Lessons learnt with hydrogen sampling

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Overview

- Fuel quality results
- Sampling methodology
- Sampling experiences
- Shipment
- Analytical comparison
- Filter analysis
- Conclusions

Introduction

- Sampling H_2 from HRS since 2012
- Experience from 38 gas and 18 particulate samples will be covered here (Hydraite + Hycora)
- 4 European countries
- 4 Sampling campaigns

  (4 years)

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Fuel quality results

- Results from analysis by SmartChemistry using ASTM methods
- **Main finding is that despite some violations the fuel quality is good**

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Fuel quality results

- Based on analysis from SmartChemistry using ASTM methods
- **Main finding is that despite some violations the fuel quality is good**
- Most common violations are components from air, and hydrocarbons
- No violations for CO, halides or sulphur
- Often an explanation for the violations
- No particulate samples above ISO limits

Fuel quality violations

Component	Limit [ppm]	Average [ppm]	Median [ppm]	Max [ppm]	Violations
O_2	5	7.3	5.7	13	7 (+1 at the limit)
N_2 + Ar	100*	527	398	1444	6
CO_2	2	5.7	5.7	5.7	1
Non Methane Hydrocarbons	2	30	30	30	1

Fuel quality violations

	HD-SC1	HD-SC1	HY-SC3	HY-SC2	HY-SC2	HY-SC2	HY-SC2	HY-SC2	HY-SC2	HY-SC1	HY-SC1
Station ID	1	2	3	4	5	6	7	8	9	3	10
THC (C1)	0.4346	0.1704	47	0.07	0.36	0.30	0.42	5.1	0.88	0.55	0.1
Methane	0.41	0.14	17	0.062	0.18	0.18	0.38	5.0	0.85	0.093	0.03
Acetone	0.009			0.0045	0.0069	0.0174	0.011	0.045	0.0072	0.0078	0.0078
O2	1.1	<1	1.8	11	5.7	5.2	5.4	13	5.4	4.1	5.7
He	<10	15			40						
N2 & Ar	237.48	234.47	452	26	18	56	378	419	76	1444	34
N2	237	234	448	26	18	56	378	416	76	1443	34
Ar	0.48	0.47	4.3					3.1		0.67	0.46
CO2	<0.1	<0.1	0.37					5.7		0.43	

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Fuel impurities within limits

Component	Count	Average excl violations [ppm]
CH_4	**38/38**	**0.77**
Acetone	**19/38**	**0.012**
Ethane	**12/38**	**0.59**
EtOH	**19/38**	**0.040**
Isopropyl Alcohol	**9/38**	**0.015**
Propane	**25/38**	**0.39**
Toluene	**8/38**	**0.0061**
Isobutane	**12/38**	**0.24**
N-butane	**5/38**	**0.0118**

Table shows number of samples where compound is identified, total samples in campaign, average value of detecte componds [ppm]

Fuel impurities within limits

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Component	Count	Average [ppm]
H_2S	**34/38**	**1.49E-5**
COS	**38/38**	**2.99E-5**
MTM	**4/38**	**6.43E-6**
CS2	**12/38**	**3.67E-6**
DMS	**8/38**	**5.19E-5**
$C_4Cl_4F_6$	**38/38**	**0.011**

Gas sampling

- Linde H2 Qualitizer
- Parallel sampling
- Sample bottles are evacuated in the lab, equipment can be purged before sampling
- Efficient sampling
- During cascade change station will do a leak-test (pressure monitoring)

  →Sample bottle have to be closed

Sample containers

Spectraseal treated 10L cylinders used

- Evacuated to 2 mbar and filled to 10 bar with 6.0 H_2 2x, and then evacuated
- Tracking of cylinders

→ No carryover

	HY-SC2-10	HY-SC3-2
THC (C1)	**5.1**	**1.7**
Methane	5.0	0.6
Acetone	0.045	
Propane	0.066	0.018
O2	**13**	
N2 & Ar	**419**	**8**
N2	416	8.3
Ar	3.1	
CO2	**5.7**	
CO	**0.015**	**0.001**
TS	**0.00011**	**0.00001**
H2S	0.000012	0.0000026
COS	0.000085	0.0000071
CS2	0.00001	
TH	**0.0033**	**0.0026**
C2Cl2	0.0023	
C4Cl4F6	0.0010	0.0026

Particulate sampling

- Hydac PSA H70
- Need H_2 amount (HRS)
- Used a 0.2um filter (ASTM) rather than a 5 um filter (iso / Hydac)
- Sensitivity is good with standard deviation 0.1 mg/kg H_2 obtained
- Sufficient to meet the ISO detection limit of 1 mg/kg
- Most samplings have been done in series with Linde qualitizer
- Purging of sampler a possible challenge

  →Addressed by redesign by HYDAC

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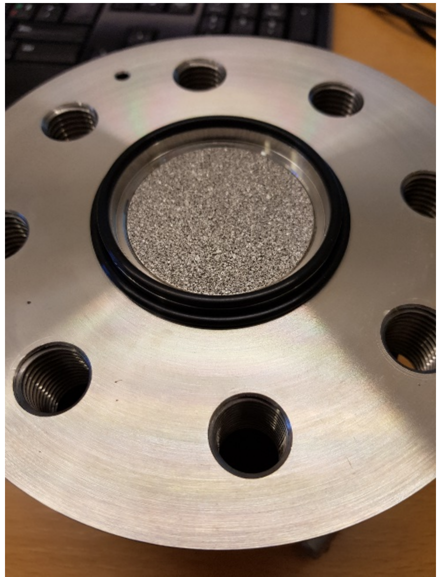
Particulate sampling

- Filter needs to be weighted, handled and changed in clean atmosphere
- Clean room in the lab
- Inflatable glovebox in the filed
- Measurements with field blanks proves the concept
- Several discarded samples, no easy way to reset equipment fast (Sampler cold, car full etc.)



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Practical experiences

- No safety incidents, and no events that lead the station to shut down
- Using Linde qualitizer and Hydac PSA H70 does not require station operators to be present (local rules might)
- Sampling will be just a regular filling seen from the station side
  - → Refuelling card can be locked after X attempts, can cause challenges due to the need for purging

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Sampling challenges

Need for empty FCEV

- Few FCEV available
- Long time to empty
- Contaminated station = contaminated car (gas)
- Most suited for routine analysis

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Combined sampling

Obtain particulate and gas sample at the same time

- One car for both samples
- Technically not a challenge
- More equipment = Pressure drop and volume
- Which device should be put first
  - → Linde first can trap particulates
  - → Hydac first can trap sulphur species (more surface)

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Sample shipment

Shipment of pressurized H_2 is challenging

- Different national rules
- Customs
- Transport companies have little experience, handover between local and global carriers a challenge
- HRS is often not a good collection point for carriers
- Using laboratories as collection points for cylinders
- Should be carried out as fast as possible

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Analysis comparison

Until Hydraite project only SC in USA were able to analyse the full standard

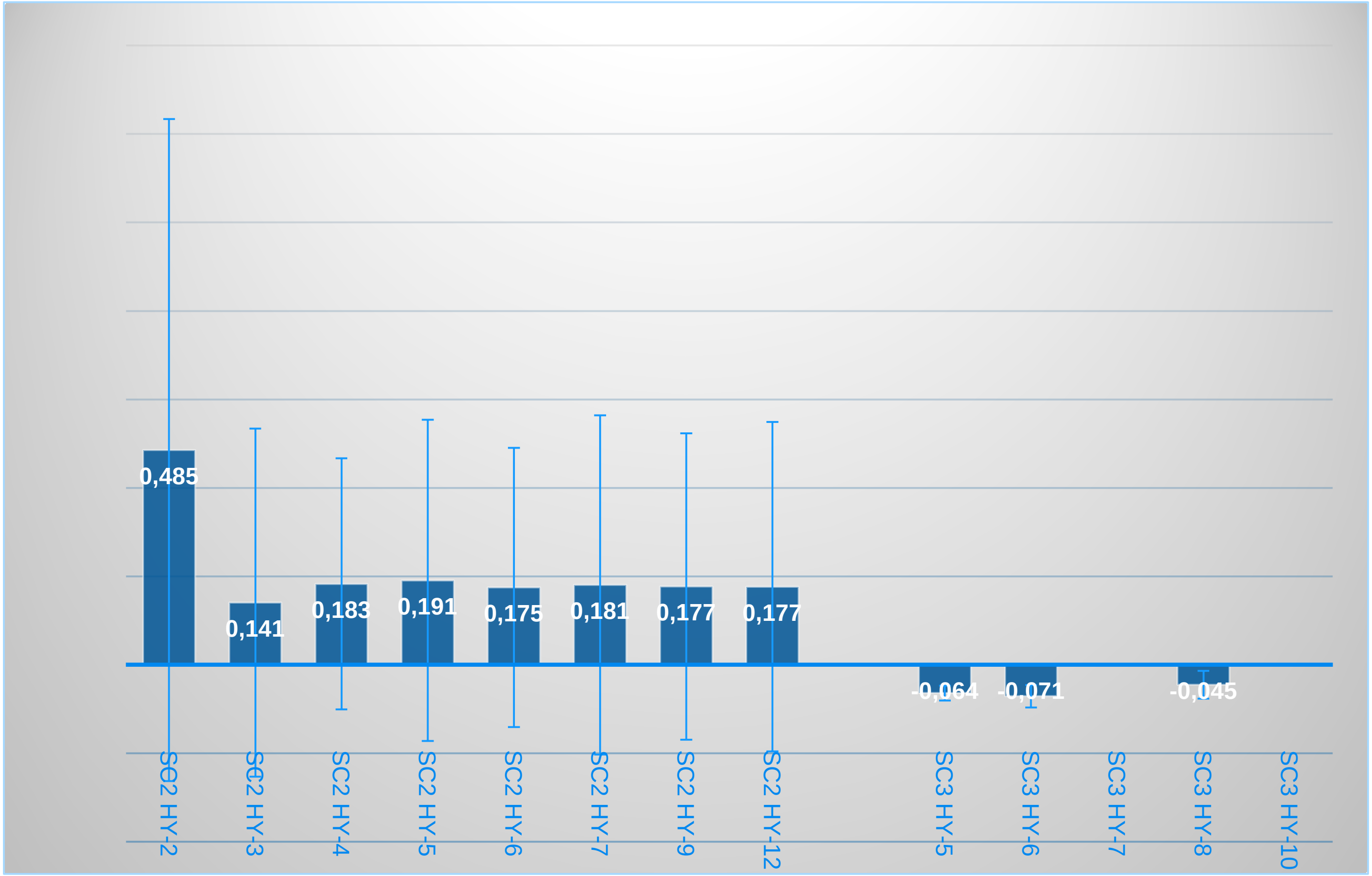
- Few options to compare data from independent labs
- Some labs could do part of the analysis
- Hydraite → Europe will shortly have 3 laboratories
- SC samples have to be transferred to smaller bottles → Increases risk for contamination

Laboratory comparison

	SC	NPL	SC	NPL	SC	NPL	SC	NPL
	HD-SC1-1		HD-SC1-4		HD-SC1-6		HD-SC1-7	
N2	75	70 ± 11	237	231 ± 22	8.9	7.96 ± 0.42	234	33.5 ± 1.8
Ar	0.75	0.628 ± 0.016	0.48	0.336 ± 0.017	< 0.4	< 0.30	0.47	< 0.30
H_2O	< 1	3.30 ± 0.20	< 1	4.29 ± 0.30	1.5	6.01 ± 0.40	< 1	7.1 ± 0.5
CO_2	< 0.1	< 0.020	< 0.1	< 0.020	< 0.1	< 0.020	< 0.1	0.040 ± 0.005
O_2	< 1	0.794 ± 0.023	1.1	< 0.030	2.3	1.105 ± 0.033	< 1	< 0.030
He	< 10	< 30	< 10	< 30	13	< 30	15	< 30
NMHC	0.14	< 0.10	0.02	< 0.10	0.03	< 0.01	0.03	< 0.1
CH_4	0.12	< 0.020	0.41	< 0.020	0.11	< 0.020	0.14	0.0194 ± 0.0040

Gravimetric filter analysis

- None of the samples were above the limit of 1 mg/kg H_2
- Standard deviation on measurement from 0.1 to 0.3*mg/kg
- Low H_2 amount increases uncertanty
- Recommended drying cycle from Hydac not sufficient for our type of filters
- Filters dried / weighted until no weight change



*Before drying procedures were improved

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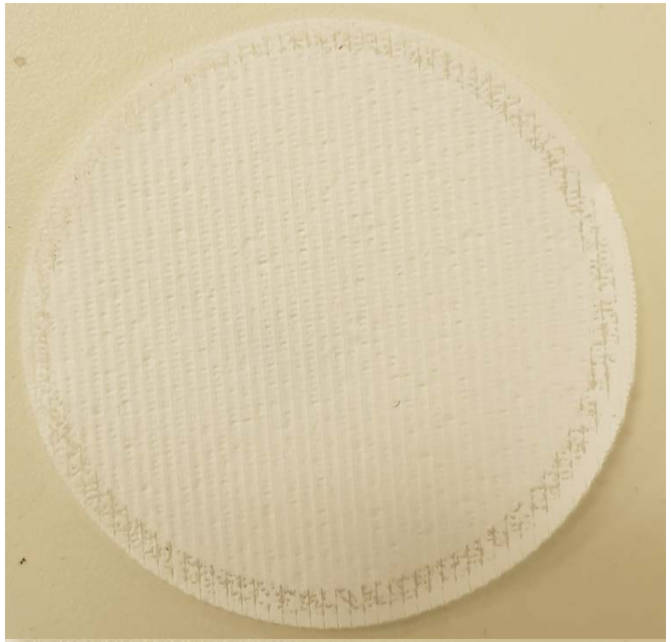
Filter SEM analysis

- Visually filters look clean, only traces in SEM
- Edge is compressed by the O-ring, but confirmed by SEM to not de-laminate (still contains same amount of fluor, but have less porosity)
- Holes in the filter indicates that particulates penetrates the filter
- Filters look noticeably different after use, but not dirty



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Conclusions

- Sampling can be carried out safely and without disrupting normal operations of the station
- Overall high purity of the hydrogen, some violations
- No obvious trends for impurities based on feedstock
  → Most regular impurities comes from operation?
- More capable laboratories will give better analysis
- Filter samples indicates low amount of particulates, but some penetration of the filter

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Available resources

- HYDRAITE deliverable D3.1
- Hycora project reporting
- Publications

[Acknowledgements…]

THANK YOU

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