METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Sampling vessels & filters

Sam Bartlett (NPL)

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

12th September 2019

EMPIR EURAMET FCH

Overview

- Parameters to consider when selecting a sampling vessels for H2
- State-of-art for commercially available sampling cylinders
- Developed procedure to prepare cylinders before sampling
- Other types of vessels: sorbent tubes
- Available resources

METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Measurement challenge

- Among the characteristics for the fuel specification listed in standard ISO14687-2, several species are reactive (e.g. halogenated compounds, ammonia, formaldehyde, formic acid, carbon monoxide) and/or may adsorb onto solid media such as cylinder walls (e.g. water).

- Therefore, it must be ensured that adequate sampling vessels are used for these species to avoid losses occurring while the sample of hydrogen is collected at the HRS station and transported to the laboratory. Losses within the vessels would lead to falsely lower levels of impurities being measured than are present in the original hydrogen

Vessels for sampling hydroge

- Must be cleaned and evacuated before sampling
- No loss of impurities during transportation (Timeline: 2-4 weeks maybe even longer if from USA)
- Sampling hydrogen may imply the presence of several species at the same time
- Vessels need to be approved for transportation
- Vessels need to be compatible with available H2-sampling devices developed to take samples at HRS stations

Component	ISO 14687 -2 µmol/mol	ISO 14687 (new) EN 17124 µmol/mol
Helium	300	300
Nitrogen	100	300
Argon	100	300
Methane	/	100
Oxygen	5	5
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Water	5	5
Total Hydrocarbons (non methane)	2	2
Total Sulfured compounds	0.004	0.004
Ammonia	0.1	0.1
Formaldehyde	0.01	0.2
Formic acid	0.2	0.2
halogenated compounds	0.05	0.05

from **INTERNATIONAL ORKSHOP METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS, Martine Carré, Air Liquide**

METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Parameters to take into account while choosing a cylinder to sample hydrogen

- Size (ex 10 L: the volume must be enough to perform all required analyses)
- Configuration: two ended cylinders, one ended cylinders
- Materials (Aluminium, steel, alloys and composite materials)
- Different inner treatments as passivation
- Compatibility with available H2-sampling devices (Limiting factor for now)
- Pressure requirements (to be certified for at least 100 bar or the sampling pressure)
- Price range

State-of-art for commercially available sampling vessels - cylinders

Multitude of methods used to passivate the internal surface of cylinders but no great deal of detail about these technologies (proprietary information). The treatments are often to make the surface inert to targeted compounds. Passivation is a technique used to occupy the active areas on the surface of a vessel.

Three categories of treatment can be distinguished:

1) Cleaning, polishing of the internal surface (electro) chemically or mechanically

2) Chemical treatment without targeting structural change of the surface

3) Multi-molecular layer coverage of the initial surface

State-of-art for commercially available sampling vessels - cylinders

Several researchers or cylinder providers have performed tests to assess the stability of the reactive impurities in different vessels show:

1) Often comparison of cylinders with and without passivation

2) Tests performed under different conditions (pressure…), using different vessels sizes and configurations, different matrices (mostly air and rarely hydrogen), concentrations often largely above the thresholds values (ISO14 687 standard)

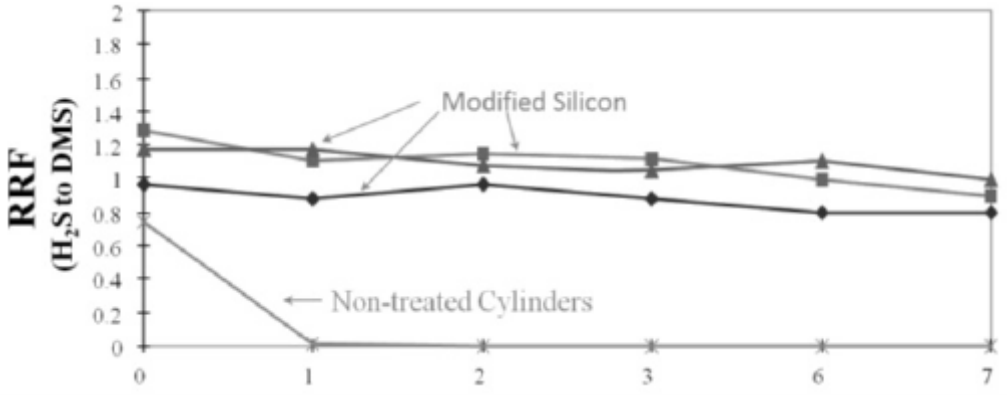
3) Information about tests conditions are often incomplete, therefore difficult to compare different studies

4) Sulfur compounds (specifically H2S) have been studied in larger extends than formaldehyde and formic acid.

State-of-art for commercially available sampling vessels - cylinders

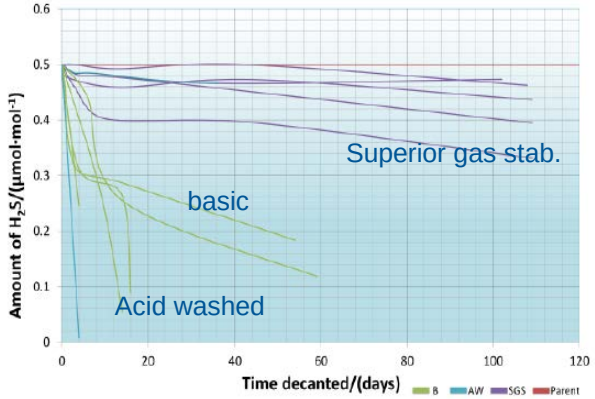
Most of the results (in aluminium or steel cylinders) show that some kind of passivation is required when storing impurities as sulfur compounds and ammonia (at least).

It is therefore of high importance to perform stability tests on these impurities in chosen cylinders and at the conditions relevant for the sampling of hydrogen in order to ensure that these cylinders are suitable for transporting the reactive impurities in hydrogen that need to be analysed for ISO 14 687 hydrogen purity.



Steel

H2S at 17 ppbv in SilcoNert®2000-coated cylinders versus uncoated stainless steel cylinder [1]



Aluminium

H2S amount fraction vs time [2]

[1] Characterizing the performance of surface modifications that enhance sensitivity, reliability, reproducibility and accuracy of analytical instruments", Silcotek notes, D. Saxton, L. Smith, M. Higgins

[2]The effect of internal surface finish of aluminium alloy cylinders on the stability of sensitive gas mixtures", A. Lomax, G. Squire, Gas Analysis conference 2017

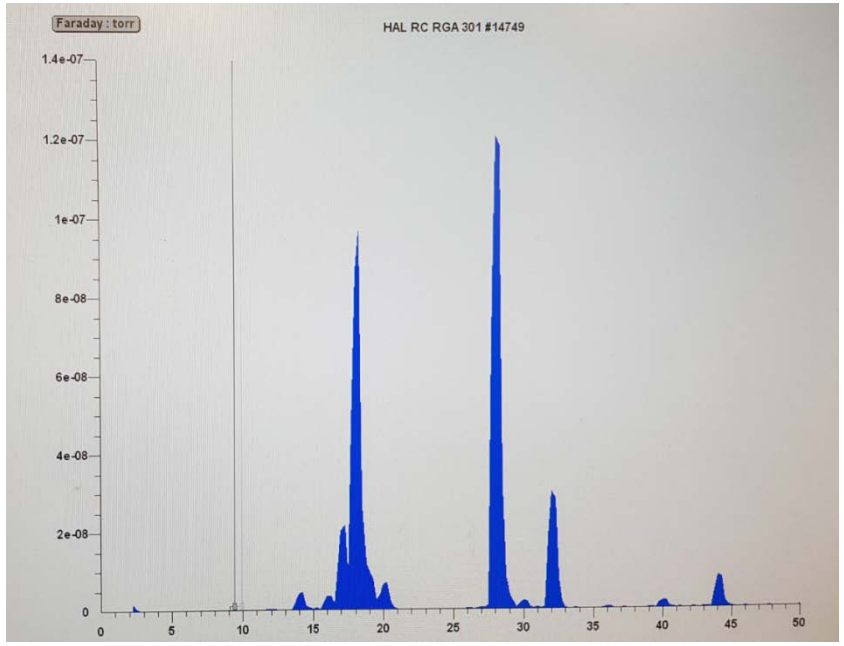
Procedure for preparing vessels before sampling

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.

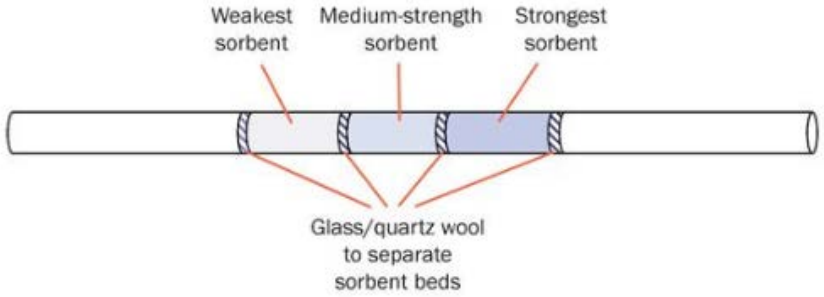
If an expected impurity remains within the system this should be removed by heating or including a subsequent hydrogen purge step.



Other types of vessels: sorbent tubes

Adequate for the organic compounds included in ”total species” (sulfur, hydrocarbons, halogenated

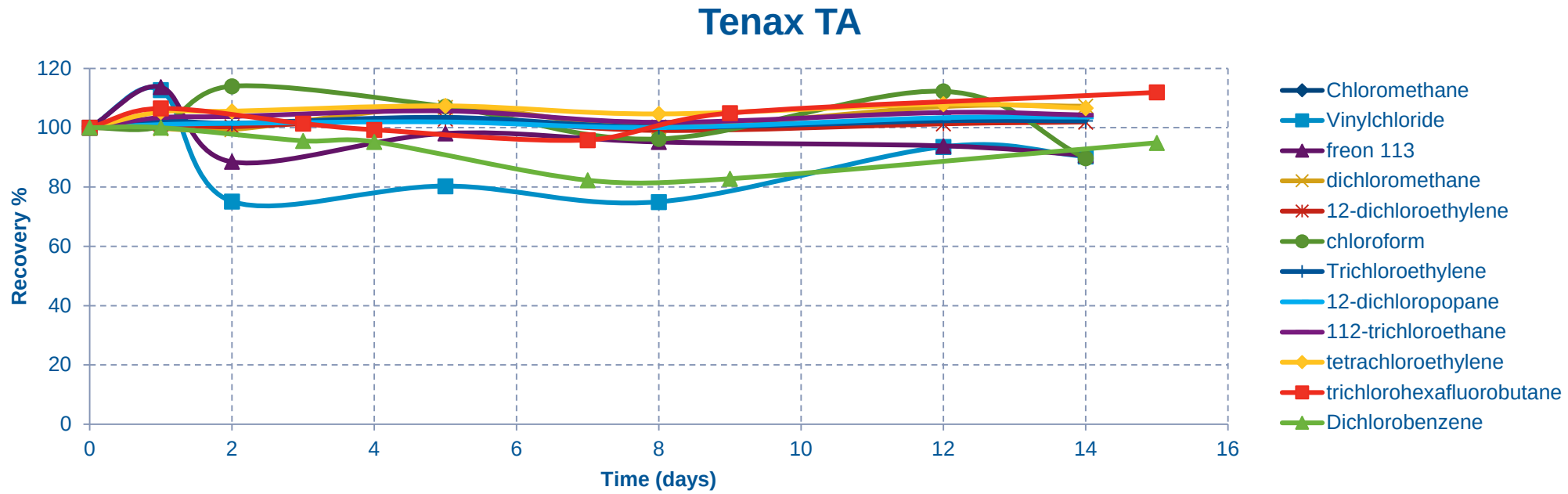
Many sorbent materials available
classified by strength + combinaison
of sorbents

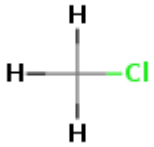


Easy to transport as the hydrogen will not be retained

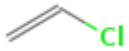
Combined with gas chromatographic techniques: will then give information on which compounds are actually present in the gas

Short-term stability studies – Preliminary results





Chloromethane
BP = -26ºC

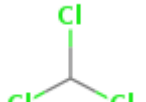


Vinylchloride
BP = -14ºC

Dichloromethane
BP = 40ºC

Trichlorotrifluoroethane
BP = 48ºC

Dichloroethylene
BP = 55ºC



Chloroform
BP = 61ºC

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.

METROLOGY for HYDROGEN VEHICLES

HYDRAITE

EMPIR Project: MetroHyVe

- Validated methods for performing traceable measurement of particles
  - Traceability to the Kg
  - Filter weighing of Hydrogen exposed filters
  - Use of NPL's Robot Weighing system

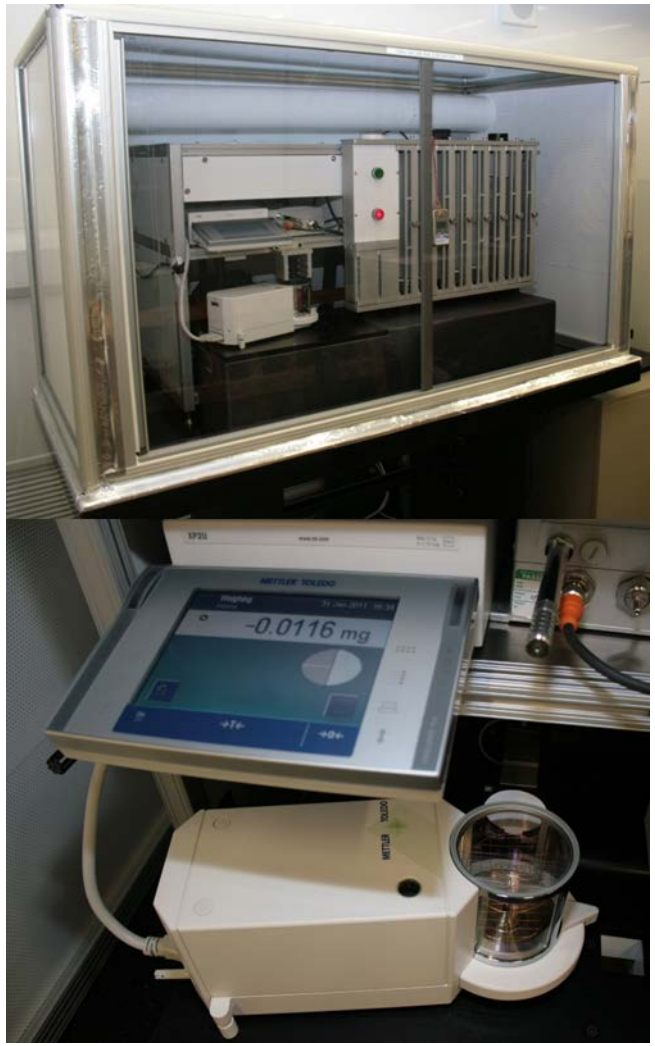
'The EMPIR Metrology for Hydrogen Vehicles will be the first large scale project of its kind that will tackle the four measurement challenges that currently prevent the industry from meeting requirements set by International Standards such as flow metering, quality control, quality assurance and sampling.'

METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Validated methods for performing traceable measurement of particles

- Repeatability on weights ±0.6µg
- Repeatability on filters ±1.0µg
- Effect of static <1.0µg
- Daily throughput 200 filters
- Max filters per batch 450
- Filter sizes 47 and 37mm
- PM_{10} (EN12341)
- $PM_{2.5}$ (EN14907)
- Traceable to the Kg



METROLOGY for HYDROGEN VEHICLES

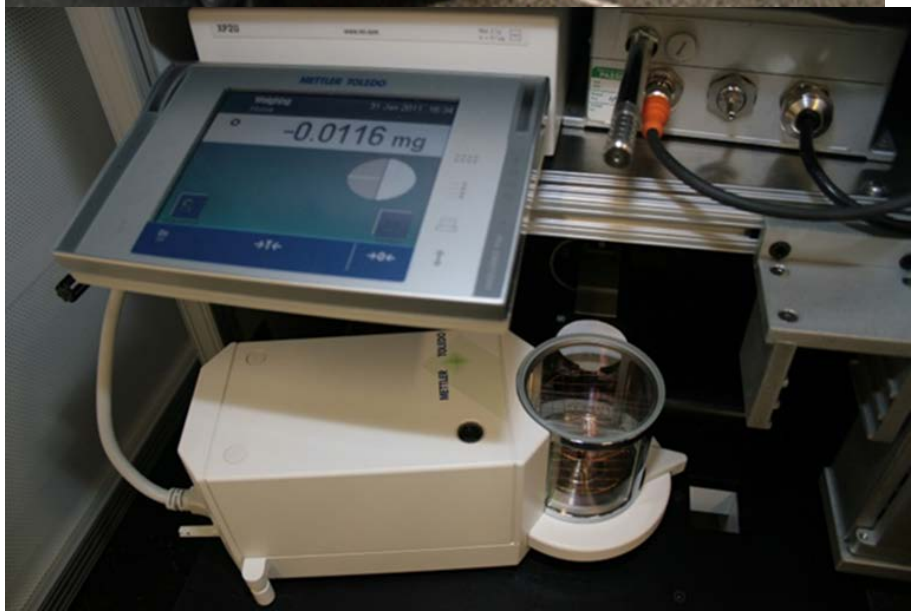
HYDRAITE

Validated methods for performing traceable measurement of particles

- Expose filters to ambient conditions at HRS

1 Hour Exposure

ITM POWER



- Weigh filters to find a pre sampling uncertainty
- The differences between filters range from -12ug to +7 ug
- The conditioning + weighing uncertainty for Emfab filters (95%, k=2) is ~17ug.

METROLOGY for HYDROGEN VEHICLES

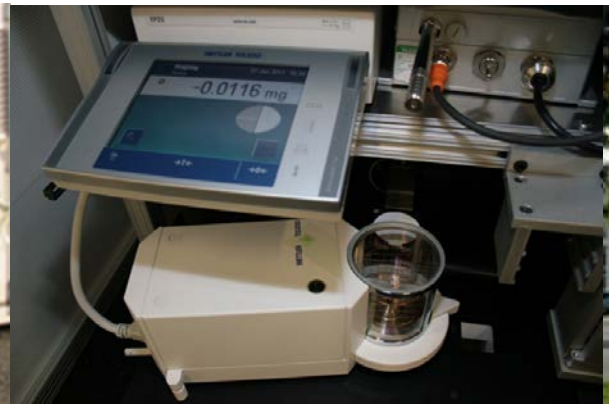
HYDRAITE

Validated methods for performing traceable measurement of particles

- Write a good practice guide for weighing, handling, shipping and storage of filters to be used as a HRS companion to ASTM D7651-10

SINTEF ITM POWER NEN Shell Air Liquide





METROLOGY for HYDROGEN VEHICLES

HYDRAITE

Available resources

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

A4.4.1: Literature review – state-of-art for the storage of reactive species in vessels

A4.1.3: Procedure for preparing sampling vessels for hydrogen sampling

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

A4.3.2: Literature review – state of art of sampling and storage of compounds selected in A4.3.1

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

THANK YOU

METROLOGY for HYDROGEN VEHICLES

metrohyve.eu

HYDRAITE

hydraite.eu