Quantitative methods for measuring H_2 concentration in natural gas mixtures and H_2 contaminants

Annarita Baldan

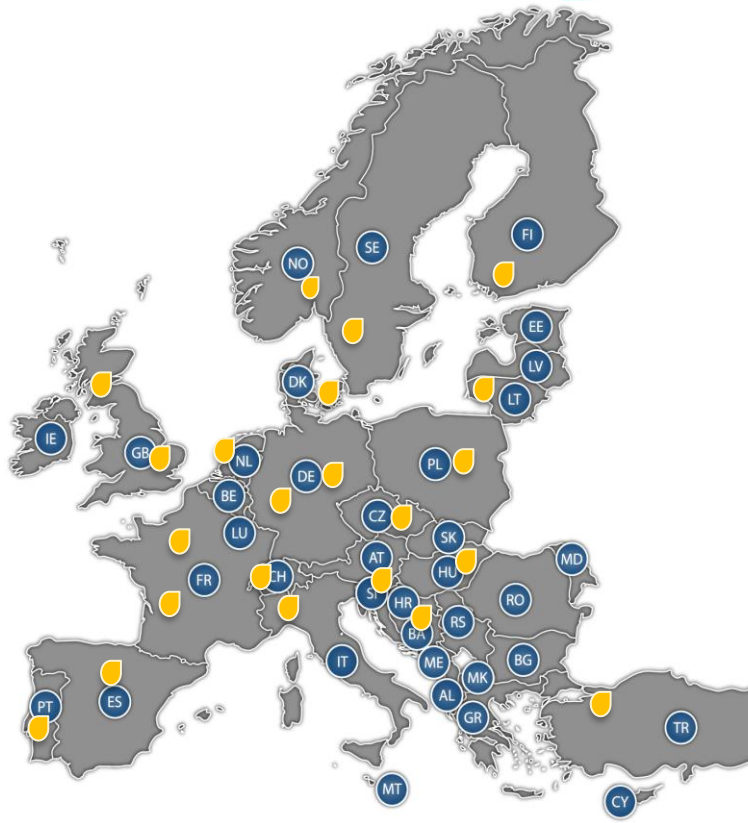
5 November 2026

ENTSOG Gas Quality Workshop

European Metrology Network for Energy Gases

- Part of EURAMET
- Focus on metering and use of energy gases: conventional fluids and fluids related to (emerging) renewable/ sustainable energy sources, including CCUS

"Improving reliability in the measurement of energy gases"



Fact sheet

Accurate measurements for quality, regulation, trade, safety, interoperability AND Innovation:

- **Act** as European metrology knowledge center
- **Boost** access to metrological services and calibration facilities
- **Promote and coordinate** measurement research based on the **EMN Strategic Research Agenda:**
  - Decarbonising natural gas
  - Decarbonising industry
  - Energy transport and storage
  - Cleaner fuel for mobility

Measurements		
	Gas composition	Calorimetry
	Reference Materials	Particles
	Flow	Humidity
	Temperature	Material data
	Pressure	Material testing



ENERGY GASES

EU Metrological Research in Energy Gases since 2010

METROLOGY PARTNERSHIP | EURAMET

NATURAL GAS	LIQUIFIED GASES	BIOGAS /BIOMETHANE	HYDROGEN	OTHER ENERGY CARRIERS	CCUS AND DECARBONISATION
1.GAS 2.MultiFlowMet	1.LNG I 2.LNG II 3.LNG III 4.CryoMet	1.BIOGAS 2.BIOMETHANE 3.Si-S/Biogas 4.BiometCAP	**1.Hydrogen** **2.MetroHyVe 1** **3.MetroHyVe 2** **4.MetHyTrucks** **5.MetroHyVe 3** 6.NewGasMet 7.MetHyInfra **8.MefHySto** **9.Met4H2** 10.H2FlowTrace	1.MaritimeMET 2.MetNH3Energy	**1.Decarb** 2.Me[illegible]CCUS 3.S[illegible]rtGasNet

ISO 14687

CEN/TS 17977



ENERGY GASES

Hydrogen content in natural gas

Feed gas for the injection into the grid comes from different sources, dependent on prevailing availability → **variable composition of the fuel gas grid**

- **Hydrogen sensors for process monitoring and control**

Robust, rapid, accurate and field-deployable

- **Hydrogen sensors for gas quality control and legal metering**

Conformity with specifications and regulations, and billing (ISO 6974)

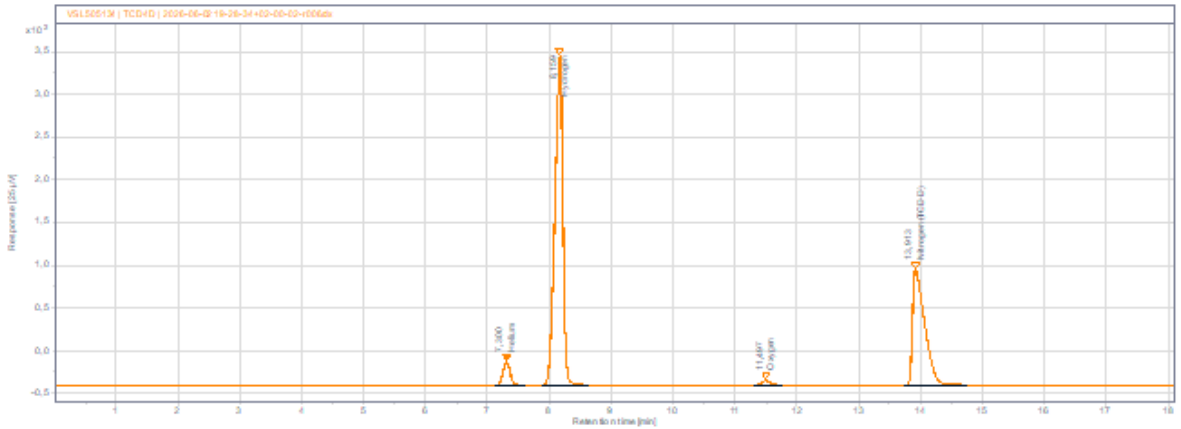
Requirements for hydrogen sensors in Natural Gas

- Measurement range hydrogen sensors: 0 - 30 mol%
- Accuracy: at least 3% for process control and < 1 % for legal metering
- Response time: < 5 min (preferably < 1 min)
- Operating conditions: up to 100 bar and 55 °C
- Method hydrogen specific and low cross-sensitivity for other components in natural gas
- Online system with continuous data acquisition
- ATEX compliance

Natural Gas Analyser based on Gas Chromatography

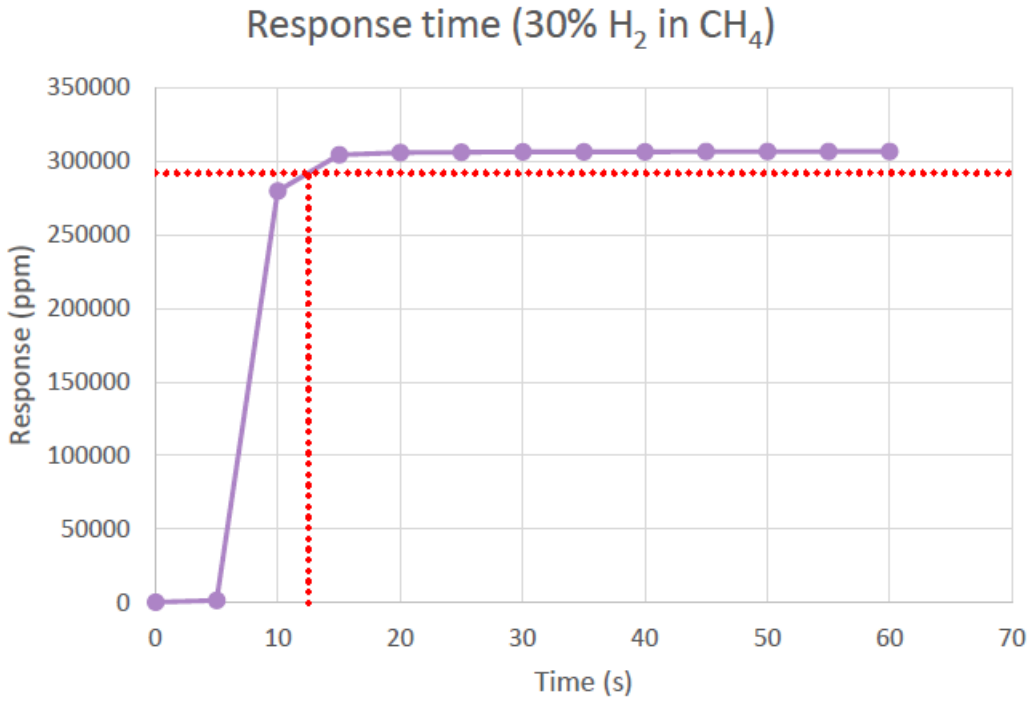
- Technology fulfils the requirements (0- 30 mol% hydrogen) for gas quality control and legal metering
- However, there is NO standard available that describes the measurement method for hydrogen content up to 30 mol%

- Discontinuous method, but fast analysis natural gas is possible within 5 minutes
- Process GCs commercially available and certified up to 20 vol % hydrogen

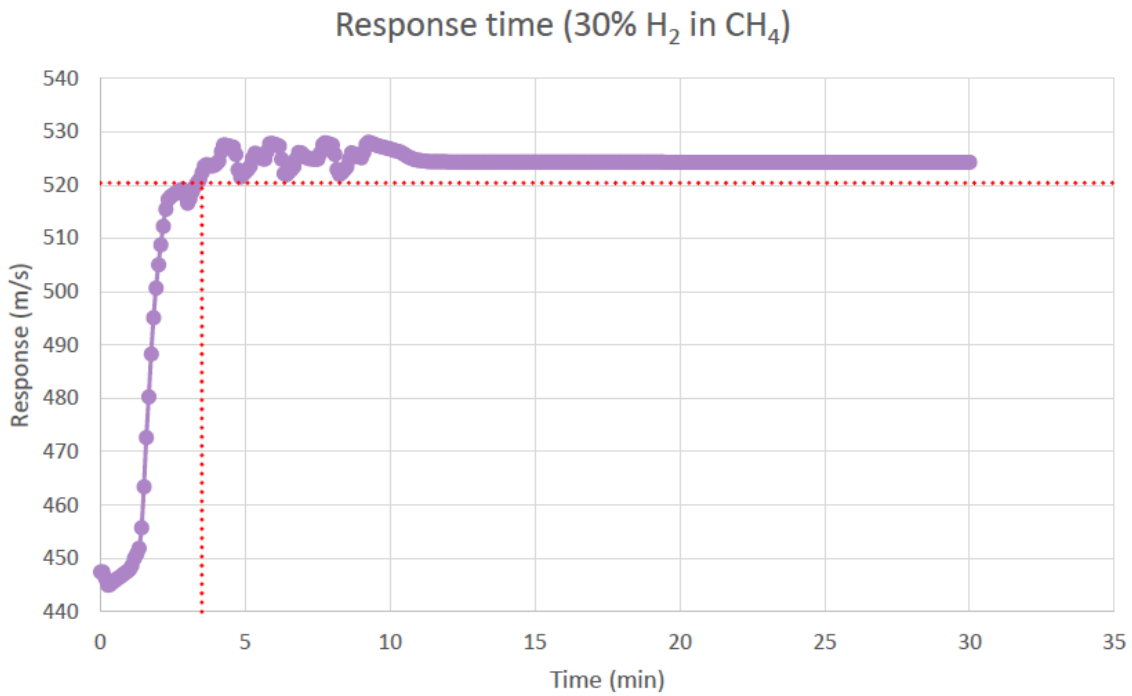


Chromatogram of NGA with 5 mol% Hydrogen in NG, GC-TCD

Sensors based on molecular transport properties



Thermal Conductivity Detector online sensor



Speed of sound online sensor (static conditions)

- Technology is not hydrogen specific! Suitable to control well-characterized process gas streams (“correlative determination”)
- Usually combined with unspecific and/or low-cost sensors for CO_2-content and density and data processed using multivariate approaches
- Eligible for process control where the tolerance of the variations of hydrogen content and gas composition is well defined

Promising technologies

- Raman spectroscopy
- Metal hydride-based sensors (palladium)



Example: Raman Rxn5 analyzer, Endress+Hauser



Example: HY-OPTIMA 5030 Series inline hydrogen process analyzer, H2scan

Hydrogen Enriched Natural Gas primary standards

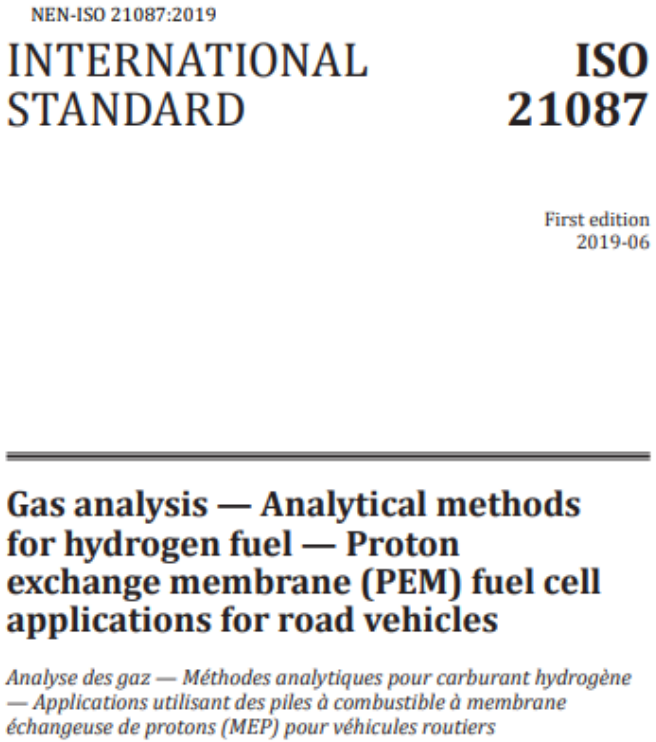
- Calibration is the basis of every reliable measurement result

Natural gas	Range, mol %	Uncertainty, %
Methane	40 – 99.9	0.1
Ethane	0.2 – 25	0.25 – 0.19
Propane	0.05 – 12	0.3 – 0.27
n-Butane	0.01 – 3.0	0.19
i-Butane	0.01 – 0.8	0.14
n-Pentane	0.01 – 0.8	0.46
i-Pentane	0.01 – 0.8	0.5
neo-Pentane	0.01 – 0.8	0.39
n-Hexane	0.01 – 0.45	0.48
Nitrogen	0.1 - 25	1.16 – 0.17
Carbon dioxide	0.05 - 20	0.75 – 0.16
Helium	0.05 – 2.5	0.28
Hydrogen	**0.05 - 30**	**0.34**



National Metrology Institute

Validation of the analytical methods



NEN-ISO 21087:2019

INTERNATIONAL STANDARD

ISO 21087

First edition
2019-06

Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles

Analyse des gaz — Méthodes analytiques pour carburant hydrogène — Applications utilisant des piles à combustible à membrane échangeuse de protons (MEP) pour véhicules routiers

Performance characteristics to be validated :

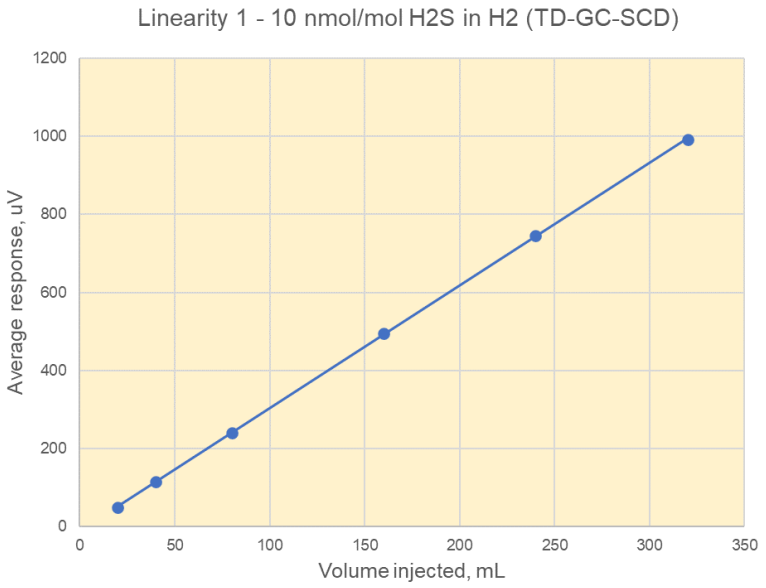
- **Selectivity**
- **Linearity in the working range**
- **Limit of Detection and Quantification**
- **Precision**
- **Trueness and measurement uncertainty**

National Metrology Institute

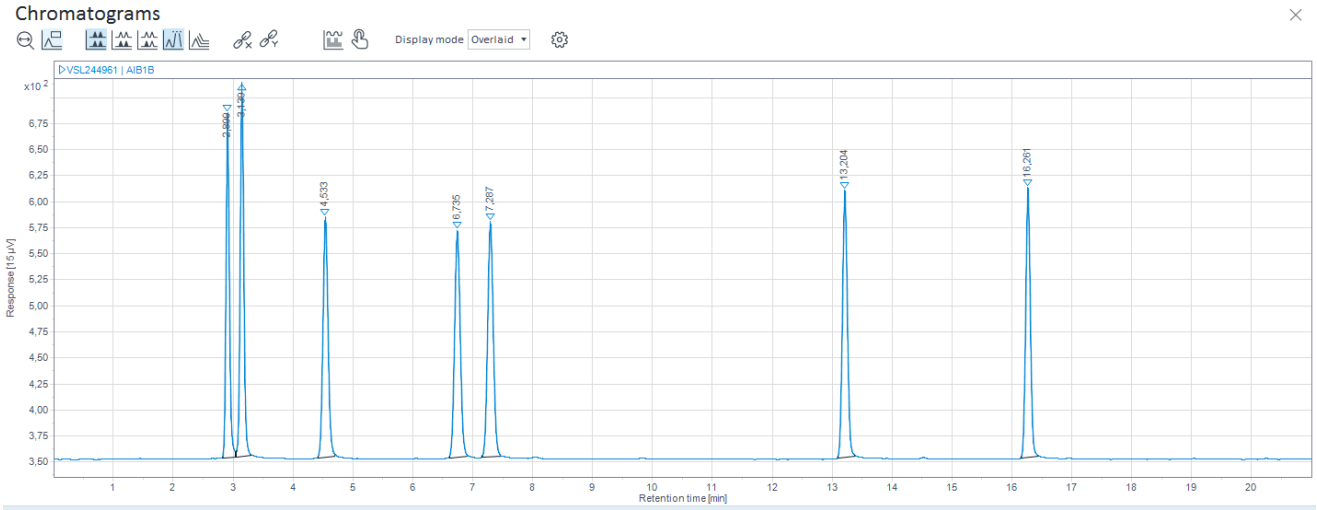
Gas standards sulfurs in H_2

- H_2S, COS, Methyl mercaptan, Ethyl mercaptan, DMS, DES, THT
- Sulfur gas standards 10 nmol/mol to 1 µmol/mol in hydrogen (ISO 14687 - Grade D and Grade A)
- Method: TD-GC-SCD



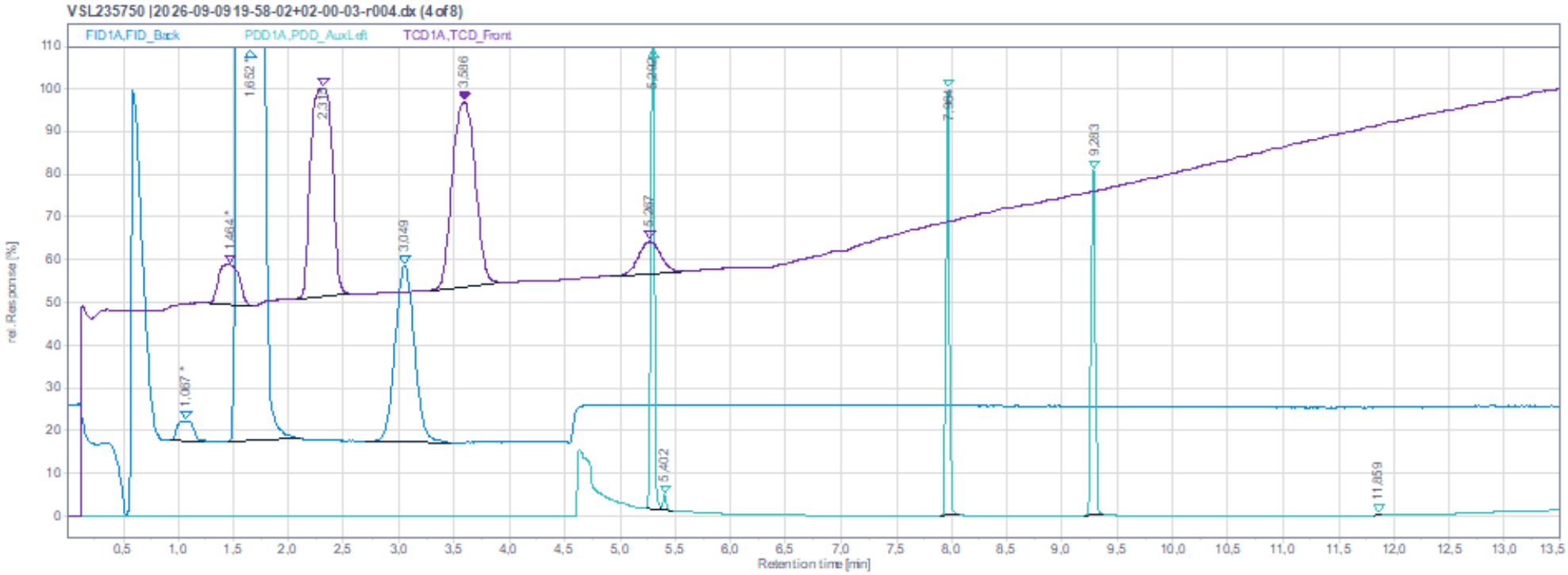


Grade A	3 µmol/mol
Grade D	4 nmol/mol



National Metrology Institute

Gas chromatography for multi component quantification



Chromatograms of the measurement of a gas standard of multi-component impurities in hydrogen (ISO 14687 Grade D threshold) on a multi channel GC

- Purple: **He**, Ar+O_2, **N_2**, CH_4 (TCD detector)
- Dark blue: **CO, CH_4, CO_2** (FID + methanizer detector)
- Light blue: **Ar, O_2**, N_2, CH_4, **CO** (PDD detector)

Offline vs online techniques



Online technique

	Offline	Online
Pros	Results are accurate, sensitive and specific	Continous measurement, fast results
Cons	Spot sampling	Large uncertainty: (response time, drift and calibration)
Notes	Dead volume of sampling system (conditioning and leakage)	Low pressure working condition (pressure reduction and cooling)
	Sampler compatibility (inertness)	Poor sensitivity and specificity
	Sample storage time	ATEX proof

Offline technique



Source: H2 sampling system, Mechatest



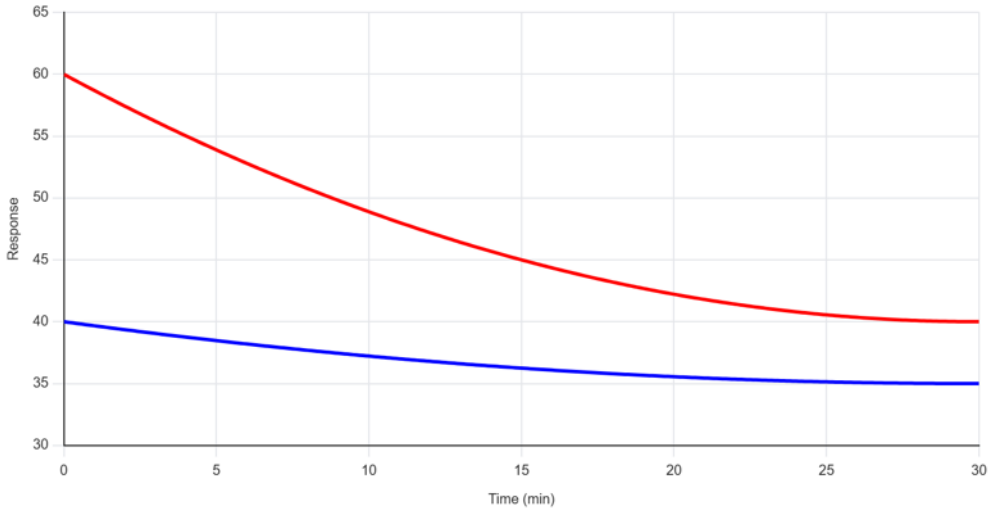


Source: H2 cylinders and offline analysis, VSL

Moisture measurement

1) above 10 µmol/mol → online and offline

2) between 1 - 10 µmol/mol → online and offline (with extra requirements)



- For case 2): discrepancy between online sensor results when positioned downstream offline sampling system + cylinder (red line) and upstream (blue line) → moisture over estimated due to the outgassing from the sampling system



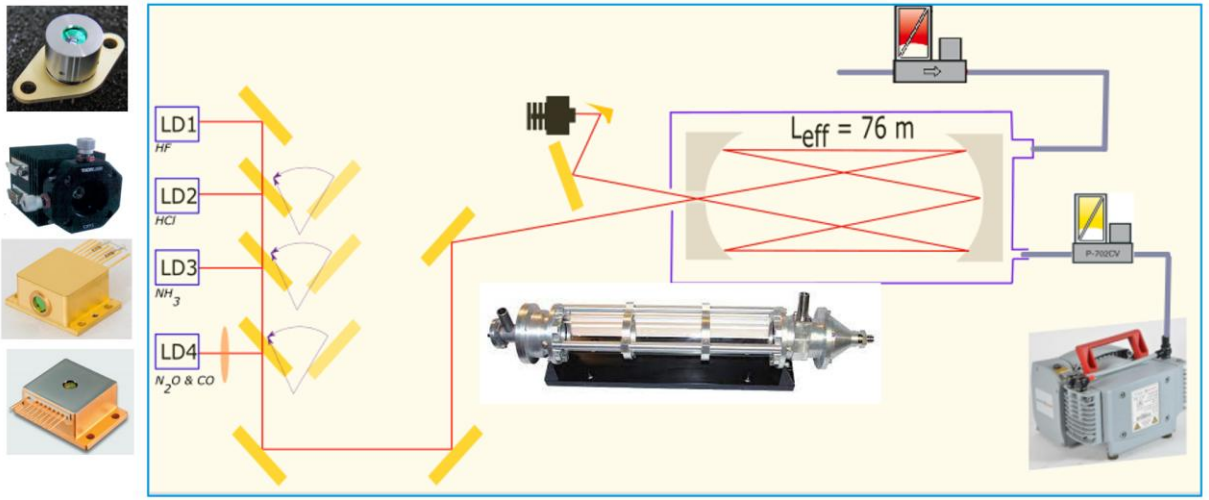


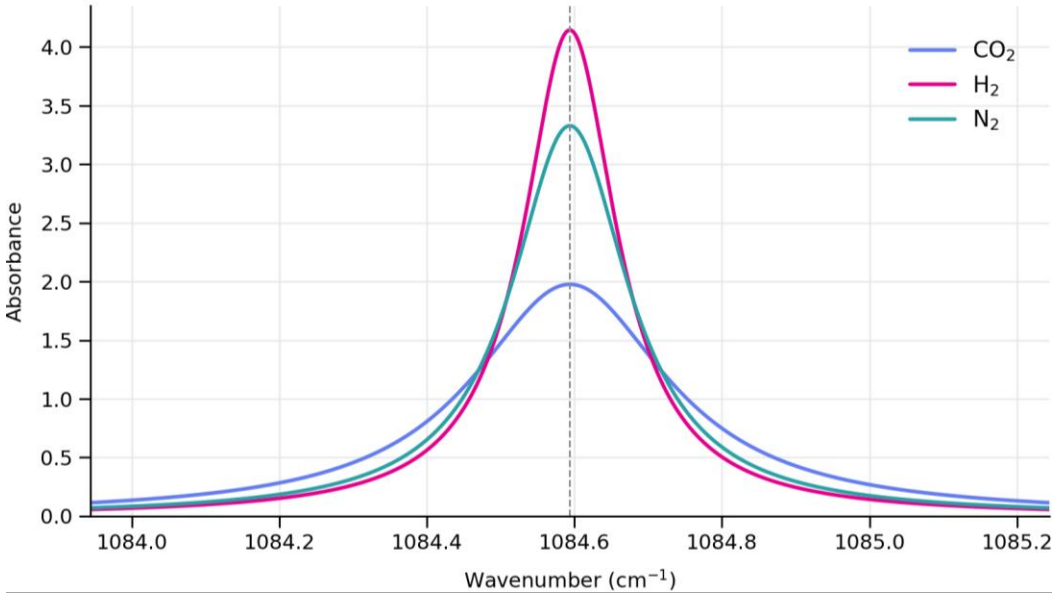


Examples of Aluminium oxide humidity sensors: a) SHAW - Model SDT – Ex Silver; b) Michell – Easidew PRO XP; c) Vaisala DMT370EX

Tunable diode laser spectrometer (TDLS)

- Instrument suitable for detection of NH_3 and other gases at trace levels in H_2
- Width of NH_3 absorption lines depends on the matrix gas





Reference: D. Zhu et al., Spectrochim. Acta A Mol. Biomol. Spectrosc. 320 (2024) 124642 *NH_3 line broadening coefficients and intensities measurement and impurities determination in emerging applications: CCUS, Biomethane and H_2*

Thank you

Acknowledgments