HyCoRA

Sampling and analysis: Lessons learned from HyCoRA

Hydraite OEM workshop

Ulm, 2018-03-07

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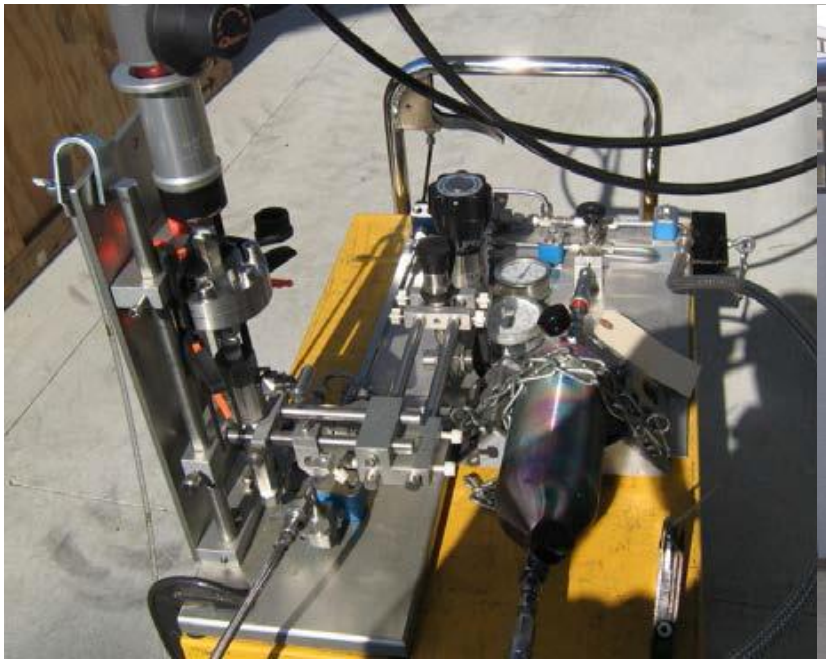
Protea
advanced monitoring
process improvement
pollution prevention

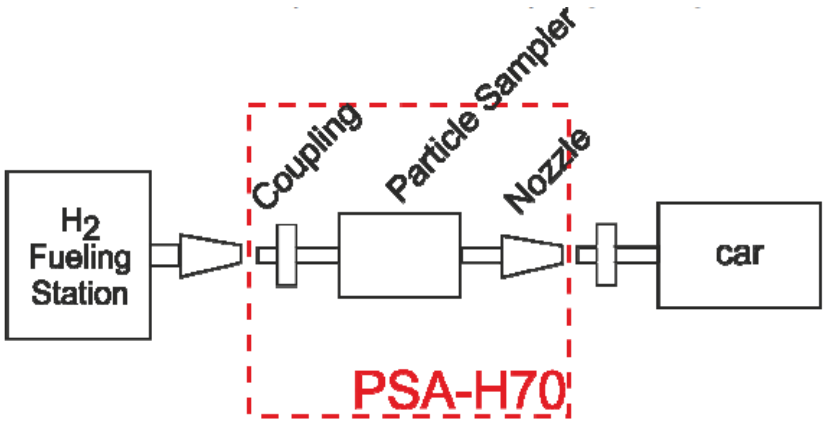
SINTEF sampling background

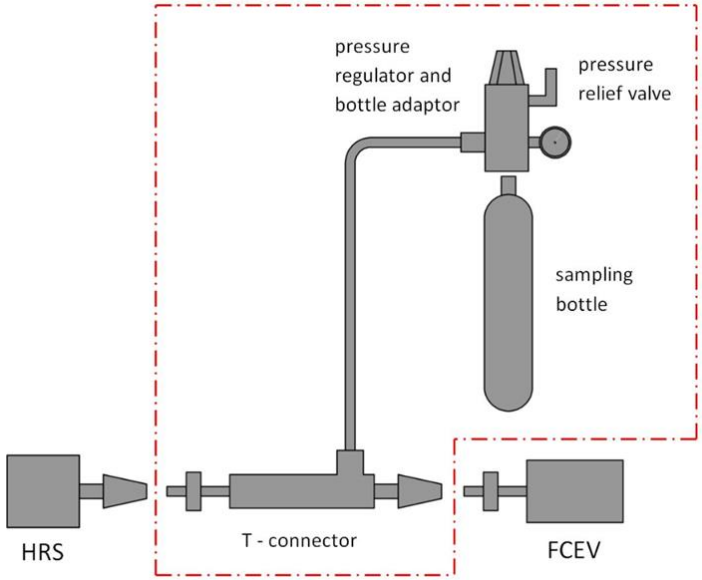
- SINTEF subcontracted Smart Chemistry for HRS QC in 2012
  - 3 HRS in Norway
- Rented sampling instrumentation from SC (ASTM D7606-11)



HyCoRA sampling strategies

- Commercial instrumentation
  - Linde: Qualitizer 70 MPa gas sampler
  - HYDAC: 70 MPa particulate sampler
- In-line strategy making use of FCEV as sink
- Instruments purchased by SINTEF





Gas sampling adapter

- Linde 'Qualitizer'
- No IrDA (limit of 60 MPa)
- Manual override of HRS safety not required

Gas sampling adapter

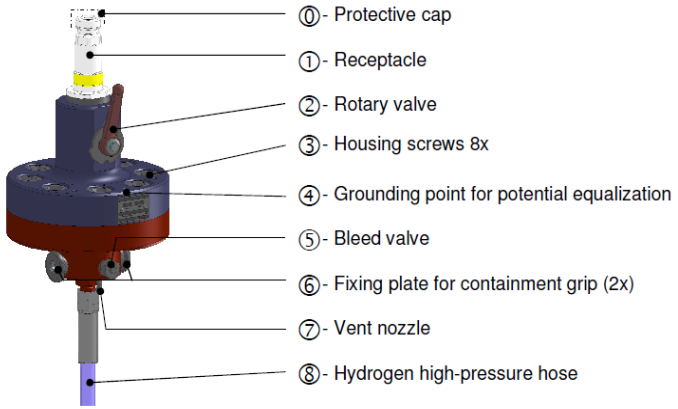
- Manual purge at 6 Mpa with UHP H_2 before first time use (to remove air)
- Hose kept slightly pressurized by check valves
- Depressurization by bleed valve
- Purge procecure by abortion of refuelling sequence and depressurization possible
- Internal volume not significant compared with the +1000 L sample.
- SINTEF has not purged instrument between samples. No indication of impurity carry over has been observed in analytical results

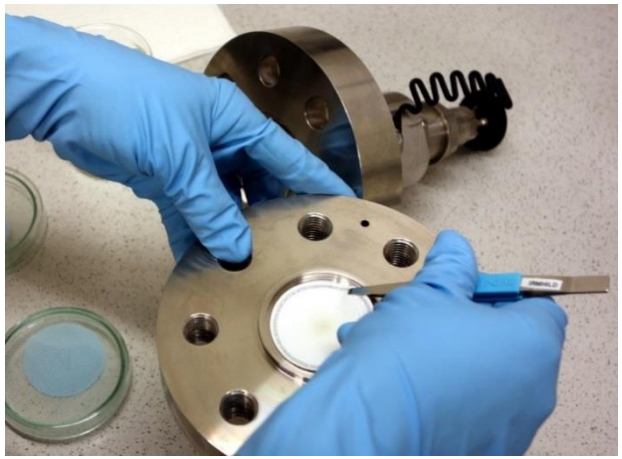
Sample cylinders

- 10L Aluminium (SS valve) Linde Spectraseal canisters
- Evacuated to 1 mbar before use
- Cleaning cycle
  - Evacuation to 1 mbar
  - Pressurization to 10 bar (UPH H_2)
  - Repeat 3x

Particulate sampler

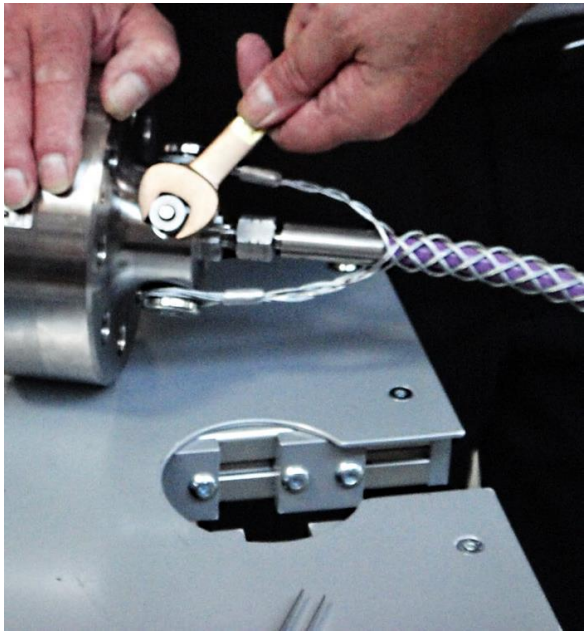
- HYDAC PSA-70
- 70 MPa sampling
- No IrDA
- Series connection with gas sampler

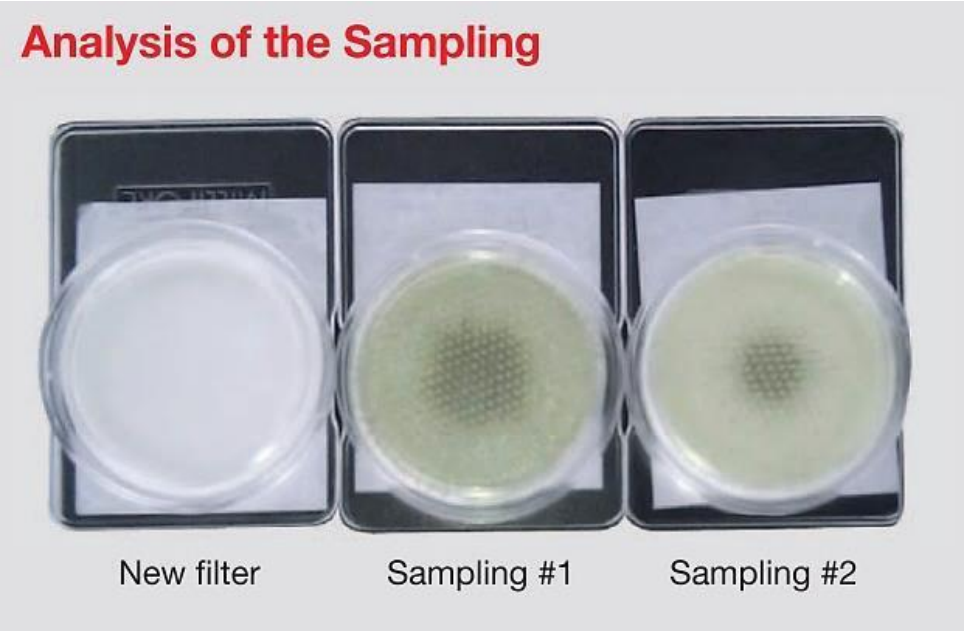




Particulate sampler

- Depressurized by bleed valve
- 0.2 and 5 µm filters available
- "Clean room" required for filter change





Sampling issues not addressed

- Sampling cylinder purging requirements
- Sampling adapter purging requirements
  - No indication of carry over observed
- Stability of samples in (lined) cylinders
- Sample tranference to other (smaller) cylinders
  - Used with shipping to US (Smart Chemistry)
- HRS back to back sampling
- Impact of serial sampling
  - Gas upstream particulates
  - Particulates upstream gas

Sampling experiences

- When supplied with a pressure >100 bar the Linde sampler will drain H_2 from the hose
  - Leak test will fail if bottle valve is not closed
- The equipment should not be used in heavy rain as ice can lock moving parts and prevent disassembly
- Equipment works without any safety override on all tested stations

Sampling stragegy downsides

- Some critics for the use of FCEV as sink
  - Need 1 (2) empty FCEV
- Depressurization to air depreciated
  - Use of HRS safety vent
  - HYDAC redesign available
- Vacuum in cylinders
  - Air leak

Strategy for analysis

- SoP: only Smart Chemistry available for analysis with full compliance with ISO 14687-2 (SAE J2719)
  - Shipping cost high
  - Time from sampling to analysis at least two weeks
- For the third sampling capaign:
  - 10 samples sent to Smart Chemistry
  - 5 samples sent to NPL
  - 5 samples sent to Protea

Smart Chemistry Analytical methods

	ASTM	Analytical technique	Pre concentration
THC (C1)	WK34574	GC-MS	Cryo/TD/Cryo
He	D1946	GC-TCD	
N_2. Ar. O_2. H_2O	D7649	GC-MS	
CO_2	D7649	GC-MS	
CO	D1946	GC-PDHID	Cryo
HCHO	D7892-15	GC-MS	Cryo/TD/Cryo
HCOOH	D5466-15	GC-ELCD	Cryo/TD/Cryo
NH_3	D5466-15	GC-ELCD	Cryo/TD/Cryo
HCl. HBr. Cl_2	D5466-15	GC-ELCD	Cryo/TD/Cryo
TS	D7652	GC-SCD	Cryo/TD/Cryo
C-X	D7892-15	GC-MS	Cryo/TD/Cryo

SC1: Diversity in feedstock

ID	Tol	HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8
Feed		WE	SMR	SMR/BIO	SMR/BIO	WE	CA	WE	WE
Storage		C	C	L	L	C	C	C	C
On-site		Y	N	N	N	Y	N	N	N
H_2O	5	< 1	< 1	< 1	< 1	< 1	2.9	< 1	< 1
THC (C1)	2	0.049	0.17	0.04	0.11	0.14	0.55	0.1	0.048
O_2	5	3.3	3.5	1.7	2.3	2.4	4.1	5.7	1.1
He	300	< 10	< 10	< 10	54	< 10	< 10	< 10	< 10
N_2 + Ar	100	24	74	10	10	14	1444	34	34
CO_2	2	< 0.2	< 0.2	< 0.2	< 0.2	0.20	0.43	< 0.2	< 0.2
CO	0.2	0.0040	0.0033	0.001503	0.000661	0.00096	0.0037	0.0014	0.0015
HCHO	0.01	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
CHOOH	0.2	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
NH_3	0.1	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
TS	0.004	0.000076	0.000051	0.000098	0.00011	0.00008	0.0004	0.00033	0.0001
TX	0.05	0.020	0.013	0.022	0.019	0.018	0.019	0.019	0.028
FI (%)	99.97	99.9973	99.9923	99.9988	99.9934	99.9983	99.8551	99.9960	99.9965

SC2: Commisioning date

ppm mol	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8	HY-9	HY-10	HY-12	LOD	Tol
Commissioned	2013	2015	2015	2015	2015	2016	2016	2015	2015	2016		
Fuel Index	99.99396	99.99750	99.99259	99.99634	99.99371	99.99384	99.99199	99.96163	99.95574	99.99180		99.97
H2O		1.5									1	5
THC (C1)	0.12	0.04	0.13	0.07	0.36	0.30	0.84	0.42	5.1	0.88		2
O2	4.9	5.0	4.9	11	5.7	5.2	4.1	5.4	13	5.4	1	5
He			51		40						10	300
N2 & Ar	56	19	16	26	18	56	75	378	419	76		100
N2	55	19	16	26	18	56	75	378	416	76	5	
Ar	0.57								3.1		0.4	
CO2									5.7		0.1	2
CO	0.0047	0.0011	0.0040	0.0014	0.0048	0.0032	0.0025	0.0016	0.015	0.0023	0.0005	0.2
TS	0.000026	0.000024	0.000020	0.000017	0.000032	0.000034	0.000039	0.000013	0.00011	0.00015		0.004
HCHO											0.001	0.01
HCOOH											0.001	0.2
NH3											0.01	0.1
TH	0.00048	0.0019	0.00042	< 0.001	0.00048	0.026	0.015	0.023	0.0033	0.0049		0.05

SC3: Time (closest to Norway)

	HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8	HY-9	HY-10	LOD	Tol
Country	NO	NO	NO	NO	DK	DK	SE	SE	NO	NO		
Fuel Index	**99.99894**	**99.999**	**99.99803**	**99.94969**	**99.99539**	**99.99457**	**99.99719**	**99.99866**	**99.99781**	**99.99714**		**99.97**
H2O				1.3							**1**	**5**
THC (C1)	**0.22**	**1.7**	**1**	**47**	**1.2**	**0.27**	**0.42**	**0.15**	**0.8**	**0.72**		**2**
THC (C1 - CH4)	**0.01**	**1.1**	**0.53**	**30**	**0.98**	**0.04**	**0.09**	**0.03**	**0.22**	**0.53**		
Methane	0.21	0.6	0.47	17	0.22	0.23	0.33	0.12	0.58	0.2		
Ethane				5.6	0.87	0.016	0.01		0.11			
Propane	0.003	0.018	0.013	8.7	0.028	0.014	0.025	0.011	0.017	0.025		
O2			**4.10**	**1.8**	**3.1**	**4.8**	**3.4**		**4.2**	**4.4**	**1**	**5**
He	**10**							**13**			**10**	**300**
N2 & Ar		**8**	**15**	**452**	**41**	**49**	**24**	**0**	**17**	**23**		**100**
N2		8.3	15	448	41	49	24		17	23	5	
Ar				4.3	0.48	0.41				0.4	0.4	
CO2				**0.37**			**0.36**			**0.2**	**0.1**	**2**
CO	**0.0022**	**0.001**	**0.00087**	**0.0093**	**0.003**	**0.0017**	**0.0015**	**0.0027**	**0.0035**	**0.0023**	**0.0005**	**0.2**
TS	**0.000016**	**0.00001**	**0.000016**	**0.000004**	**0.000015**	**0.000016**	**0.00002**	**0.000022**	**0.000017**	**0.000018**		**0.004**
HCHO											0.001	**0.01**
HCOOH											0.001	**0.2**
NH3											0.01	**0.1**
TH	**0.00067**	**0.0026**	**0.0037**	**0.0062**	**0.0028**	**0.0035**	**0.002**	**0.0038**	**0.0042**	**0.01**		**0.05**
C4Cl4F6	0.00067	0.0026	0.0037	0.0062	0.0028	0.0035	0.002	0.0038	0.0042	0.0100	**0.001**	

Comparison of analytical results

	#1		#2		#4			#5		#6	
	SC	NPL	SC	NPL	SC	NPL	SINTEF	SC	NPL	SC	NPL
Water	< 1	2.93	< 1	2.51	1.3	13.2		< 1	3.44	< 1	1.38
Nitrogen	< 5	4.8	8.3	18.3	452	579		41.0	89.3	49.4	87.7
Argon	< 0.4	< 1	< 0.4	< 1	4.3	< 1		0.48	< 1	0.51	< 1
Helium	10	< 20	< 10	< 20	< 10	< 20		< 10	< 20	< 10	< 20
Oxygen	< 1	0.59	< 1	0.67	1.8	< 0.5		3.1	4.84	4.8	0.272
Carbon dioxide	< 0.1	< 0.02	< 0.1	< 0.02	0.37	0.316	0.250	< 0.1	0.0306	< 0.1	< 0.02
Carbon monoxide	0.0022	< 0.02	0.0010	< 0.02	0.0093	< 0.02		0.0030	< 0.02	0.0017	< 0.02
Methane	0.21	< 0.02	0.60	0.0491	17	14.28	12	0.22	0.242	< 0.2	< 0.02
Ethane					5.6	319	400				
Propane					8.7	0.117	1				
N-butane					15	0.46	1				
Total hydrocarbons	0.22	< 0.02	1.7	< 0.02	47	> 200		1.2	< 0.02	0.27	< 0.02
Total Sulfur	0.000016	< 0.001	0.000010	< 0.001	0.0000042	< 0.001		0.000015	< 0.001	0.000016	< 0.001
Total halogenates	0.00067	< 0.052	0.0026	< 0.052	0.0062	< 0.052		0.0028	< 0.052	0.0035	< 0.052

HRS QC time trends

- HRS Gothenburg from "bad to good" 2016 -> 2017
- HRS Porsgrunn N_2 improvement

Porsgrunn	Chlor-alkali					
	2012	**2014**	**2017**			
Fuel Index (%)	**99.7195**	**99.85512**	**99.94969**			
N2	2800	1443	448			
CO2	3.3	0.43	0.37			
Ar	0.77	0.67	4.3			
THC	0.8	0.55	30	Ethane, Buthane, N-butane		
CH4	0.39	0.093	17			
H2O	< 1	2.9	1.3			
O2	< 2	4.1	1.8			
CO	0.0097	0.0037	0.0093			
TH	< 0.002	0.019	0.0062			

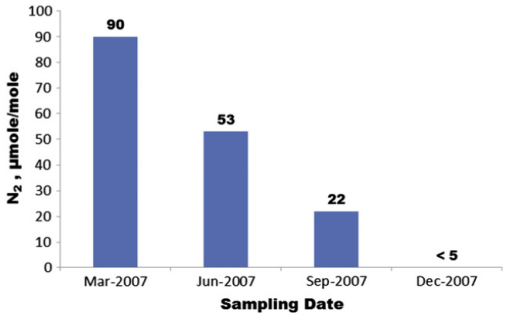


Fig. 10 – N_2 in Station #7 H_2.

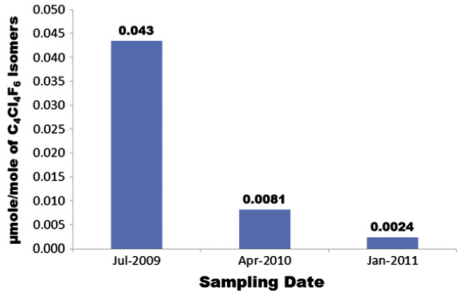
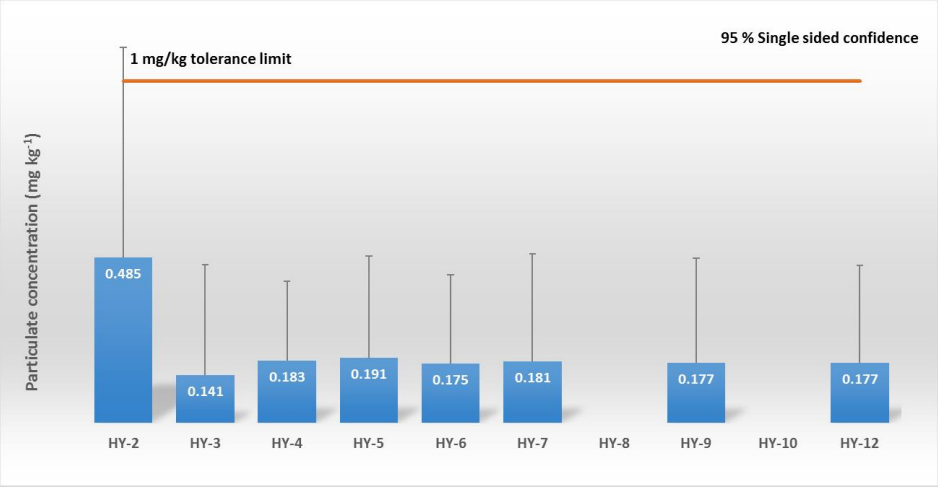


Fig. 9 – $C_4Cl_4Cl_6$ in Station #1 H_2.

Particulates

- Big difference upstream vs downstream collection
- Independent sampling (2x FCEV) until further clarification



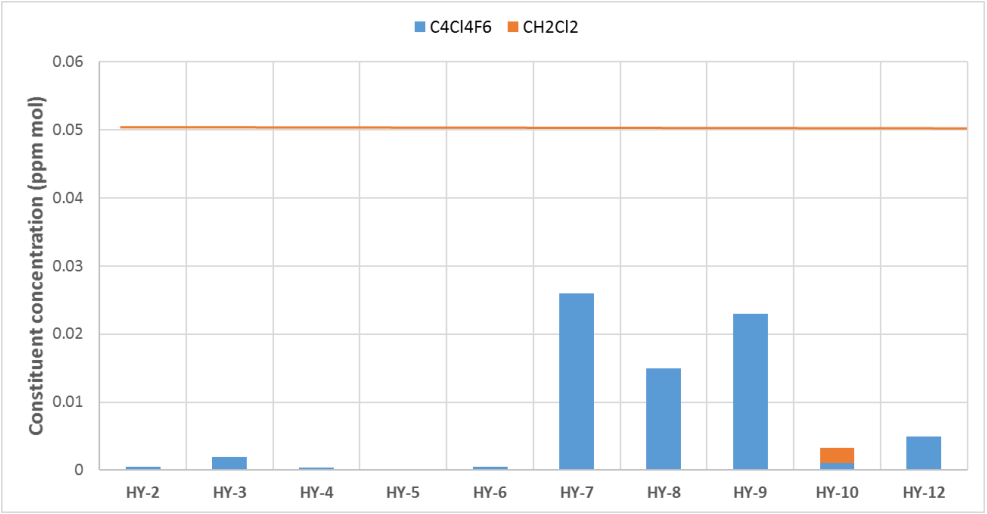
Upstream

	Mean before [mg]	Mean after [mg]	Difference [mg]	2x Std Dev [mg]	kg H_2 filled	Weight gain per kg H_2 [mg]	2xStd Dev / kg H_2 [mg]
HY-5	100,403	100,153	-0,250	0,066	3,915	-0,064	0,017
HY-6	97,210	96,933	-0,277	0,098	3,900	-0,071	0,025
HY-7	100,520	100,430	-0,090	0,057	NA	NA	
HY-8	100,687	100,540	-0,147	0,10	3,266	-0,045	0,031
HY-9	99,963	99,893	-0,070	0,10	NA		
Field Blank	99,937	99,830	-0,107	0,059	NA		

Downstream

Halogenates

- ISO 14678 revision
  - "total halogenates" removed
  - Exemplified by HCl and R-X (CEN TC 268)
  - Cl-ion basis justification? Cl_2 -> HCl OK but CH_2Cl_2?
- Presence and stability of $C_4Cl_4F_6$



Uncertainty of analysis

RSD	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8	HY-9	HY-10	HY-12
Fuel Index										
H2O		9.8								
THC (C1)										
O2	**4.9**	**17**	**7.0**	**15**	**5.8**	**7.9**	**12**	**8.4**	**15**	**8.1**
He			**6.2**		**1.2**					
N2 & Ar										
N2	2.9	12	9.1	18	17	2.3	0.53	2.7	7.6	3.7
Ar	6.5								11	
CO2									**8.7**	
CO										
TS										
HCHO										
HCOOH										
NH3										
TH										

Comparison of twin samples

ppm	HY-1	HY-9
City	Gausstad	Gausstad 2
Fuel Index	**99.99894**	**99.99781**
H2O	**<1**	<1
THC (C1)	**0.22**	**0.8**
THC (C1 - CH4)	**0.01**	**0.22**
Methane	0.21	0.58
Ethane		0.11
Propane	0.003	0.017
Isobutane	0.0064	0.027
N-Butane		0.011
Isobutene		0.052
O2	**<1**	**4.2**
He	**10**	**<10**
N2 & Ar		**17**
N2	<5	17
Ar	<0.4	<0.4
CO2	**<0.1**	**<0.1**
CO	**0.0022**	**0.0035**
TS	**0.000016**	**0.000017**
H2S	0.0000051	0.00001
COS	0.000011	0.000011
HCHO		
HCOOH		
TH	**0.00067**	**0.0042**
C4Cl4F6	0.00067	0.0042

Sample carry-over?

	SC2	SC3
	HY-10	**HY-2**
Country	SE	NO
Fuel Index	**99.95574**	**99.999**
H2O	ND	
THC (C1)	**5.1**	**1.7**
Methane	5.0	0.6
Acetone	0.045	
Ethane		
EtOH		
Isopropyl Alcohol		
Propane	0.066	0.018
Toluene	0.0027	
Isobutane		1.1
N-Butane		
Isobutene		
O2	**13**	
He		
N2 & Ar	**419**	**8**
N2	416	8.3
Ar	3.1	
CO2	**5.7**	
CO	**0.015**	**0.001**
TS	**0.00011**	**0.00001**
HCHO		
CH3COOH		
NH3		
TH	**0.0033**	**0.0026**
Cl2		
HCl		
HBr		
C2Cl2	0.0023	
C4Cl4F6	0.0010	0.0026

	SC1	SC2
	HY-6	**HY-6**
Country	NO	DE
Fuel Index	**99.8551**	**99.99371**
H2O	**2.9**	ND
THC (C1)	**0.55**	**0.36**
Me	0.093	0.18
Ac	0.0078	0.0069
Ethane	0.38	NA
EtOH	0.0038	0.017
Isoprop	0.0036	NA
Propane	0.063	
Toluene	NA	0.0032
O2	**4.1**	**5.7**
He		**40**
N2 & Ar	**1444**	**18**
N2	1443	18
Ar	0.67	
CO2	0.43	
CO	0.0037	**0.0048**
TS	**0.00040**	**0.000032**
H2S	0.000086	0.000011
COS	0.00015	0.000021
MTM		
ETM		
DMS	0.0001	
TH	**0.038**	**0.00048**
TOH	0.019	
C4Cl4F6	0.019	0.00048

Quality Conclusions

- Hydrogen fuel quality generally good
  - Few violations observed since 2012
- Significant impurity levels observed for
  - N_2, He
  - O_2, CO_2, H_2O, THC
  - $C_4Cl_4F_6$
- Impurities does not correlate with H_2 feedstock
- No correlation between commissioning date and fuel quality found
  - Maintenance schedule probably important

HYDRAITE
Sampling strategy

- 1st half: Standardized (ISO 19880-1) sampling strategy will be adapted from HyCoRA project
- HYDRAITE in close interaction with development of new sampling strategies
  - a goal in several projects (Hy-Lab, MetroHyVe)
- 2nd half: HyCoRA sampling strategy will be compared with other sampling strategies
  - At least two applied in parallel in HRS
- 30 samples in total
  - 10 first split for SC and three HYDRAITE laboratories (WP4) for comparison
  - 20 following HYDRAITE laboratories