DAIMLER

HYDRAITE 1st OEM Workshop
Hydrogen quality from an OEM´s point of view

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H2 Quality Status – ISO 14687-2 Standard

- The current Standards (ISO 14687-2 and SAE J2719) are based on investigations, conducted in Japan, France and US around 2004.
- Modern MEA configurations are not properly considered within ISO 14687-2.
- The ISO standard 14687-2 is based on the evaluation of single contaminants. The effect of an "ISO-cocktail (*" has not been evaluated.
- The current standard only considers contaminants, which are originated from the hydrogen production process. Contaminants from transportation or hydrogen refueling station technology are not sufficiently considered.
- The measurement methods, used during the ISO pre normative research phase, were not appropriate for proper prediction of the lifetime impact on an automotive fuel cell stack.

* ISO Cocktail: *Mixture of 99,97% Hydrogen and contaminates, according to the ISO 14687-2*

HYDRAITE – Project

The HYDRAITE Project main contents:

I) H_2 supply chain contamination risk assessment

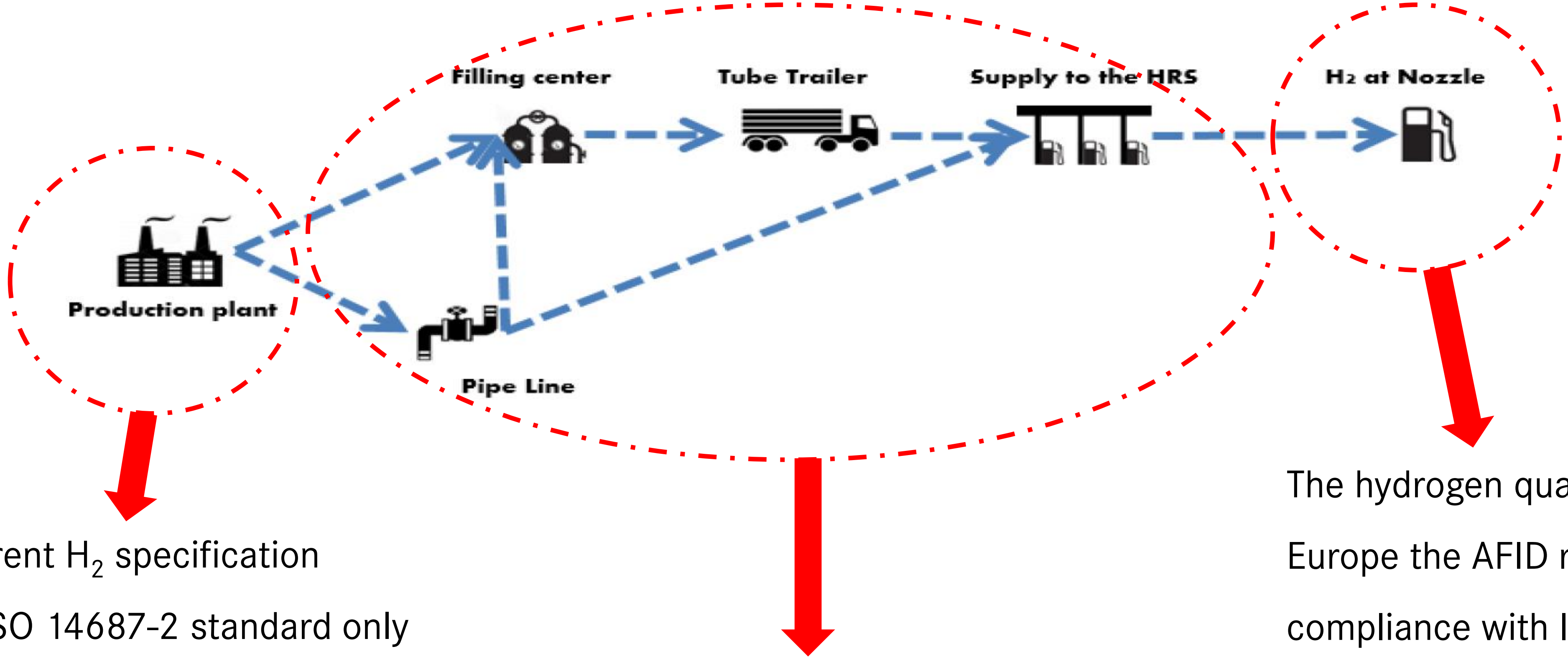
II) H_2 quality monitoring at HRS (sampling and online analysis)

III) Establishing expert H2 purity laboratories

IV) Fuel cell measurements

I) H_2 supply chain contamination risk assessment

Potential sources of contamination



The current H_2 specification within ISO 14687-2 standard only considers contaminants, which are originated from the hydrogen production process.

Contaminants from transportation or hydrogen refueling station technology are not sufficiently considered.

The hydrogen quality at HRS: In Europe the AFID requires the compliance with ISO 14687. California has defined the SAE hydrogen standard SAEJ2719 for their HRS.

I) H_2 supply chain contamination risk assessment

- The entire chain from production to filling nozzle should be considered.
- The Standard ISO 19880-8 for hydrogen quality control currently under development should be taken as starting point und taken into account.
- What additional impurities beyond the current ISO 14687-2 should be considered?
- An on board hydrogen purifier is not an appropriate risk mitigation.
- Recommendations for a revision of ISO 19880-8 should be made from project results.

II) H_2 quality monitoring at HRS

- In Europe the AFID requires a hydrogen quality according to ISO 14687. National implementation is ongoing.
  California has defined the SAE hydrogen standard SAEJ2719 for their HRS.

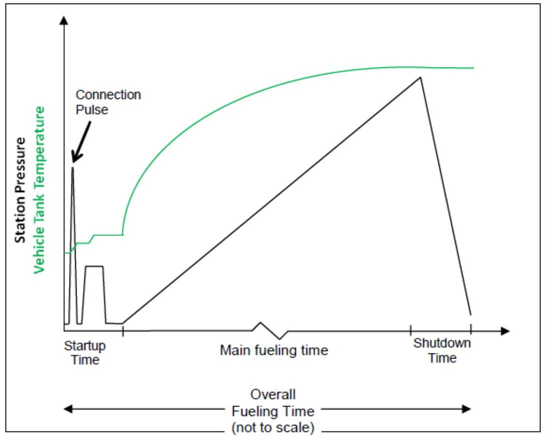
- Today, typically only a hydrogen delivery quality (e.g. Fuel index 99,999) at the HRS is agreed.

- The combination of a high hydrogen delivery quality and the use of not appropriate gas sampling and analysis methods creates a wrong impression of the current hydrogen quality at HRS in Europe.

- It is still a big challenge to proper evaluate the contamination level of hydrogen. Most of the measurement methods do have a too high detection limit. Furthermore solids and liquids are only summarized with a maximum gravimetric value. Their effect on the fuel cell power train is neglected.

II) H_2 quality monitoring at HRS

- Sampling in the bypass or in the main stream to be clarified.
- Sampling must be suitable for all impurities. Impurities include gases, liquids and solid particulates!
- Sampling must be able to detect all potential contaminants indentified in the risk assessment.
- The sampling should comprise the Overall Fueling Time according to SAE J2601.



- Online Analysis must be able to respond within one fueling process.
- Online Analysis should focus on “canary species”/”marker”, e.g. CO.

III) Establishing expert H_2 purity laboratories

Characteristics (assay)	Type I, Type II
	Grade D
Hydrogen fuel index (minimum mole fraction)[a]	99,97 %
Total non-hydrogen gases	300 µmol/mol
Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol/mol
Total hydrocarbons[b] (Methane basis)	2 µmol/mol
Oxygen (O_2)	5 µmol/mol
Helium (He)	300 µmol/mol
Total Nitrogen (N_2) and Argon (Ar)[b]	100 µmol/mol
Carbon dioxide (CO_2)	2 µmol/mol
Carbon monoxide (CO)	0,2 µmol/mol
Total sulfur compounds[c] (H_2S basis)	0,004 µmol/mol
Formaldehyde (HCHO)	0,01 µmol/mol
Formic acid (HCOOH)	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

a The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

b Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

c As a minimum, total sulphur compounds include H_2S, COS, CS_2 and mercaptans, which are typically found in natural gas.

d Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

- Standard and quality control at HRS are focused on gaseous contaminants, according to ISO 14687-2.
- Particles are not defined in detail. Liquids are only mentioned in conjunction with particles.
- Current H_2-specification does not comply with the requirements from Gas Industry and Automotive Industry
- Current revision of ISO 14687-2 ongoing within ISO/TC 197/WG27. Revised ISO 14687 expected to be published in 2018.

III) Establishing expert H_2 purity laboratories

What we expect to be addressed by pre-normative research projects

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Total sulfur compounds[c] (H_2S basis)	0,004 µmol/mol
Formaldehyde (HCHO)	0,01 µmol/mol
Formic acid (HCOOH)	0,2 µmol/mol
Ammonia (NH_3)	0,1 µmol/mol
Total halogenated compounds[d] (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg
Oil, Siloxane, Ionic Liquids	tbd
Metal Ions	tbd

known

new

Gaseous Contaminants

- Threshold values of critical contaminants, e.g. THC, CO, NH_3, sulphur compounds, and halogenated compounds to be checked.
- Sate of the art MEA design and threshold value must match.
- Analysis methods for H_2 quality assurance needed.

Maximum Particulates Concentration

- Threshold value to be checked
- Clear and unambiguous specification of solids and liquids

New Contaminants

partly liquid (aerosol), partly solid?, gaseous?

Liquids are currently not measured.

Solids are not specified.

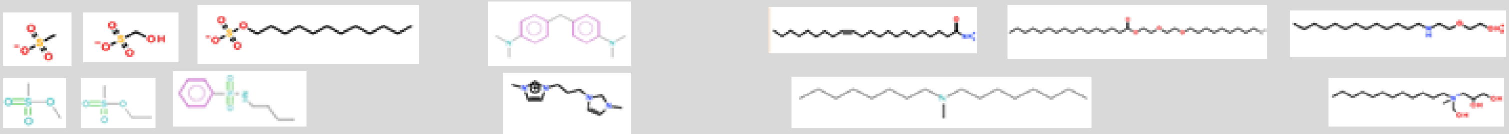
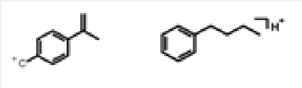
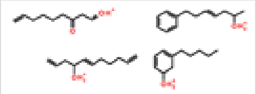
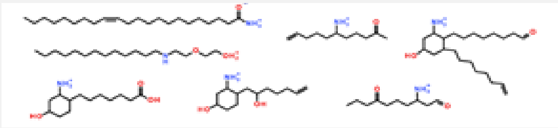
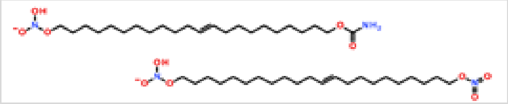
- **Cleanser**
- **Solvents**
- **Lubricants**
- **Siloxanes**
- **Metal / Metal Ions**

Different components from the **ionic liquid** and their decomposition products

Others
(Acids, abrasives, etc.)

III) Establishing expert H_2 purity laboratories

New Contaminants – what we already have found at HRS

	collected contaminates
Particulates	Steel, Aluminium Alloy, Copper Alloy, Plastic, Abrasives (SiC, SiO, Al2O3,...)
Metal Ions	Aluminium, Lead, Boron, Calcium, Iron, Potassium, Cadmium, Copper, Magnesium, Manganese, Molybdenium, Nickel, Silver, Silicium, Titan, Zinc, ...
Ionic Liquid (incl. Additives and Decomposition Products)	
Lubricants	Aromates und Alkenes with one to three double bonds oxidised Alkenes 
Cleanser	
Solvents (possibly from the manufacturing of the ionic liquid)	
Others (e.g. Acids, Nitrate, Siloxane, ...?)	HNO3, H2SO3, .. 

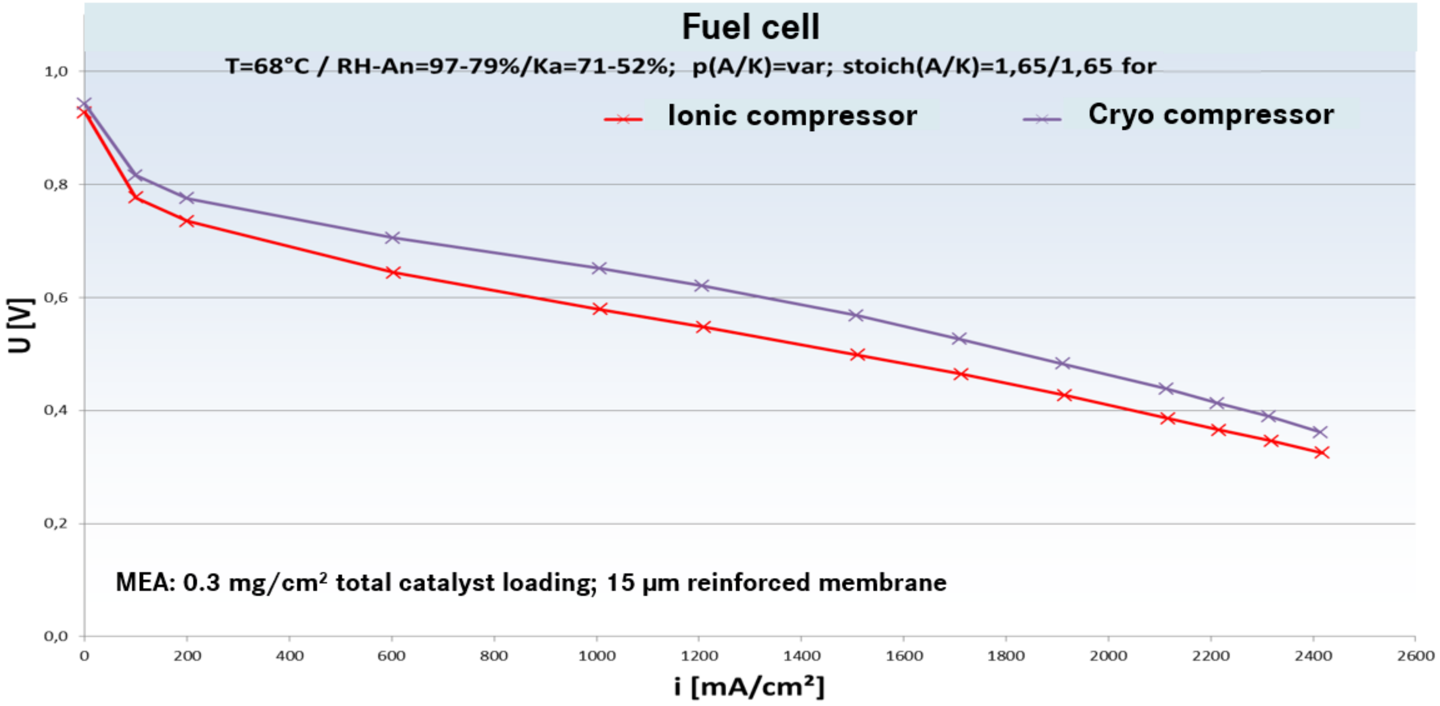
III) Establishing expert H_2 purity laboratories

- Offline analysis should be able to check the overall specification according to ISO 14687.
- Detection/determination limits of analysis methods should not define the threshold value. → Optimization of detection/determination limits needed.
- Analysis cost must be reduced.

IV) Fuel cell measurements

Performance loss in a single cell (50 cm²) - Cryo Compressor vs. Ionic Compressor

- Single Cell, H2/Air Polarization Test was conducted with Normal Operating Conditions.

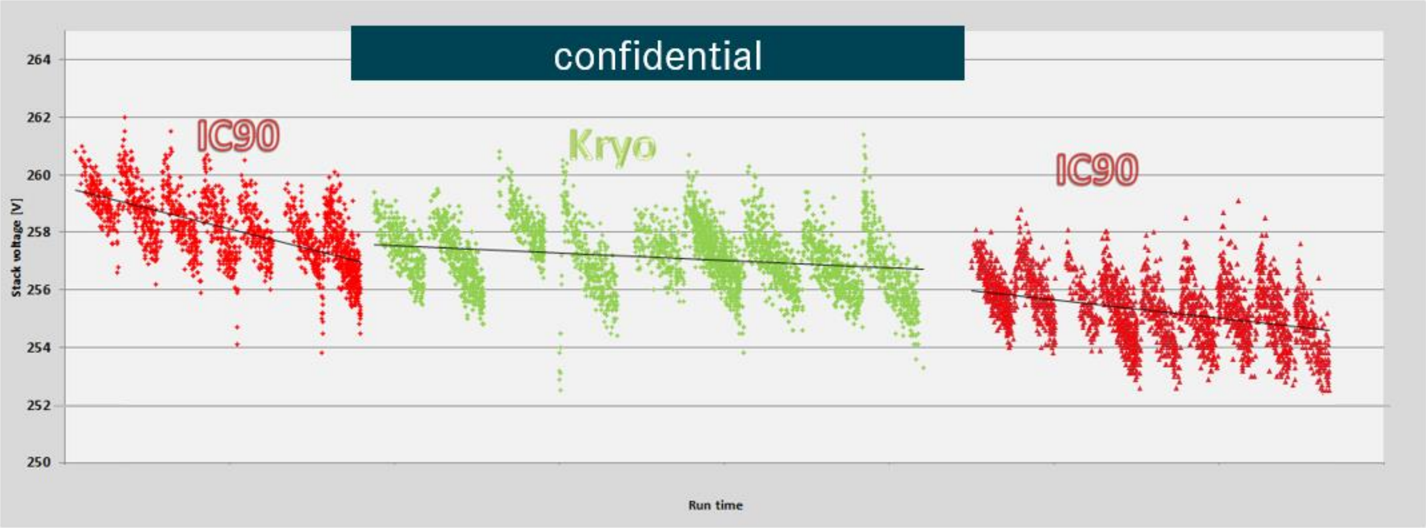


- Fuel cell, operated with hydrogen from an ionic compressor, shows a reduced performance.

IV) Fuel cell measurements

Performance degradation in a fuel cell drive train - Cryo Compressor vs. Ionic Compressor

- Test with a fuel cell drive train has been conducted with hydrogen from different HRS.
- The test was conducted with a typical load cycle.
- The test was interrupted regularly with a typical recovery procedure.



- The performance degradation with Hydrogen from HRS with Ionic compressors is significantly higher. Reasons are not identified yet.

IV) Fuel cell measurements

Selecting a representative fuel cell system for the investigations is not easy:

- Gradient free operation is only possible in a single cell
- Anode recirculation results in a not defined operation compared to flow-through
- With anode recirculation an exact impurity concentration can not be set

How will the project draw conclusions about impurity threshold values from these measurements with a system under "automotive operating conditions"?