A German Hydrogen Quality initiative

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HYDRAITE 1st OEM workshop
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Motivation

- EU directive 2014/94/EU – AFID, Annex II 2.2.

  The hydrogen purity dispensed by hydrogen refueling points shall comply with the technical specifications included in the ISO 14687-2 standard.
- Until now there exist no independed laboratory in Germany that has the capability to analyze according to the ISO standard.
- Nevertheless a quality control has to be performed at the existing, planned and actually being build up HRS

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Development of two independed laboratories for H2 quality measurement according to international standards

Partner: ZBT (coordination), ZSW & CEP (ass.)

Start: April 2017 (Duration: 2,5 years)

Nationales Innovationsprogramm Wasserstoff- und Brennstoffzellentechnologie

Gefördert durch: Bundesministerium für Verkehr und digitale Infrastruktur

Koordiniert durch: NOW Nationale Organisation Wasserstoff- und Brennstoffzellentechnologie

- **Elaboration of analytic methods for measuring the hydrogen quality according to ISO 14687**
- **Optimization of the actual sampling method**
- Analysis of hydrogen from different sources (HRS etc.)
- Identification of canary species
- Inter comparison with other international labs
- Concept on FC based online sensor
- Support of normative activities in Germany and EU

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Analytics – Evaluation of updates of quality standard

Component	ISO 14687-2 2012 *	prEN 17124: 2017
Hydrogen fuel index (min mol fraction)[a] / %	99,7	99,7
Impurities	300	300
Water (H_2O)	5	5
Total hydrocarbons (THC)[b] (excluding Methane)	2	2
Methane (CH_4)	-	100
Oxygen (O_2)	5	5
Helium (He)	300	300
Nitrogen (N_2)	100	300
Argon (Ar)	100	300
Carbon dioxide (CO_2)	2	2
Carbon monoxide (CO)[c]	0,2	0,2
Total sulfur compounds (H_2S basis)	0,004	0,004
Formaldehyde (HCHO)[c]	0,01	0,2
Formic acid (HCOOH)[c]	0,2	0,2
Ammonia (NH_3)	0,1	0,1
Halogenated compounds[d] (Halogenate ion basis)	0,05	0,05
Maximum particulates concentration / mg/kg	1	1

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

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).

c Total of CO, HCHO, HCOOH shall not exceed 0,2 µmol/mol

d Halogenated compounds include, for example, hydrogen chloride (HCl), and organic halides (RX). Species will be checked according to the Quality Assurance.

* Type 1: Gaseous Type 2: Liquid; Grade D: PEM fuel cells for road vehicles

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Analytics – ZBT analytic configuration

Impurity	ISO 14687 [µmol/mol]	Analytical Method	Detection Limit * [µmol/mol]
Water	5	Quartz crystal microbalance (QCM)	0,1
		IMR-MS	< 5
Total Hydrocarbons	2	GC-PED	0,01
		IMR-MS	0,5
Methane	100	GC-PED	0,01
		IMR-MS	0,125
Oxygen	5	GC-PED	0,01
		IMR-MS	3
Helium	300	EI-MS	200
Argon	300	GC-PED	0,05
		EI-MS	< 100
Nitrogen	300	GC-PED	0,1
Carbon Dioxide	2	IMR-MS	0,5
Carbon Monoxide	0,2	GC-PED	0,001
		IMR-MS	0,06
Total sulphur compounds	0,004	TD-GC-SCD	< 0,001
		IMR-MS	0,001 (H_2S)
Formaldehyde	0,2	IMR-MS	0,0022
Formic Acid	0,2	IMR-MS	0,05
Ammonia	0,1	IMR-MS	0,003
Halogenated compounds	0,05	IMR-MS	< 0,009

* Manufacturer Specification

Ion-Molecule Reaction Mass Spectrometry (IMR-MS)
Electron Ionization (EI-MS)

GC with Sulfur Chemiluminescence Detector (SCD) with Thermo desorption (TD)

GC with Plasma Emission Detector (PED)

Quartz Crystal Microbalance (QCM)

Pictures: MS4 Analysetechnik, cmc Instruments, Perkin Elmer & Michell

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Analytics – Calibration system

ISO/DIS 21087:2018 Analytic methods (ISO TC 158/JWG 7)

- Maximum uncertainty for impurity measurement
  - 50 % for total sulphur and formaldehyde
  - 10 % for others

To be defined

- Dilution of singular species or mixtures?
- Availability of gas standards?
- Acceptable uncertainty of calibration gases?
- Usage of which calibration system?

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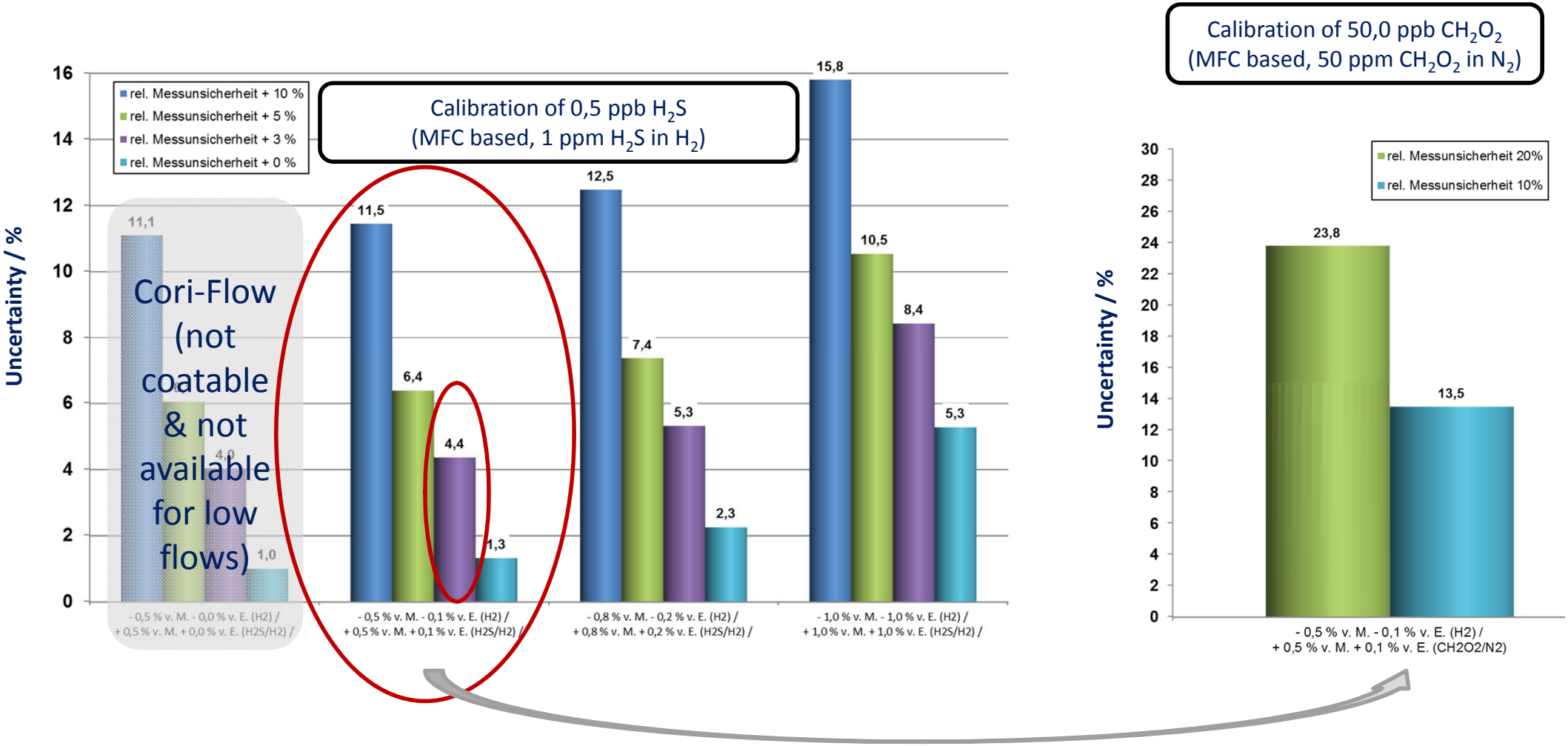
Analytics – Calibration system

Calibration uncertainty depending on

- Impurity concentrations and uncertainties in calibration gases
- Dilution system



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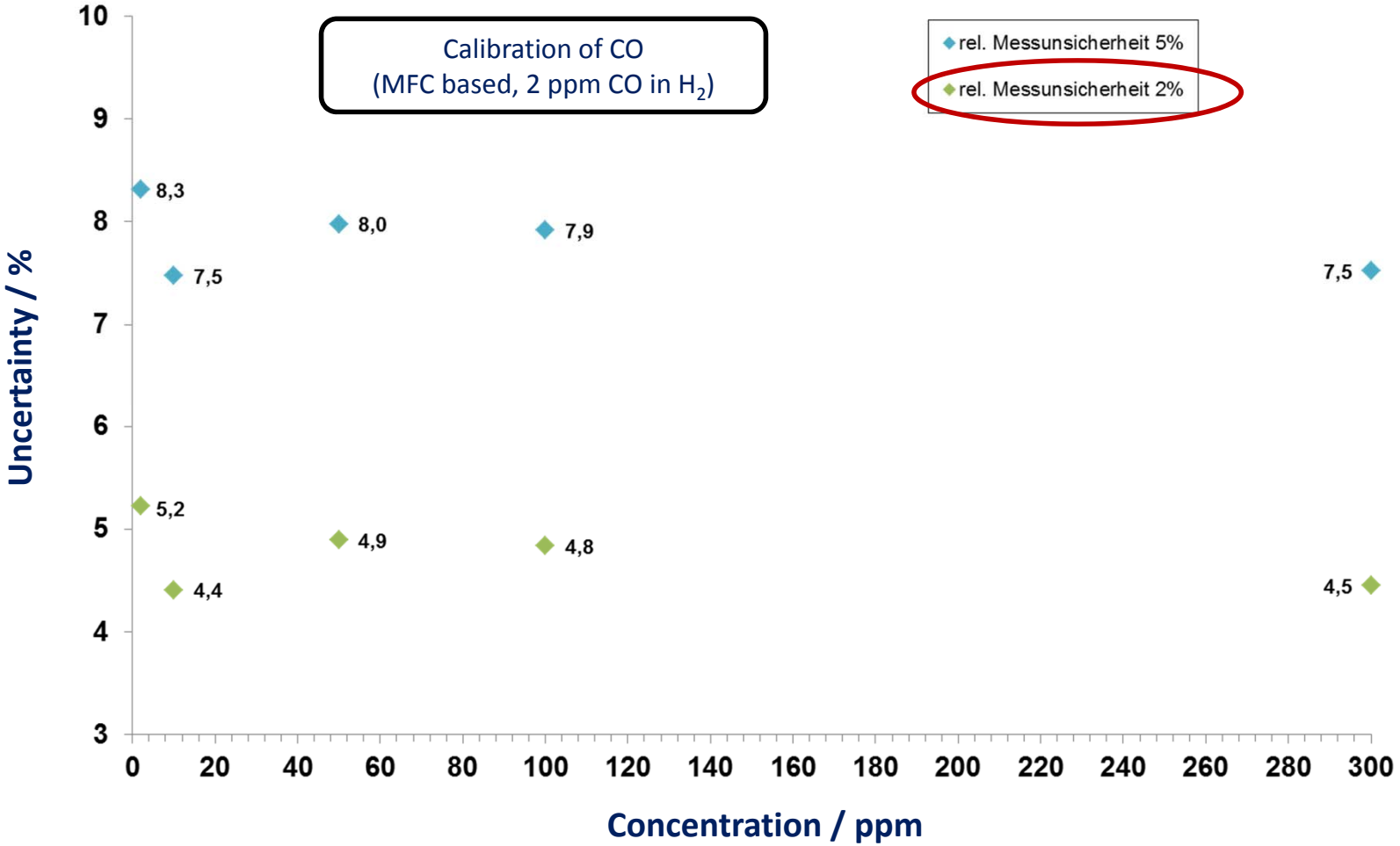
Analytics – Calibration system



Costs for calibration gas (depending on species/mixtures, concentrations & uncertainties)

- Up to > 1.000 € for single species
- Up to approx. 3.000 € for mixtures

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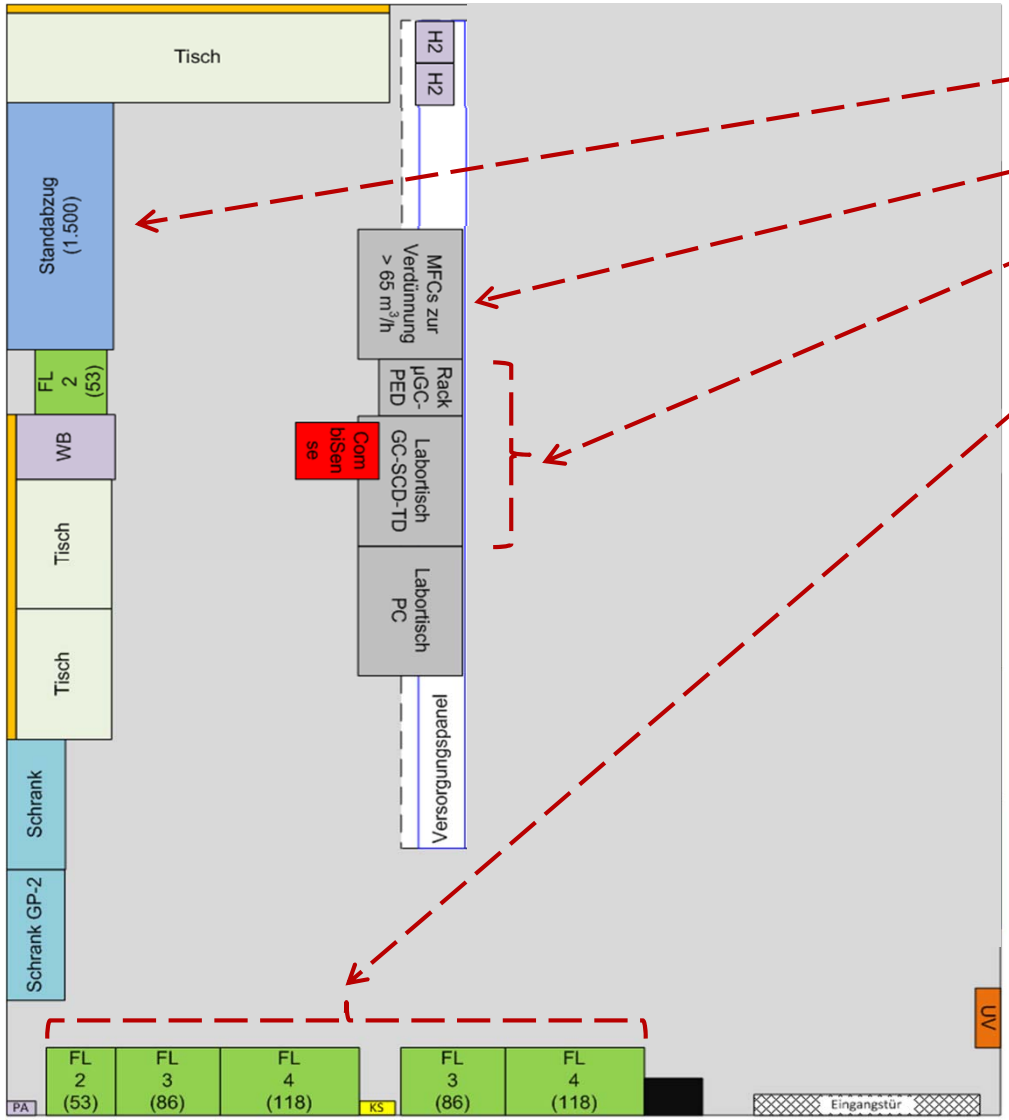
Analytics – ZBT lab planning's

Online approx.
in Q IV / 2018



- Conditioning of sample cylinders
- Calibration system
- Analytic devices
- Calibration gas supply

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Gas sampling

- Evaluation of existing approaches according to ISO 19880-1 and from Linde, Air Liquide etc.
- Iterative process
  - Concept development (incl. support of notified body)
  - Compliance with HRS manufacturers, operators & OEMs, (national & international)
  - Identification of suitable manufacturers
- Purchasing devices and equipment and elaboration of regulations and certification
- Validation

H2 Qualitizer

Japan

US

Pictures: ZBT, 2016; Idemitsu Kosan Co., Ltd., 2015; Smart Chemistry 2018

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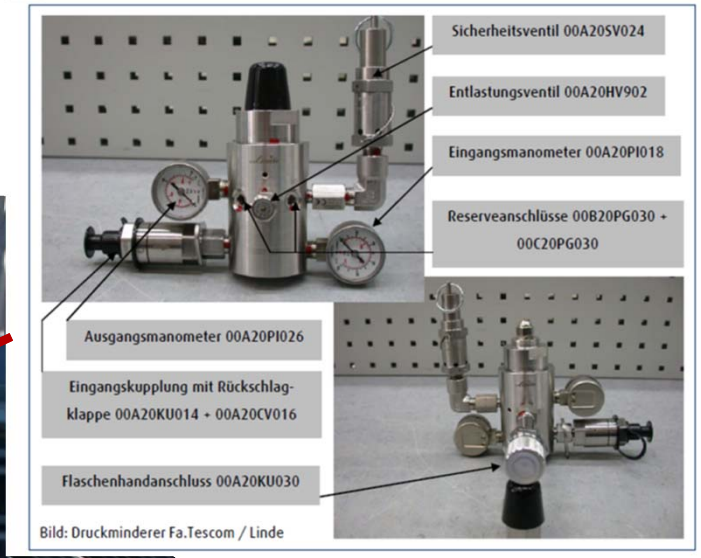
Gas sampling – Linde H2 Qualitizer (FCEV as sink, parallel, no override)



Pictures: ZBT, 2016; Linde 2013

Features	Problem	Consequences
FCEV necessary as sink	Availability of empty cars	Not feasible for higher number of HRS
	Single sampling per FCEV fueling	Multiple samples (QM) requires more FCEVs
Uncoated parts	Wall effects	Uncertainties in measuring S, H_20 etc.
H_2 purging necessary (close to dispenser) for pressure release	Potentially / hazardous explosive atmosphere	Avoidance of sources of ignition, classification of hazardous areas…
Release of H_2 @700 bar (in case of pressure reducer failure)	hazardous explosive atmosphere	!?!

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Sampling – Proposals of solutions

Short term with FCEV as sink

- Gas
  - H2 Qualitizer (possibly adapted)
  - AL device
- Particulates
  - Downstream sampling (Hydac PSA)

Long term without FCEV

- Option 1
  - Gas: Buffer tank as sink plus venting of surplus H_2
  - Particulates: parallel sampling (Hydac PSA)

- Option 2
  - Gas: Modification of the SAE J2601 (“Sampling” protocol) or overriding fueling protocol
  - Particulates: No parallel sampling (Hydac PSA)

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Gas sampling – Hydrogen qualities

Sampling and analysis of hydrogen from different sources
(production, logistics, CEP-HRS etc.)

- 2 sampling campaigns at HRS in 2018 planed
  - 1st: Only CEP limits possible, sampling with HQSA by ZBT/ZSW & analyzing by ZSW
  - 2nd: Target ISO limits, sampling with HQSA (?) & analyzing by ZBT/ZSW
- Identification of impurities and their sources from hydrogen production to dispenser
- Identification of canary species

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Thank you

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