

Sampling and Analysis of hydrogen fuel from HRS in Europe

2nd HyCoRA OEM WS
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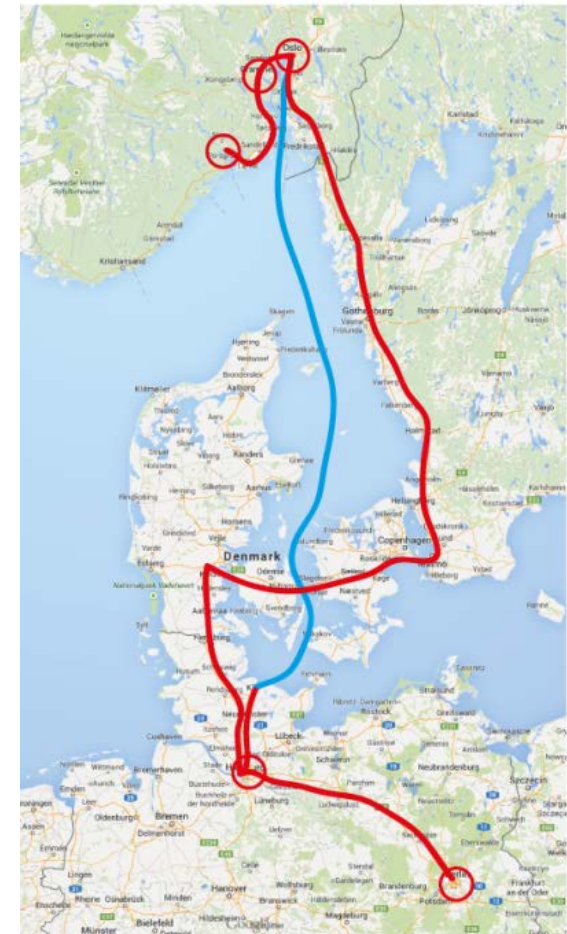
WP3(T3.1) HRS sampling campaign #1

- Initial plan to use FCHEV to collect samples
- Goal to make feedstock as diverse as possible
- Five HRS available for refuelling in northern Germany
 - Daimler strict approval of HRS for their vehicles
- Five HRS available in .de
- Added three HRS from Norway
- Switched to ICE transport
 - CEP provided empty FCHEV at each HRS
 - No approval for FCHEV/sample transport on ferries



Route

- Norway HRS: MB F-Cell
- Oslo-Kiel ferry with empty samples
- 2000 km drive Berlin-Oslo



Gas sampling unit (Linde)

- Linde 'Qualitizer'
- No IrDA: maximum 600 bar sampling in .de
- Manual override of HRS safety not required



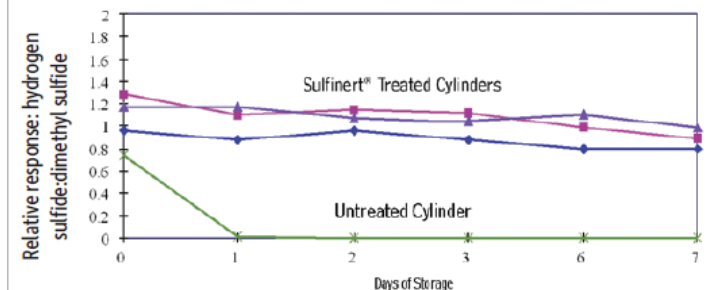
Sample cylinders

- 8x 10L Aluminium (SS valve) Spectraseal canisters)
- Analysis volume requirements
 - Pre-concentration
- Cylinder lining requirement
 - Feedback from VSL, NPL and Linde
 - Different types of linings
 - Spectraseal
 - Sulfinert
 - Silonite



Sulfur compounds are stable in Sulfinert® treated stainless steel systems.

17 ppbv hydrogen sulfide in 500 mL cylinders



Sample list

- 8 samples sent for analysis by Smart Chemistry
- Sampling instrument works well
 - 3 HRS/day possible
 - 1000-1300 NL sample collected
 - Affected by vehicle and refuelling rate

Station	Date	Feedstock	Storage	Sample ID	Sample pressure (bar)
Porsgrunn	28.11.2014	Chlor-alkaline	Compressed	HY-6	133
Drammen	28.11.2014	Water electrolysis (trucked in)	Compressed	HY-7	135
Oslo	31.10.2014	Water electrolysis (trucked in)	Compressed	HY-8	130
Hamburg, Hafencity, Oberbaumbrücke	09.12.2014	Water electrolysis (on-site)	Compressed	HY-1	100
Hamburg, Bramfelder Chaussee	09.12.2014	SMR	Compressed	HY-2	130
Berlin, Sachsenendamm	10.12.2014	SMR/Bio	Liquid	HY-3	130
Berlin, Holzmarktstrasse	10.12.2014	SMR/Bio	Liquid	HY-4	95
Hamburg, Schnackenburgallee	11.12.2014	Water electrolysis (on-site)	Compressed	HY-5	120

Cost of QA

- Smart Chemistry analysis cost: € 2,300 / sample
- Shipment of pressurized hydrogen sample expensive
 - € 2000 for 8 samples Norway to US
- 8 x 10 L Spectraseal cylinders: € 12,500
- Linde 'Qualitizer' sampler: € 37,500
- Customs declarations (international)
- Man hours ...
 - 2-3 HRS/day given empty FCHEV availability

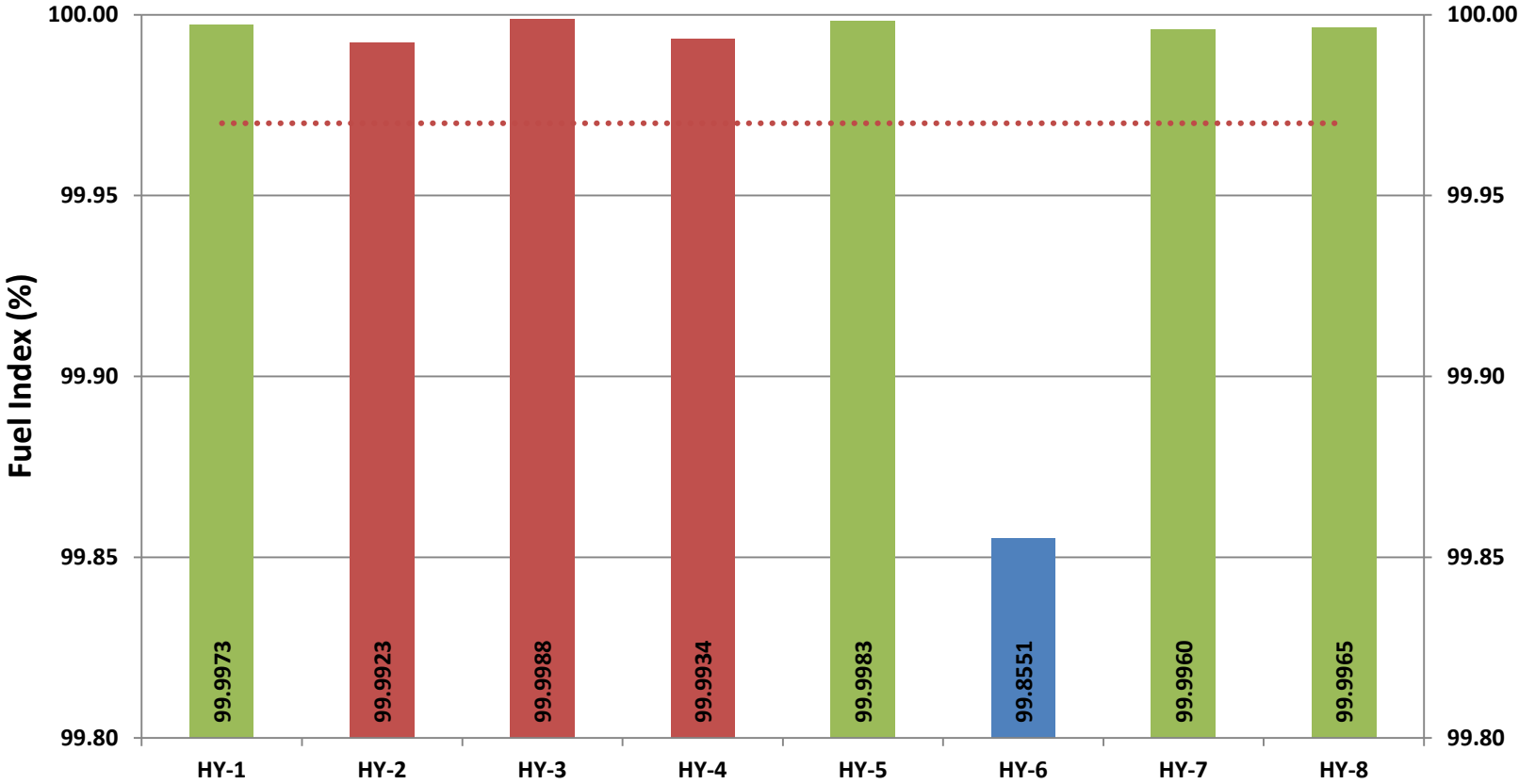
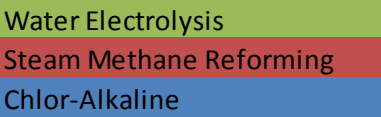
Analytical Methods applied by Smart Chemistry (US)

	ASTM	Analytical technique	Pre concentration
THC (C1)	WK34574	GC-MS	Cryo/TD/Cryo
He	D1946	GC-TCD	
N ₂ , Ar, O ₂ , H ₂ O	D7649	GC-MS	
CO ₂	D7649	GC-MS	
CO	D1946	GC-PDHID	Cryo
HCHO	WK34574	GC-MS	Cryo/TD/Cryo
HCOOH	WK34574 (v1)	GC-ELCD	Cryo/TD/Cryo
NH ₃	WK34574 (v1)	GC-ELCD	Cryo/TD/Cryo
HCl, HBr, Cl ₂	WK34574 (v1)	GC-ELCD	Cryo/TD/Cryo
TS	D7652	GC-SCD	Cryo/TD/Cryo
C-X	WK34574	GC-MS	Cryo/TD/Cryo

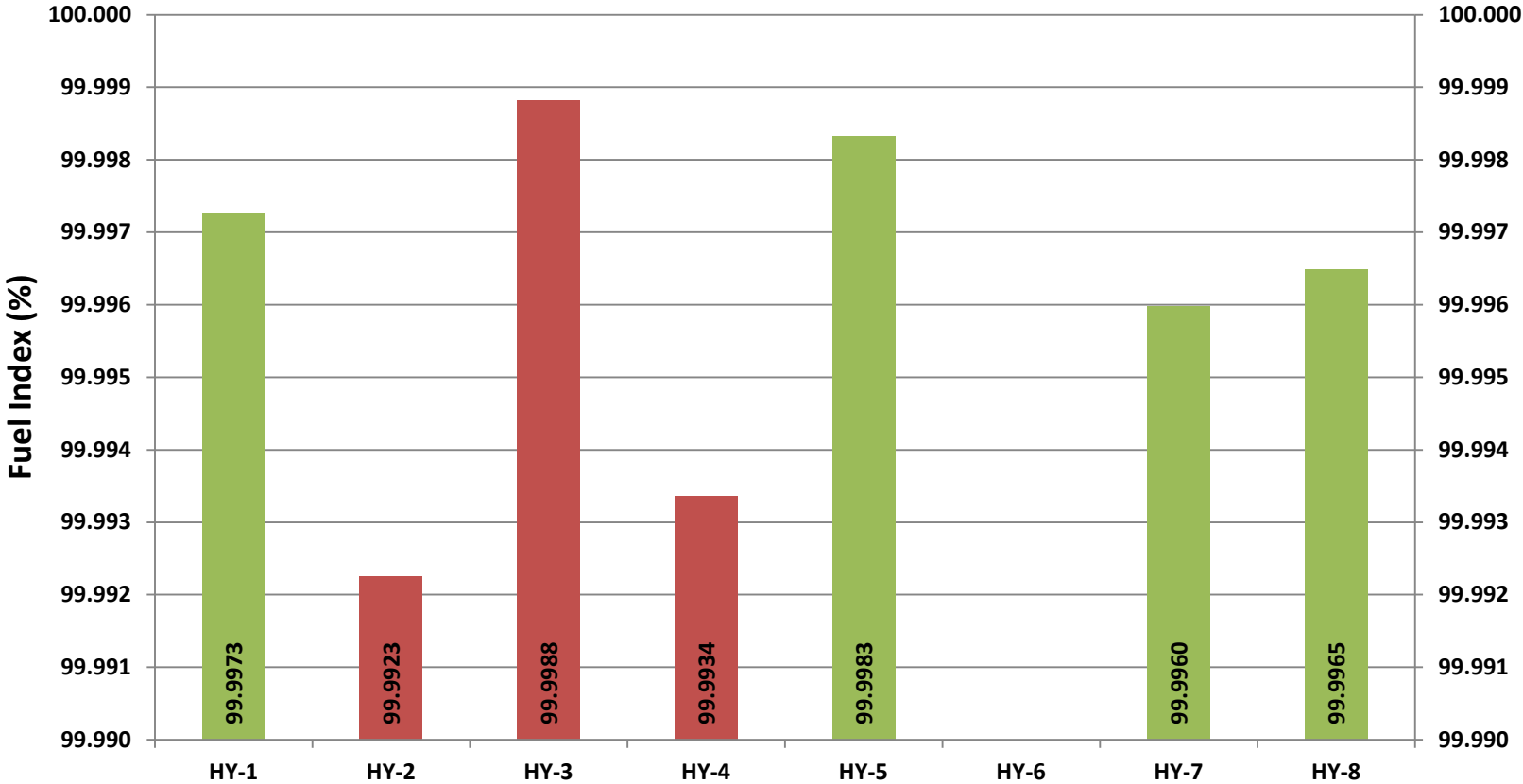
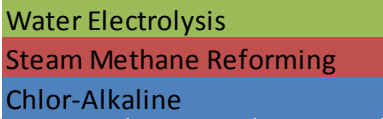
Results

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 ₂ O	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

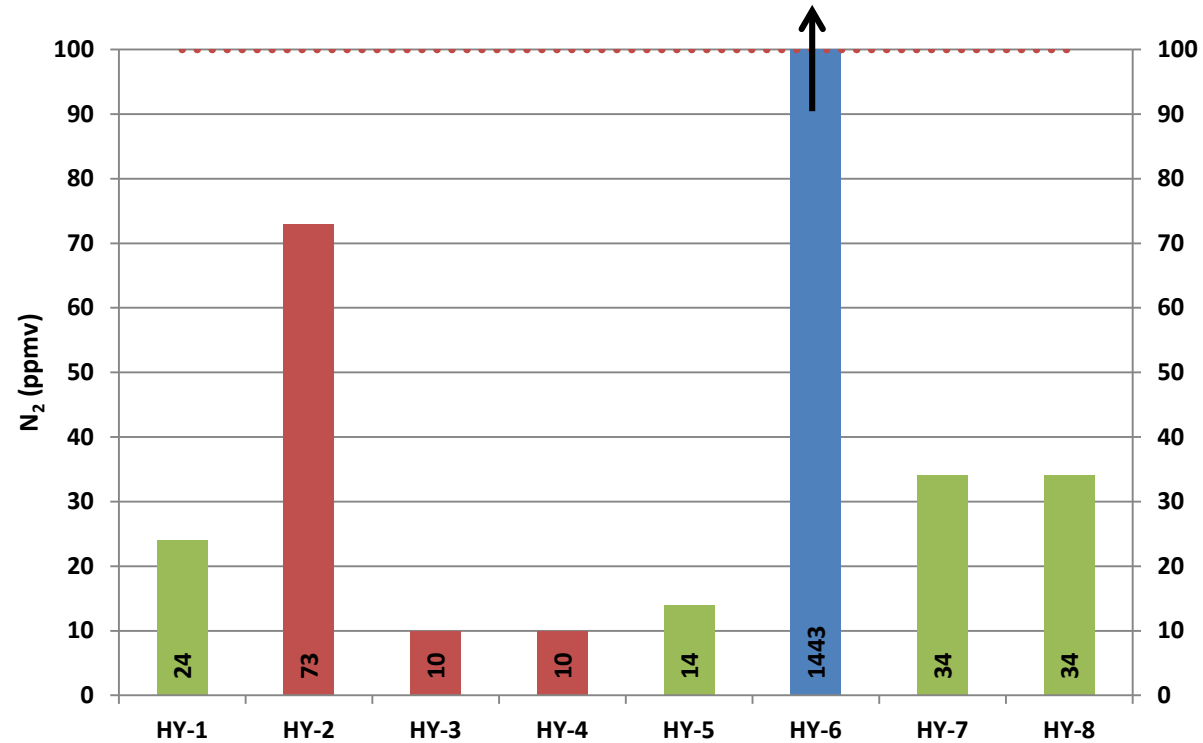
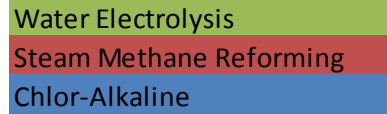
Fuel Index



Fuel Index



Fuel dilution dominated by N₂



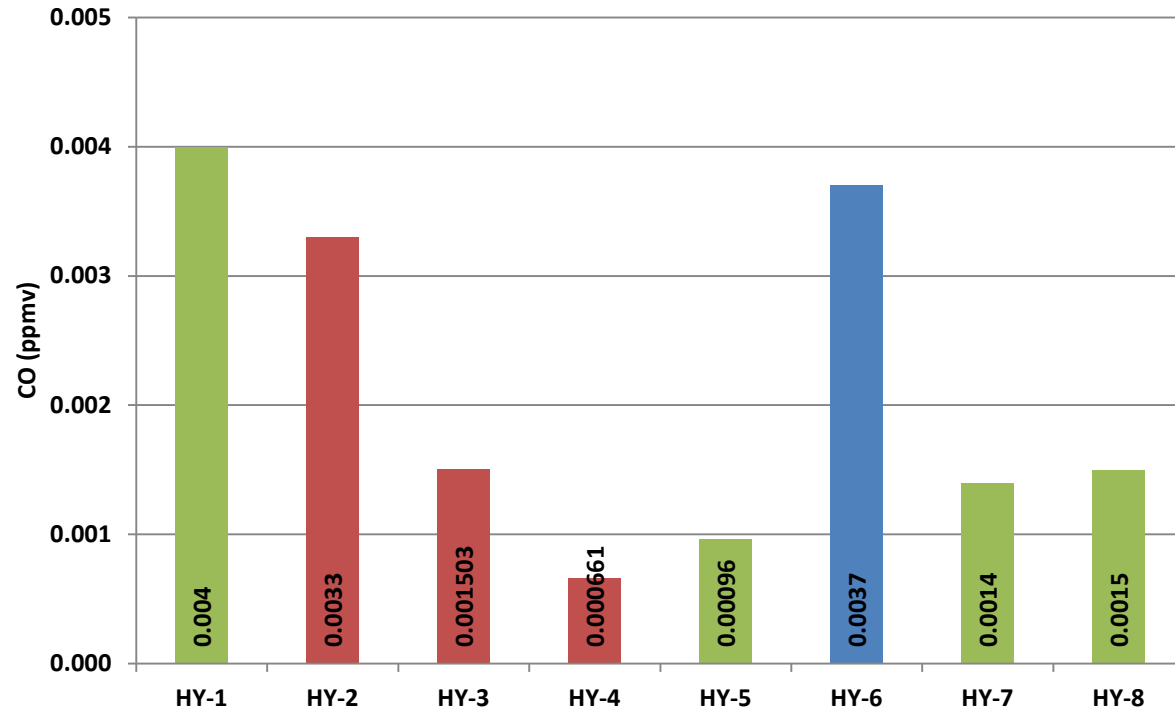
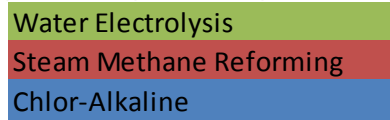
ID	Tol	HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8
O ₂	5	3.3	3.5	1.7	2.3	2.4	4.1	5.7	1.1
He	300	< 10	< 10	< 10	54	< 10	< 10	< 10	< 10
N ₂	100	24	73	10	10	14	1443	34	34
Ar		< 0.5	0.75	< 0.5	< 0.5	< 0.5	0.67	0.46	< 0.5
Sum		27	77	12	66	16	1448	40	35

Sample air contamination?

- Characteristic ratios of air components should be recognized
- Some O₂ reactivity could alter ratios
- Water measurement not sensitive (LOQ 1 ppm) for enough for evaluation

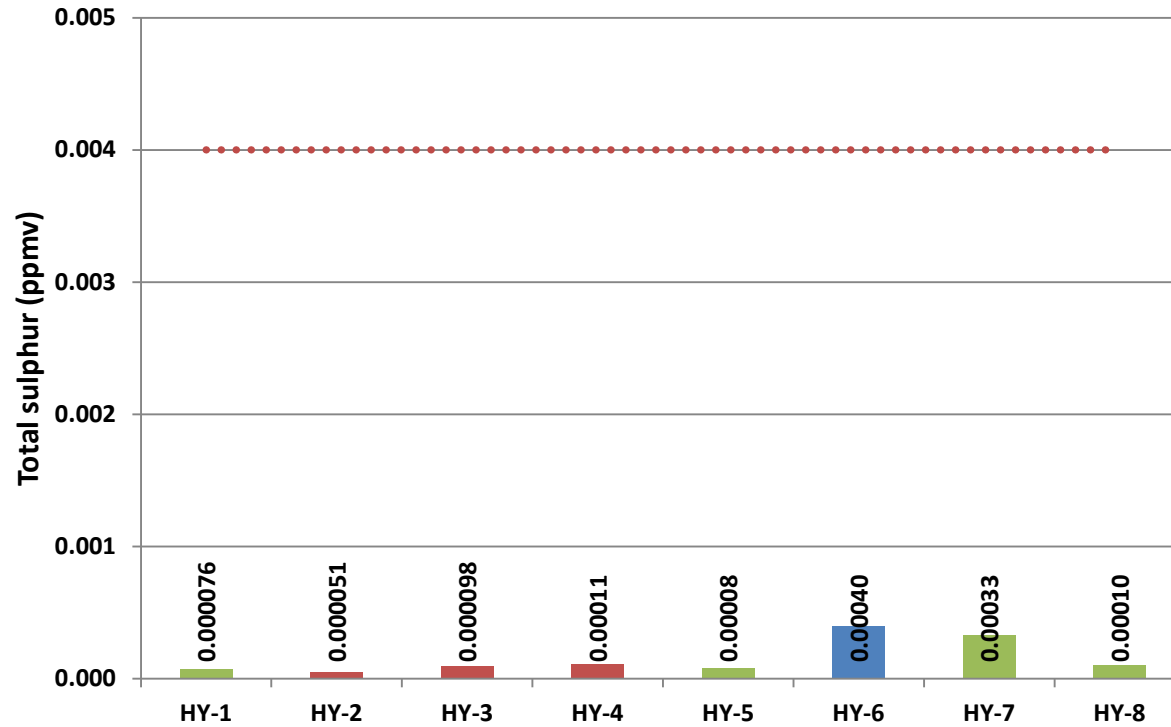
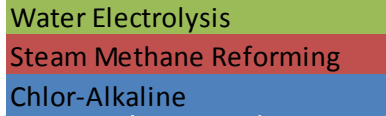
Ratio	Air	HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8
N ₂ :O ₂	3.7	7	21	6	4	6	352	6	31
N ₂ :Ar	84		97				2154	74	
O ₂ :Ar	22		5				6	12	

Canary CO concentration?



Ratio	HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8
CO ₂ :CO					208	116		
O ₂ :CO	825	1061	1131	3480	2500	1108	4071	733
THC:CO	12	52	27	166	146	149	71	32
TS:CO	0.02	0.02	0.07	0.17	0.08	0.11	0.24	0.07
N ₂ :CO	6000	22121	6653	15129	14583	390000	24286	22667

Sulphur distribution

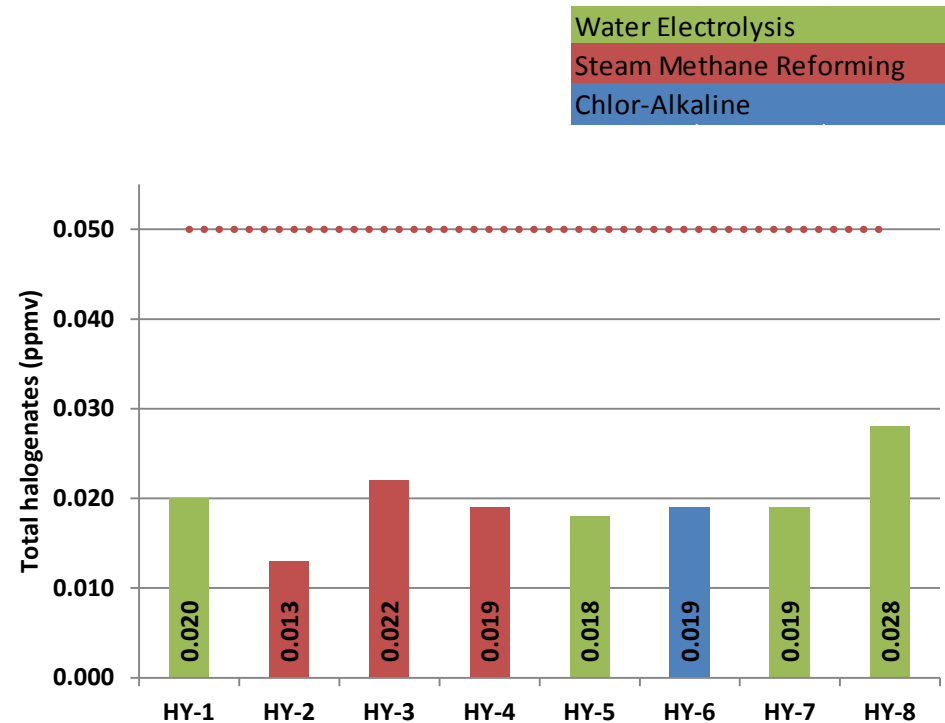


US: same species

ID		HY-1	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8
TS	ppmv	0.000076	0.000051	0.000098	0.00011	0.000080	0.000400	0.000330	0.00010
H ₂ S	frac	0.25	0.37	0.23	0.19	0.30	0.22	0.27	0.39
COS	frac	0.36	0.29	0.59	0.35	0.28	0.38	0.30	0.39
CS ₂	frac	0.38	0.33	0.17	0.50	0.43	0.25	0.42	0.23

Total halogenates

- Only $C_4Cl_4F_6$ found
- Source: SS liner PCTFE?
- Decomposition (HCl basis) would violate total halogenate basis
- Test for $C_4Cl_4F_6$ stability required
- Is F part of inventory?
 - HF harmless to fuel cell



QC Norway 2012

Table 1: SmartChemistry QC results. All results in ppmv unless specifically noted. Tolerance levels are in accordance with SAE J2719. Results in red are in conflict with the standard.

Constituent	Tolerance	Porsgrunn	Gaustad	Økern
Total Hydrocarbons (C1 basis)	2	0.80	0.035	0.049
Nitrogen	100*	2800	7.7	< 5
Argon	100*	0.77	< 0.5	1.9
Carbon Dioxide	2	3.3	< 0.5	< 0.5
Carbon Monoxide	0.2	0.0097	0.0047	0.0010
Total Sulphur	0.004	0.00022	< 0.0001	< 0.0001
Total Halogenates	0.05	< 0.002	0.0042	0.014
Particulate Concentration	1 mg kg ⁻¹	0.042	0.14	0.21
Number of particles		11	48	7
Hydrogen Fuel Index	99.97 %	99.7195%	99.9992 %	99.9998%

*The sum N and Ar required to be less than 100 ppm.

WP3 Planning

- Planning of new campaign in 2016
 - New HRS available
 - Support (FCHEV availability)
- Use HYDAC particle sampler in series with qualitizer



Thank you!

