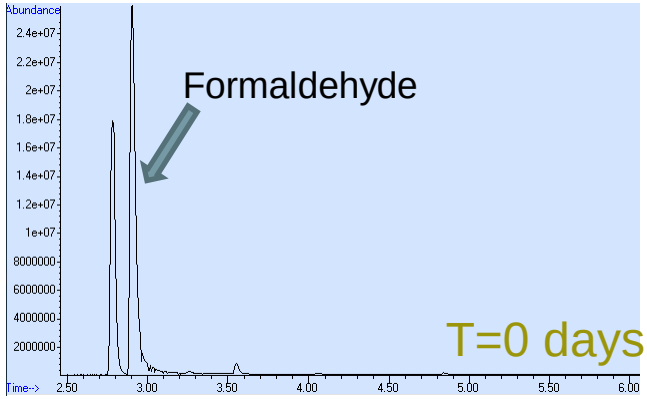
10 ppm formaldehyde
in H_2

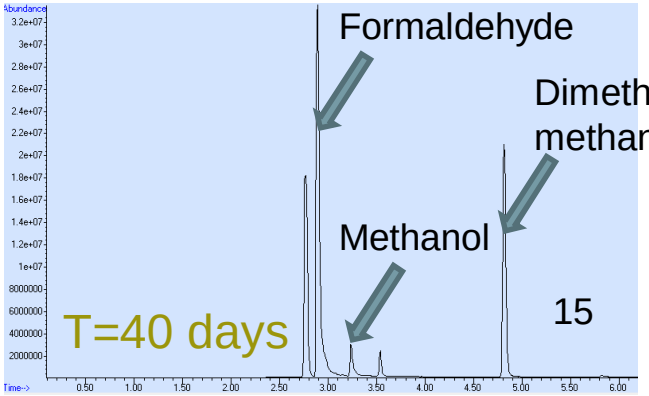
Degradation monitoring: FTIR, GC-MS, methaniser GC-FID



Slow degradation

(loss of 10 – 20 % within 2 months)





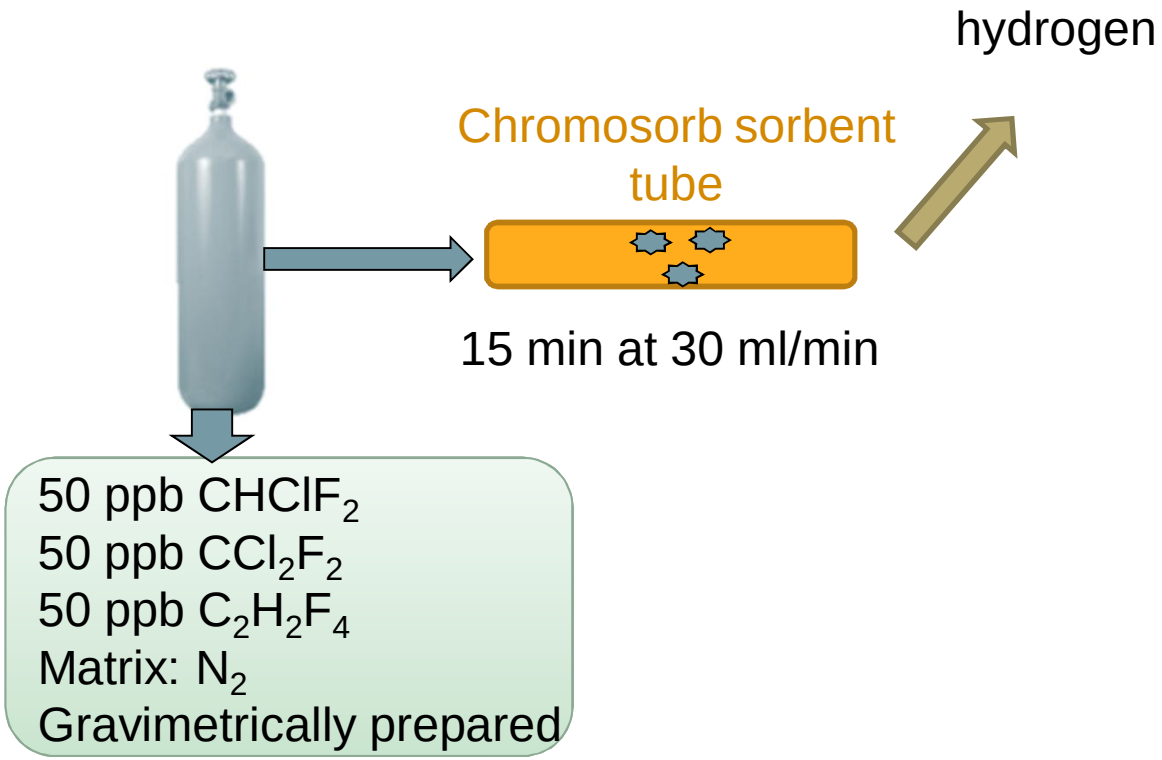
Formaldehyde analysis - Summary

- Analysis of formaldehyde in hydrogen
  - Several methods under development/validation
  - Gas standard for Formaldehyde in H_2

- Stability of formaldehyde in hydrogen
  - 2 ppm formaldehyde in H_2 → 0 % after 3 months
  - 10 ppm formaldehyde in H_2 → stable after 1 month
    - Study ongoing until complete degradation

Halogenated compounds in hydrogen

- Analysis of 3 freons gases ($CHClF_2$, CCl_2F_2, $C_2H_2F_4$) in N_2 using ThermoDesorption GC-MS (TD-GC-MS)



TD-GC-MS

Halogenated compounds in hydrogen

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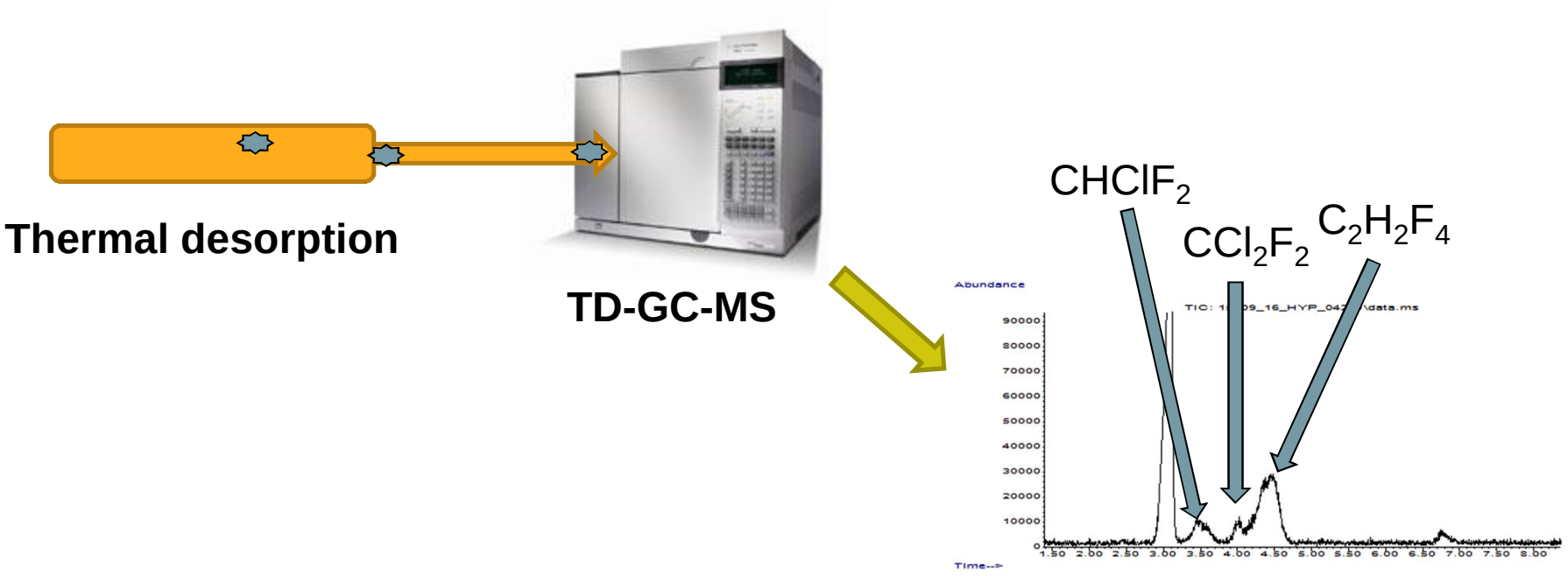


Chromatogram

Halogenated compounds in hydrogen

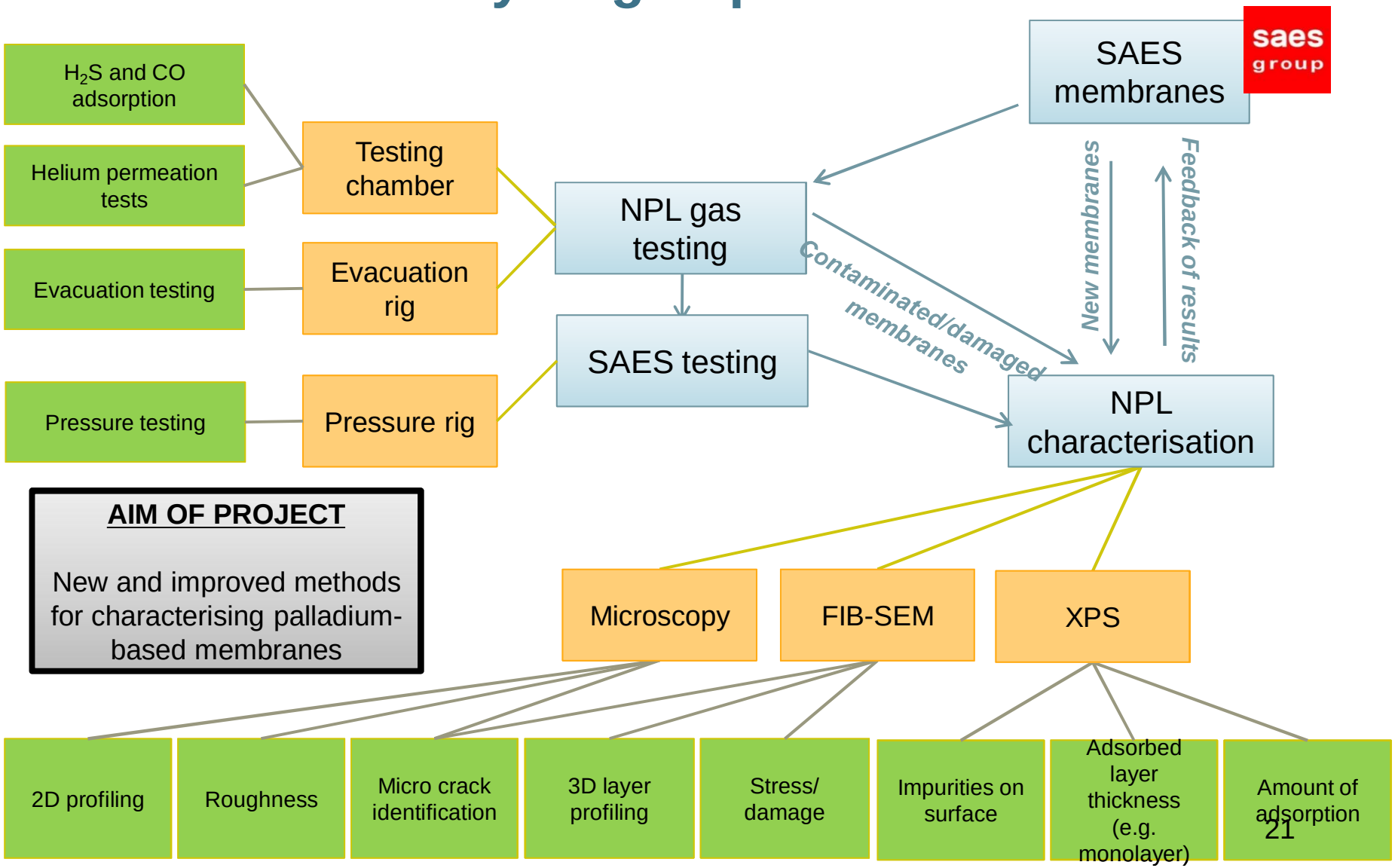
- Capability to analyse halogenated compounds at low concentration in gas

- Preparation of standard of halogenated compounds in hydrogen → to be evaluated
  - Purchasing pure compounds
  - Oxy-flame mixture
  - Stability

- Improvement of procedure → Funding required!

- New developments on hydrogen impurities
- **New capability at NPL**
- Perspective NPL enrichment device

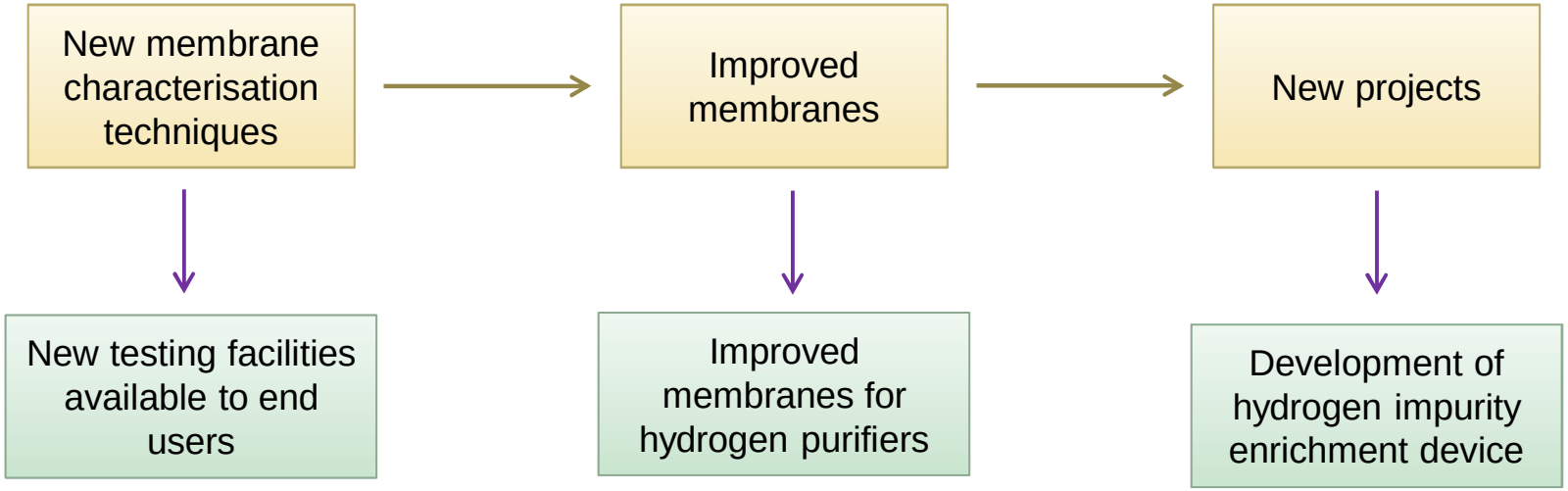
Characterisation of palladium-based membranes for hydrogen purification



Characterisation of palladium-based membranes for hydrogen purification

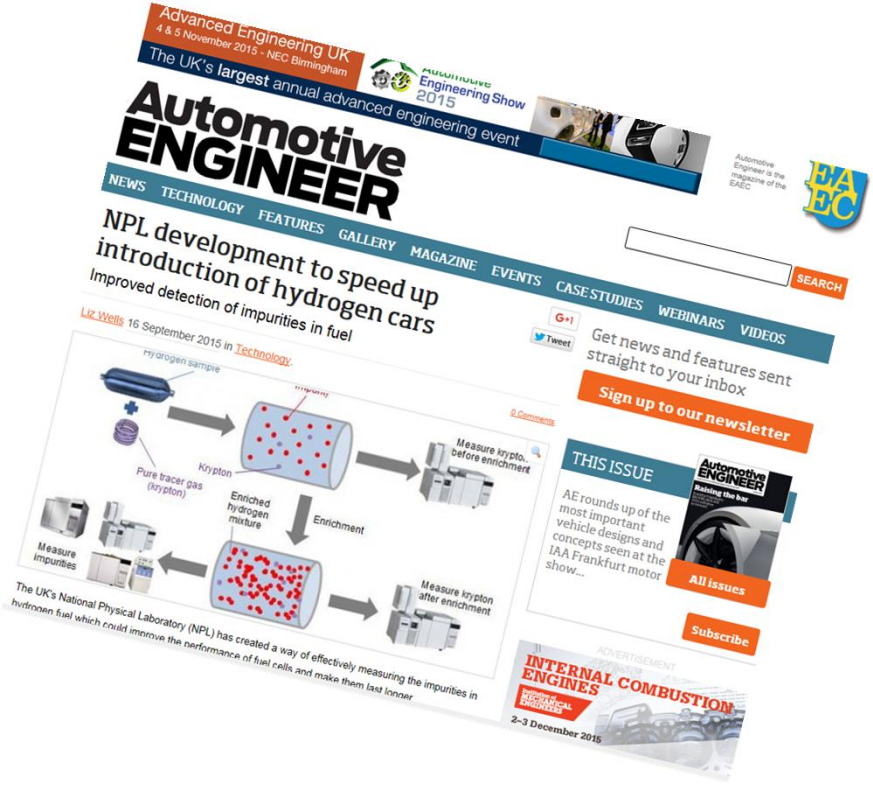
NPL National Physical Laboratory

Project outcomes



- New developments on hydrogen impurities
- New capability at NPL
- **Perspective NPL enrichment device**

Perspective NPL enrichment device



- Private partner needed for the commercialisation of the device

Conclusion

- New development on hydrogen impurities
  - Water analysis almost extensively validated and traceable to SI
  - Formaldehyde in Hydrogen: 1 month stability ensured
  - Halogenated analysis:
    - Organo-halogenated compounds analysed by TD-GC-MS
    - Investment needed to continue further

- New capability at NPL

  New service: Characterisation of palladium-based membranes for hydrogen purification

- Perspective NPL enrichment device
  - Private laboratory partner needed to commercialise the device

Progress in other projects…

- Report of analysis for impurities in hydrogen under UKAS ISO17025 accreditation in process

- New development ongoing for
  - ammonia, formaldehyde (GC-MS),
  - formic acid and formaldehyde (GC-PDHID)
  - new binary standards in hydrogen in preparation

- Participation in project proposal EMPIR co-normative call – Project proposal called Hydrogen

Acknowledgement

Hydrogen Quality control Innovate UK

Innovate UK

CASCADE TECHNOLOGIES

ITM POWER
Energy Storage | Clean Fuel

NPL
National Physical Laboratory

Gas and Particulate Metrology group
Humidity group

Thanks,

Questions?