METROLOGY for HYDROGEN VEHICLES

16ENG01 – MetroHyVe “WP4 – Sampling”

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SAB meeting

24th of January 2018

EMPIR EURAMET

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

WP4 - Sampling

WP4 aims at optimizing and developing best practices approaches for sampling of hydrogen gas and particulates

Representative sample taken and transported

- Avoid overestimating (shut down the station) or underestimating (failure of the fuel cell vehicle)
- Pressure and volume sampled suitable to full range of analytical techniques needed

WP4 deliverables – good practice guides

- D7 " Effective sampling and transportation of hydrogen from the refuelling station as required by ISO 14687
- D8 "Suitability of vessels and gas cylinders for sampling hydrogen as required by ISO 14687

WP4 - Sampling

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Task 4.1

Suitable sampling techniques at the hydrogen refueller (RISE, Air Liquide, FHA, ITM, SINTEF, NPL)

Aim: Develop a standardised approach for sampling at the HRS to obtain a representative sample of hydrogen (and avoid contamination with air or water)

Task 4.2

Validation of particulate sampling using filters (NPL, Air Liquide, ITM)

Aim: Develop a robust sampling system for the collection of particulates onto filters in a stream of hydrogen at the HRS

Task 4.3

Efficiency of sorbent tubes (VSL, RISE, NPL, SINTEF, IFE)

Aim: Determine the efficiency of TD sorbent tubes for the ”total” measurements (halogenated, sulphur, hydrocarbons)

Assess performance of the sorbent tubes and trapping mediums (DL, efficiency)

Task 4.4

Assessing suitability of commercial available sampling vessels (RISE, NPL, VSL, IFE)

Aim: Assess the suitability of commercially available sampling vessels for transporting the reactive impurities in H2 (H2S, CO, NH3, HCHO, HCOOH)

WP4 - Sampling

Task 4.1: Suitable sampling techniques at the hydrogen refueller (**RISE**, Air Liquide, FHA, ITM, SINTEF, NPL)

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Task 4.4: Assessing suitability of commercial available sampling vessels (**RISE**, NPL, VSL, IFE)

Task 4.1

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WP4 - Sampling

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Task 4.1: Suitable sampling techniques at the hydrogen refueller

- Full risk assessment to understand possible contaminants and issues
- Survey to understand the sampling requirements at the labs contra working conditions at the HRS
- Procedure for preparing vessels before sampling
- Test of purging techniques at Teddington HRS (air and water) + recommendations on number of purges required

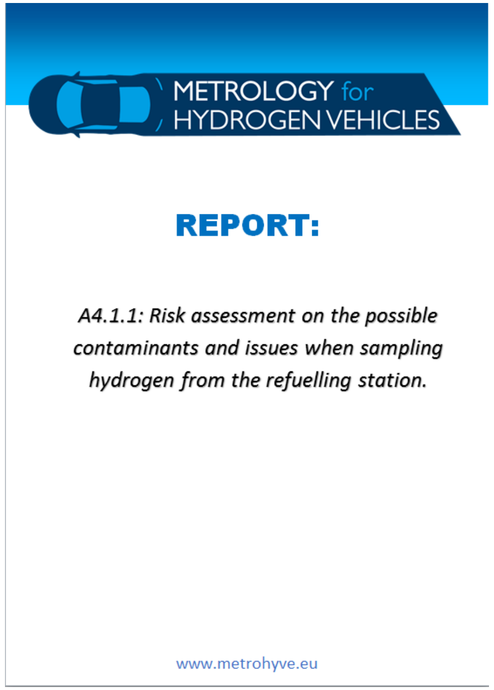
Good practice guide on effective sampling and transportation of hydrogen from the refuelling station as required by ISO14687 (D7)

Full risk assessment to understand possible contaminants and issues

Report ” *Risk assessment on the possible contaminants and issues when sampling hydrogen from the refuelling station.*”
Delivered in December 2017

Outcomes presented as follows:

- Introduction
- Overview of a HRS
- Standards (sampling)
- Sampling methods (parallel sampling, series sampling, available sampling devices, available sampling vessels)
- Risk assessment sampling
- False positives
- False negatives
- Current recommendations
- Future work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REPORT:

A4.1.1: Risk assessment on the possible contaminants and issues when sampling hydrogen from the refuelling station.

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Existing sampling devices

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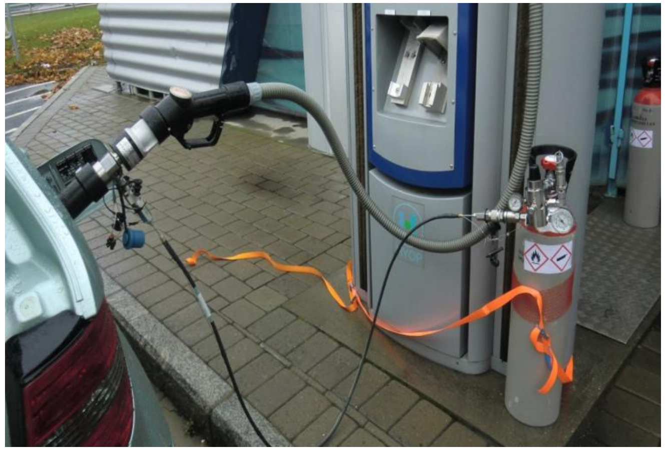
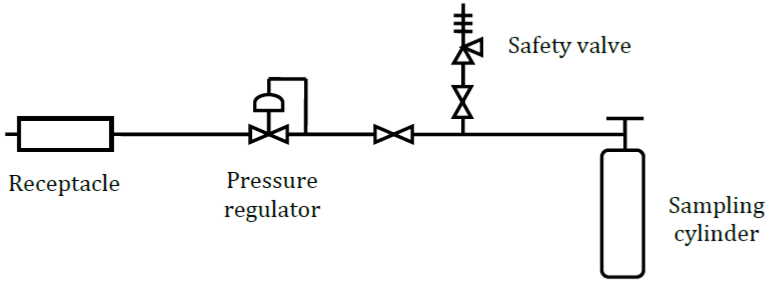


HyCoRa project

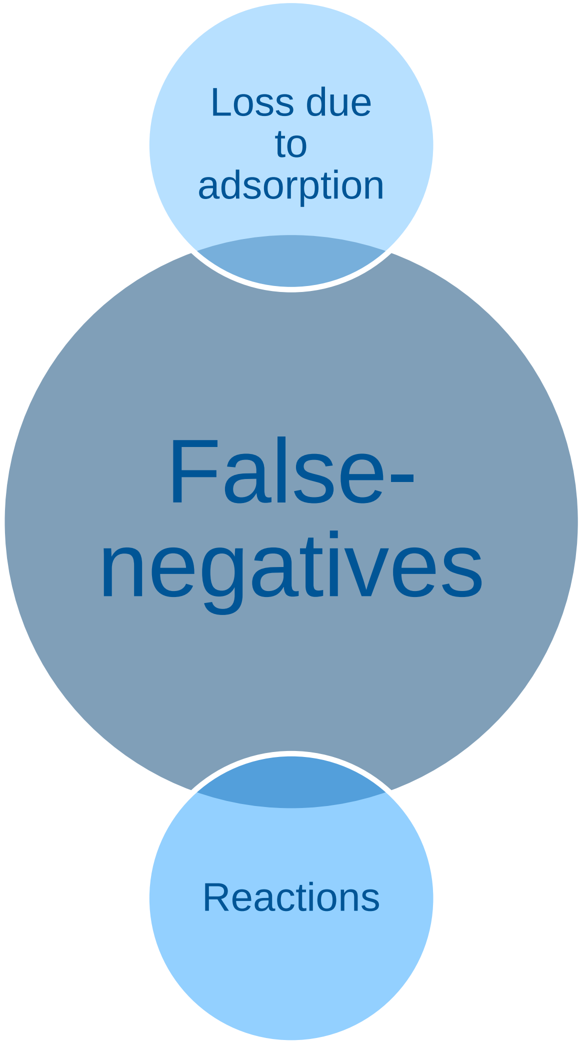
Smart Chemistry



HQSA used in Japan

Full risk assessment to understand possible contaminants and issues

METROLOGY for HYDROGEN VEHICLES



WP4 Survey to understand the sampling requirements at the labs contra working conditions at the HRS

- Survey for the gas lab analysis sent to 7 labs in December 2017
- Survey for the HRSs sent to HRSs in January 2018
- Answers to be compiled
- These results will be used to form a recommendation for the conditions for sampling including vessel size and fill pressure that suit both the refuelling stations operators and gas analysis laboratories, Feb-Mars 2018

WP4 Survey to understand the sampling requirements at the labs contra working conditions at the HRS

METROLOGY for HYDROGEN VEHICLES

Parameter	On site (HRS)	Laboratory	Technique	LLOQ
Hydrogen pressure				
Hydrogen volume				
Hydrogen flow				
Particulates in H_2				
CO				
CO_2				
Total sulfur compounds				
O_2				
H_2O				
Total hydrocarbons except CH_4				
CH_4				
He				
N_2				
Ar				
HCHO				
HCOOH				
NH_3				
Halogenated compounds				
Other:				
Other:				

Comments:

* LLOQ expressed in µmol/mol or please indicate the corresponding units

For gas analysis labs

Maximum stored pressure			MPa
Serving pressures at HRS			MPa
			MPa
			MPa
			MPa
Working range temperature	min.		ºC
	max.		ºC
Maximum flow supplied			kg/h

Comments

Other important aspect is the connections available in your HRS to supply hydrogen to vehicles. Which hydrogen receptacles do you have:

ISO 17268:2012	H11 - 11 MPa at 15 °C,	☐
	H25 - 25 MPa at 15 °C,	☐
	H35 - 35 MPa at 15 °C,	☐
	H35HF - 35 MPa at 15 °C (high flow for commercial vehicle applications),	☐
	H70 - 70 MPa at 15 °C,	☐
Other, specify		☐
		☐
		☐
		☐

For HRSs

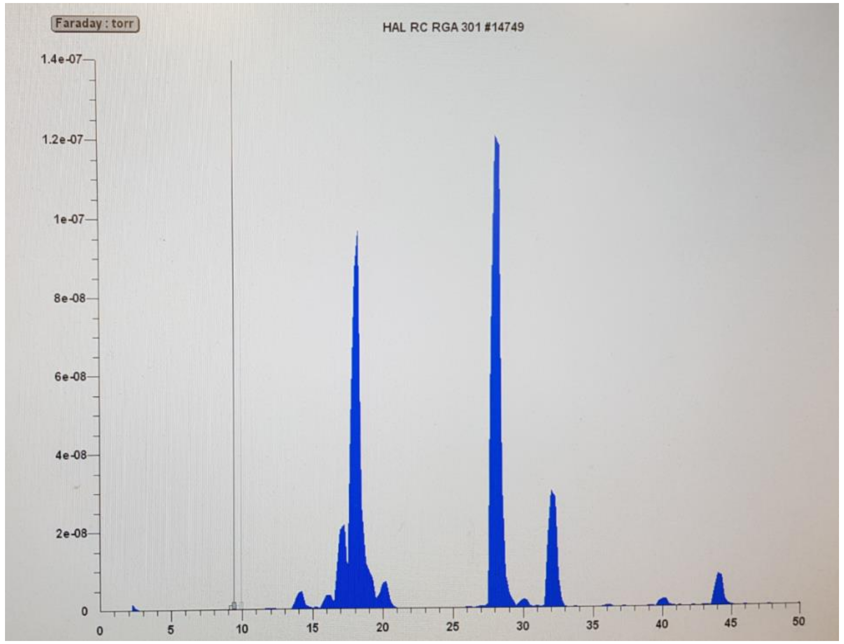
WP4 - Procedure for preparing vessels before sampling

NPL's evacuation rig in operation

Evacuation with a turbo pump to 1 x 10^{-7} mbar.

Residual gas analyser to monitor outgassing of air, moisture and any remaining contaminants.

If an expected impurity remains within the system this should be removed by heating or including a subsequent hydrogen purge step.



WP4 - Sampling

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WP4 - Sampling

METROLOGY for HYDROGEN VEHICLES

Task 4.2: Validation of particulate sampling using filters

- State-of-art in particulate sampling (literature review, required steps for method validation, availability of commercial devices)
- Development of a system (lab) that can produce a contineous stream of particles in H_2. The system will include a with pressure regulator and OPC
- Test of device especially made for collecting particulates at HRS (SINTEF) and filter sampling with system from A4.2.2. Comparison with OPC (reference)
- Good practice guide for performing particulate sampling at HRSs (P, sampling set-up, flow rates, time, calibration)

Literature review

NPL will perform a literature review of existing particulate sampling techniques. The review will highlight the state-of-the-art in particulate sampling and the required steps for validating these methods. The availability of commercial devices for this application will also be investigated.

- Identify current sampling techniques used at HRSs.
    - Sampling pressure
    - Existing particle loss determinations
    - Whole system overview

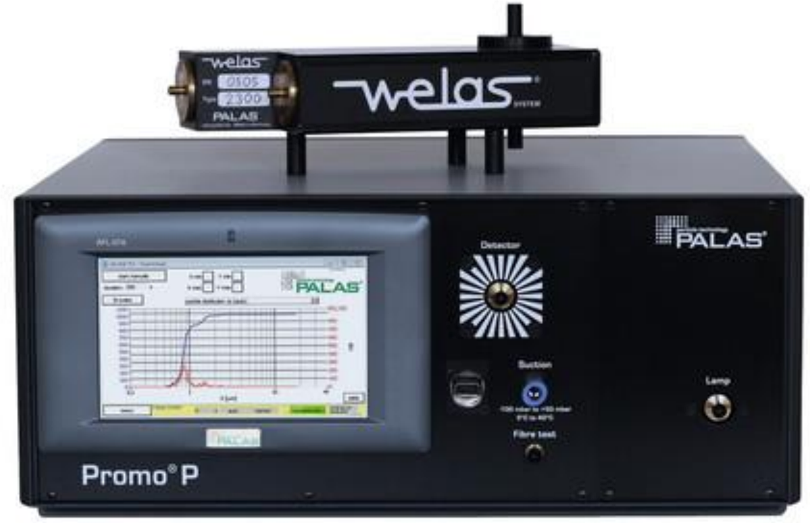
Final report completed by the end of January 2018

Losses due to pressure regulation

NPL will develop a system in the laboratory that can produce a continuous stream of particles in hydrogen at 2 bar or 5 bar (or the highest pressure that the OPC can operate at). The system will use a two-way valve to allow the hydrogen to switch between passing the hydrogen through a pressure regulator (set at lower pressure) then OPC or directly to the OPC. This set up will allow tests to be performed to determine the amount of particles that are lost to the pressure regulator.

- Develop a system to determine particle losses in Hydrogen due to pressure regulation.
  - Develop a high pressure atomiser
  - High pressure OPC head up to 10 Bar
  - Switchable system between different pressures
  - Loss determination within a standard regulator

  Laboratory work to begin in January 2018



PALAS Promo 2000 P - Automatic flow regulation for over pressures from 2 to 10 Bar

Particle loss determination of field devices

NPL will perform at least one test at 2 bar or 5 bar (or the highest pressure that the OPC can operate at) comparing a filter connected to a pressure regulator set at 1 bar and a filter connected to a sampling device especially made for collecting particulates at the HRS (provided by SINTEF). The mass of particulates collected by both sampling devices will be compared to determine the particulate losses from each, and to make an assessment of the device efficiencies for accurately capturing particulates. Both devices will be compared to measurements from the OPC which will provide the reference.

Determine particle losses in commercially available sampling devices

- Use high pressure OPC as a reference
- Use as many of sampling devices found in A4.2.1 as possible
- Use the set-up developed in A4.2.2 for comparisons

Particle sampling guide

NPL with input from Air Liquide and ITM will write a good practice guide providing recommendations for performing particulate sampling at HRSs including recommended pressures, sampling set up, flow rates (including methods for ensuring traceability for this measurement), flow time and calibration for the final particulate measurement.

- Write a good practice guide for particle sampling at HRSs.
    - Pressures and associated losses
    - Optimal set up to avoid losses
    - Possible system loss determination set-ups

WP4 - Sampling

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Efficiency of sorbent tubes (VSL, RISE, NPL, SINTEF, IFE)

Aim: Determine the efficiency of TD sorbent tubes for the "total" measurements (halogenated, sulphur, hydrocarbons)

Assess performance of the sorbent tubes and trapping mediums (DL, efficiency)

WP4 - Sampling

METROLOGY for HYDROGEN VEHICLES

Task 4.3 : Efficiency of sorbent tubes

- Selection of target compounds (3-5 per family: sulfur, halogenated, hydrocarbons) and 3 best sorbents (literature review of hydrogen purity analyses, sorbent properties…)
- Short-term (1-2 weeks) stability studies on the selected sorbents for the selected hydrocarbons, sulfur, halogenated
- Peer-reviewed paper (results + conclusion for the suitability of each sorbent tube tested
- Assessment of feasability of direct sampling (at HRS) on sorbent tubes

“Total” measurements specified in ISO 14687

- Quantifying “total” is challenging due to the large number of compounds possible covering a wide range of properties
- Sorption tubes are widely used to sample a wide range of compounds in environmental analysis
- Assessment of the usability of sorbent tubes is the main topic of task 4.3

- Total compounds comprise
  - halogenated compounds
  - sulphur compounds
  - hydrocarbons

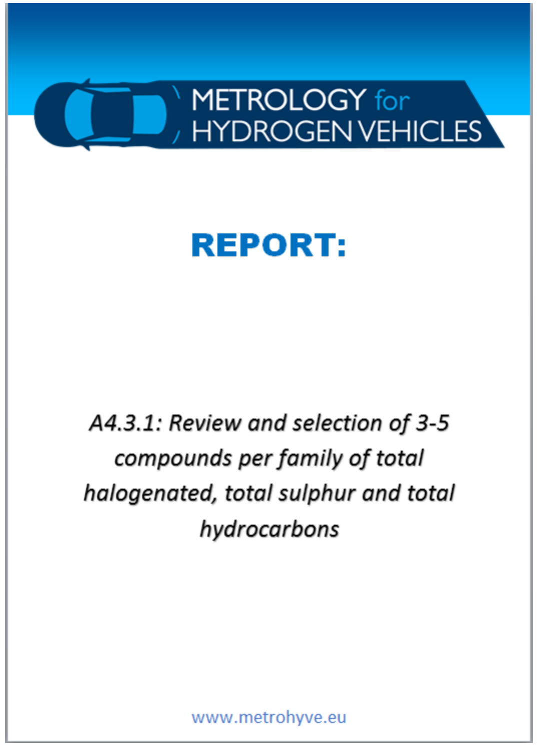
Existing hydrogen purity reports

Report ” *Review and selection of 3-5 compounds per family of total halogenated, total sulphur and total hydrocarbons*” delivered in December 2017

Totally 32 hydrogen purity reports from 24 different stations (SM, chlor-alkaline and electrolysis processes) have been reviewed.

Sources:

- HyCoRa
- Smart Chemistry
- H2moves Scandinavian
- H2Protocol.com
- NPL feedback


METROLOGY for HYDROGEN VEHICLES

REPORT:

A4.3.1: Review and selection of 3-5 compounds per family of total halogenated, total sulphur and total hydrocarbons

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Existing hydrogen purity reports

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Hydrocarbons	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3 SC2											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
Methane																									
Acetone																									
Ethane																									
Ethanol																									
Isopropyl alcohol																									
Propane																									
Heptane																									
Cyclohexane																									
n-butane																									
Isobutane																									
Octene																									
Decene																									

SC: Sampling campaign
HRS8 and HRS12 in the HyCora project are the same station but two different sampling and analysis (the same day)
CSU H2 HRS1 and HRS2 are the same station

Hydrocarbons	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
Methane										
Acetone										
Ethane										
Ethanol										
Isopropyl alcohol										
Propane										
Heptane										
Cyclohexane										
n-butane										
Isobutane		2	3	4						
Octene										
Decene										

HRS1 and HRS9 are the same station but two different sampling and analysis (within 3 weeks)

Existing hydrogen purity reports

Sulfur	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
H2S																									
COS																									
CS2																									
TBM																									
THT																									

H2S: hydrogen sulphide
COS: carbonyl sulphide
CS2: carbon disulphide
TBM: Tert-butyl mercaptan
THT: Tetrahydrothiophene

Sulfur	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
H2S										
COS										
CS2										
TBM										
THT										

Existing hydrogen purity reports

METROLOGY for HYDROGEN VEHICLES

Halogenated	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
Cl_2																									
HCl																									
HBr																									
C4Cl4F6																									
CH_2Cl_2																									

Cl_2: Chlorine
HCl: Hydrogen Chloride
HBr: Hydrogen Bromide
C4Cl4F6: tetrachlorohexafluorobutane
CH_2Cl_2: dichloromethane

Halogenated	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
Cl_2										
HCl										
HBr										
C4Cl4F6										
CH_2Cl_2										

Compounds selected for work on sorbent efficiency

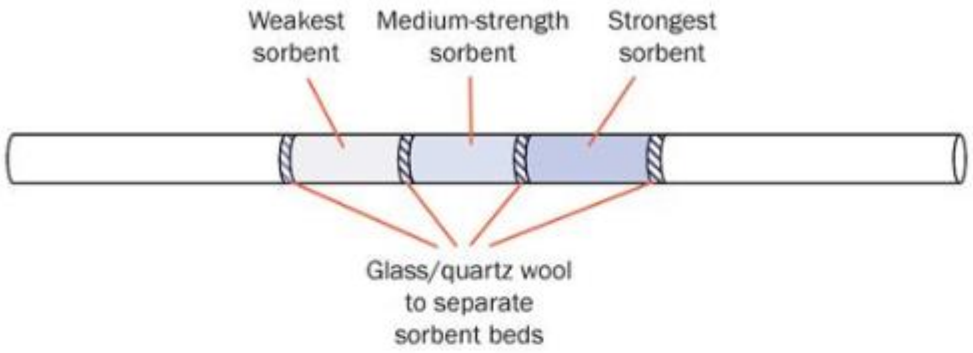
METROLOGY for HYDROGEN VEHICLES

Hydrocarbons	Sulfur	Halogenated
Methane	Carbonyl sulphide*	Tetrachlorohexafluorobutane
Ethane	Carbon disulphide*	Dichlorobenzene
Propane	Tert-butyl mercaptan	Dichloromethane
Butanes	Methyl mercaptan	Tetrachloroethylene
Acetone	Tetrahydrothiophene	Chloroform*
Methanol		
Ethanol		
Octane		
Decane		

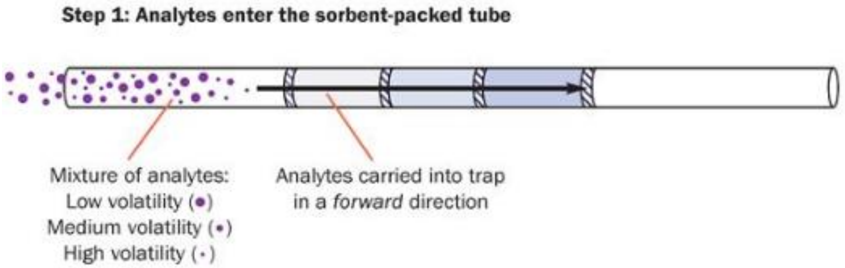
* If proven possible

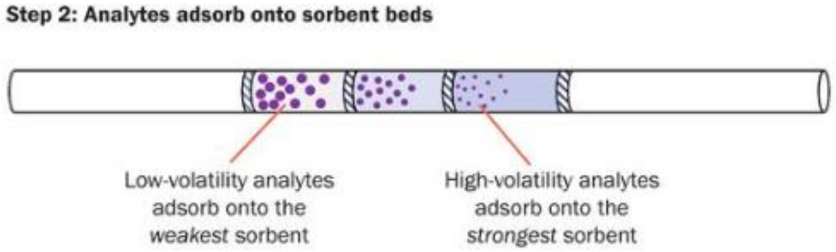
Selection of 3 best sorbents per family

Many sorbent materials available classified by strength + combinaison of sorbents:

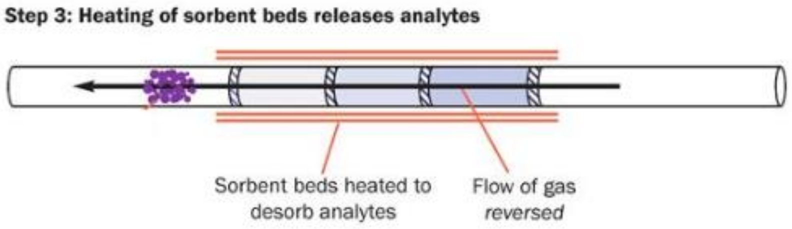


Trapping (sampling)





Release (analysis)



Selection of 3 best sorbents per family

Use breakthrough volumes tables when available for targeted compounds

Tenax TA with Alcohols

Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300
Methanol	1.30	0.362	0.140	0.055	0.023	0.011	0.006	0.003	0.002	0.001						
Ethanol	7.90	1.80	0.481	0.152	0.055	0.021	0.010	0.005	0.003	0.002	0.001					

Tenax TA not appropriate for methanol, ethanol

Carbosieve SIII with Alcohols

Temperature	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360
Methanol	12.0	7.50	4.00	2.30	1.30	0.750	0.400	0.230	0.130	0.070	0.037	0.023	0.013	0.009	0.005	0.003	0.003	0.002	0.001
Ethanol	100	55.0	30.0	17.0	9.00	5.00	2.70	1.60	0.800	0.450	0.262	0.136	0.077	0.045	0.028	0.019	0.012	0.008	0.006

Carbosieve SIII appropriate for methanol (Low T) and ethanol

The **Blue highlighted** areas indicate acceptable value for the trapping of the organic compound at that temperature.

The **Red highlighted** areas are good temperatures to assure complete desorption of the organic compound off the adsorbent resin during the thermal desorption process.

Assessment of feasability of direct sampling (at HRS) on sorbent tubes

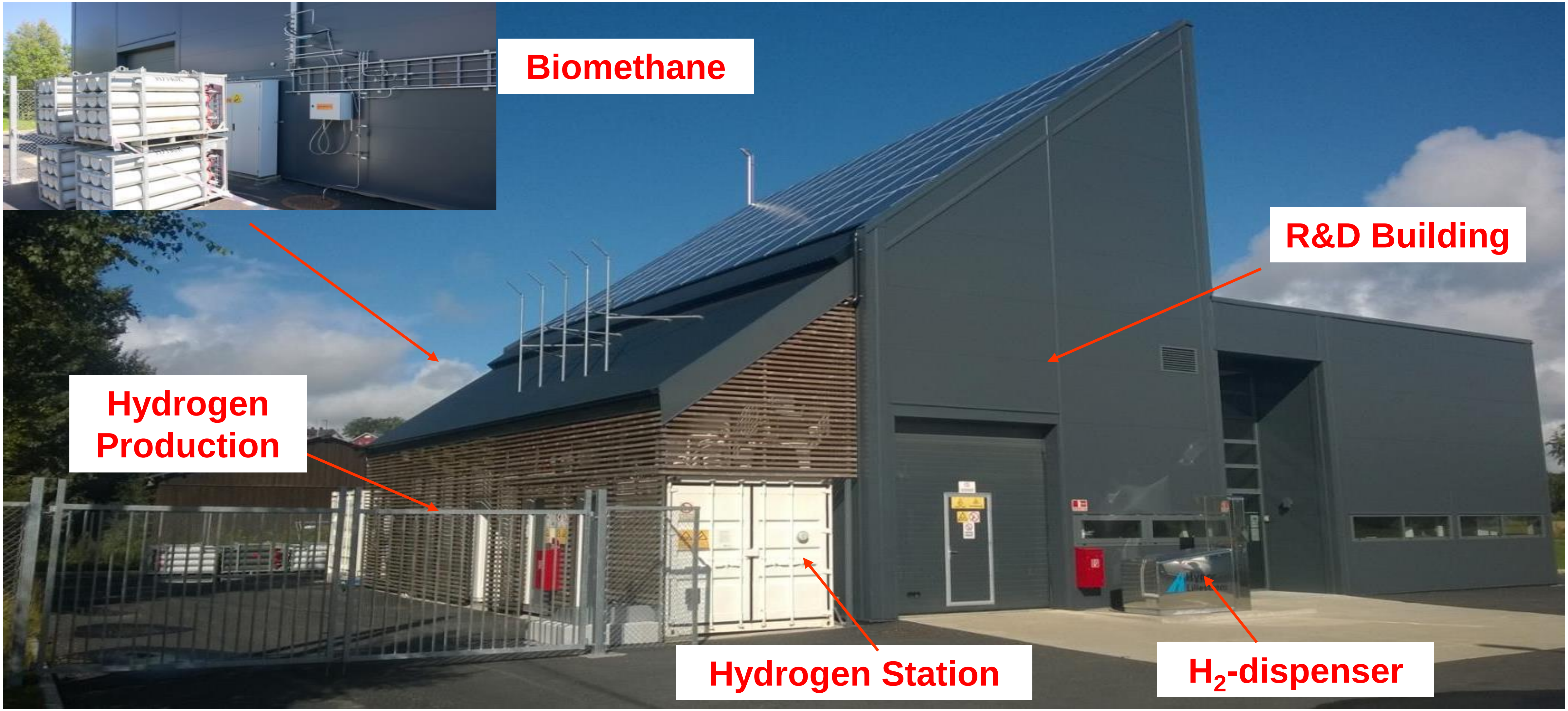
- **IFE Hynor Hydrogen Technology Center** (IFE Hynor) is a fuel cell and hydrogen technology test center owned and operated by IFE.

- The test center includes a small-scale **hydrogen refueling station** (HRS) capable of high-pressure (700 bar) and fast refueling (3 minutes) of PEM-based (Proton Exchange Membrane) fuel cell electric vehicles (FCEVs).

- The IFE Hynor test facility also includes the possibility to supply various qualities of biogas and hydrogen (on-site production or bottled gas) and advanced gas analysis equipment.

www.mozees.no
www.ife.no/en/ife/laboratories/ife-hynor-hydrogen-technology-center/ife-hynor-hydrogen-technology-center
www.ife.no/en/ife/laboratories/n-fch-systems-laboratory/n-fch-systems-laboratory

IFE Hynor Hydrogen Technology Center



Sorbent tube attachment to a HRS

Linde Qualitizer or other with DIN-Swagelok adapter

Two-step Pressure reducer?
P_{out} (100-200 kPa)

6 mm conditioned Thermal Desorption tube train with teflon ferrules

Flow 50-200 mL/min
(Depends on sorbent)

Filling duration:
3-5 minutes
During this time:
Purge + sampling

Flow meter with volume integration functionality and temperature metering

Connecting tubing has to be clean and non-reactive. Purging is important!

Downstream pressure control is essential due to pressure step up and initial spike during filling

Temperature control may be required since outdoors (Peltier element?)

Leak-detector

WP4 - Sampling

METROLOGY for HYDROGEN VEHICLES

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Assessing suitability of commercial available sampling vessels (RISE, NPL, VSL, IFE)

Aim: Assess the suitability of commercially available sampling vessels for transporting the reactive impurities in H2 (H2S, CO, NH3, HCHO, HCOOH)

WP4 - Sampling

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Task 4.4: Assessing suitability of commercial available sampling vessels

- State-of-art for the storage of reactive species in vessels (size, comfiguration, passivation treatment, vessel preparation, pressure, cost)
- Design of experimental protocol to prepare H2-containing relevant amount fractions of reactive impurities
- Design of experimental protocol to perform short-term stability studies (2 different vessels per partner, different impurities, tested pressure)
- Short-term stability studies (1-2 weeks) as defined in A4.4.3

Good practice guide on the suitability of vessels and gas cylinders for sampling hydrogen as required by ISO14687 (D8)

WP4 - Sampling

- Two ended cylinders
- One ended cylinders
- Different inner treatments as passivation
- Different materials

Assessing suitability of commercial available sampling vessels

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- Literature survey on the current state-of-the-art for the storage of reactive species in vessels including information of their size, configuration, passivation treatment, vessel preparation, sampling pressure and cost

- RISE will organise a teleconference to discuss plan of actions for this task (Aug. 2018)

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THANK YOU