SAMLING AND ANALYSIS OF HYDROGEN FROM REFUELLING STATIONS IN EUROPE

Thor Aarhaug, PhD, Senior Scientist

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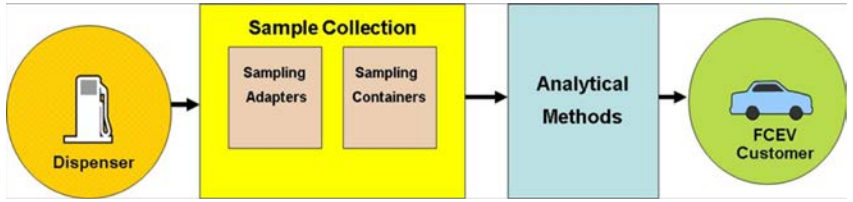
Outline

- Sampling strategies for H_2 from HRS nozzle
  - Methods described by ISO 19880-1 Annex K
  - Sampling cylinders and preparation thereof
- Analysis of H_2 samples
  - Fuel quality requirement as defined by ISO 14687
  - Analytical methods
    - Requirements set by ISO 21087
  - Results from HyCoRA project
    - 28 gas samples, 13 particulate samples collected
    - Comparison of analytical results from two (three) laboratories

Sampling strategies

ISO 19880-1 Annex K: Sampling procedures and hardware for hydrogen fuel quality analysis

Method	Sampling time	HRS fueling override	Sink	Sample Cylinder volume (example)	Reference Sample pressure
Gas Parallel	~ 3 min	No*	FCEV or test CHSS	≤ 10 L	< 16 MPa
Gas Serial	< 1 min / cylinder	Yes	Vent system	≤ 2 L	< 7 MPa
Gas Direct	<10 min	Yes	Vent system	47 L	< 12 MPa
Particulate Direct	~ 3 min	Yes	Vent system	not applicable	APRR according to SAE J 2601**
Particulate series	~ 3 min	No *	FCEV or test CHSS	No applicable	APRR according to SAE J 2601**



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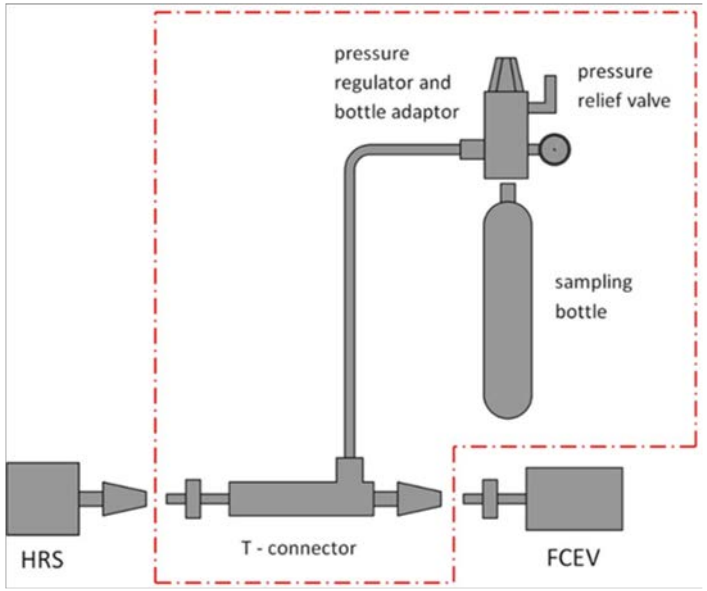
Gas parallel sampling

- Linde Qualitizer 70 MPa adapter
- FCEV used as sink
- No IrDA
- Normal HRS operation while sampling
- Bleed valve depressurization



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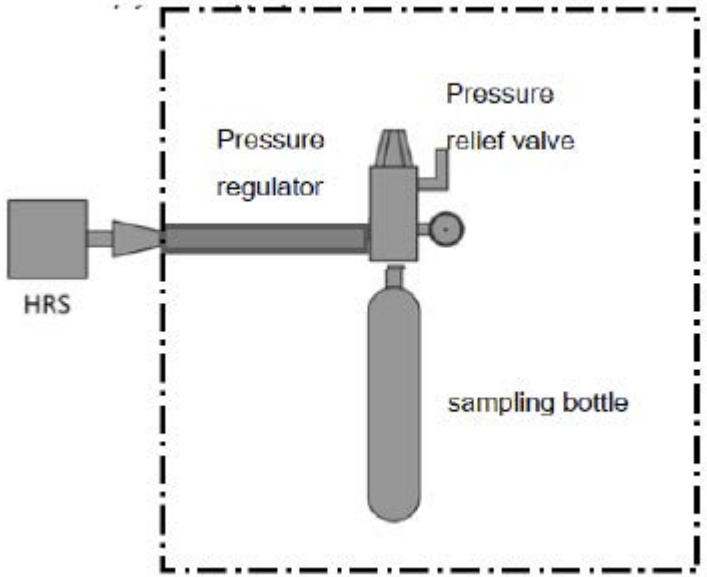
Gas parallel sampling

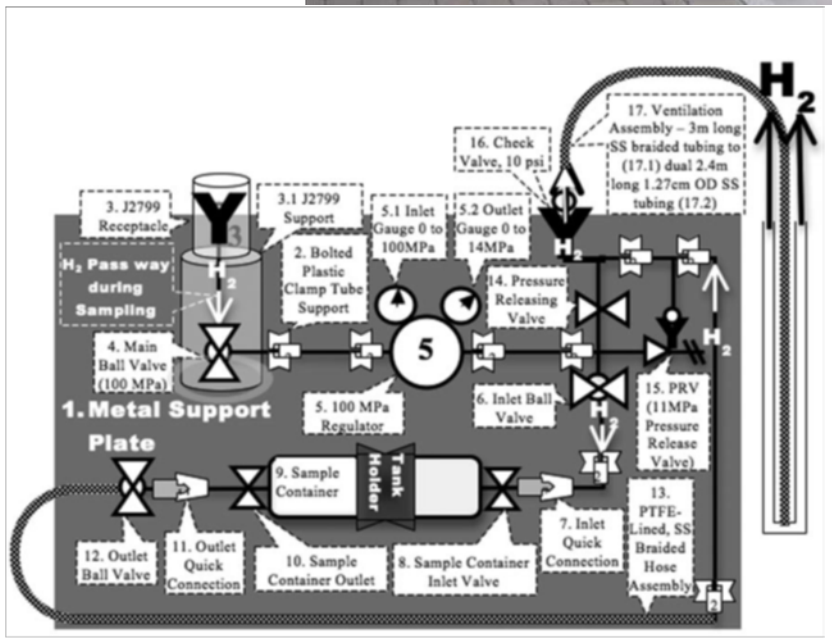
Gas sampling direct method

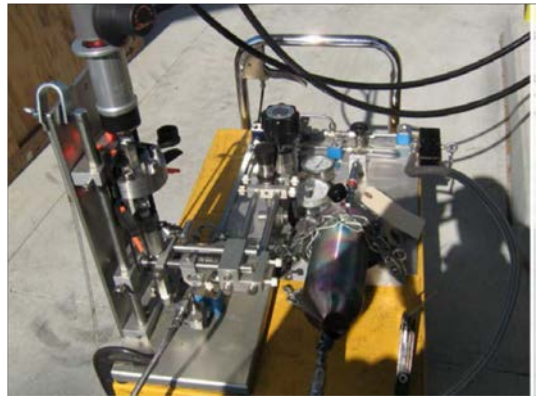
- Japanese approach
- Large volume, low pressure cylinder
- P, T monitoring
- Purging on-site
- HRS override



Gas serial sampling

- ASTM D7606-17
- Sample cylinder purge-through
- Sample collected at ca. 7 Mpa
- Venting of large volume of H_2
- HRS override





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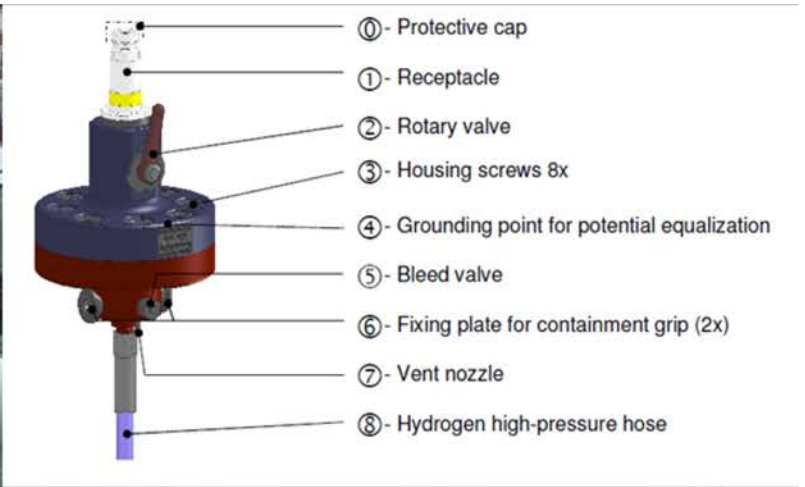
Particulate sampling

- HYDAC PSA-70
- 70 Mpa sampling
- No IrDA
- Vent valve



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Sample cylinders

- Linde Qualitizer throttled to fill 10 L bottle during refuelling
- Linde spectra-seal (lined) cylinder used
- Cylinders prepared by
  - Pressurization to 6-10 bar
  - Evacuation to 2 mbar
  - Repeat sequence 2 times

ISO/DIS 14687 Fuel specification

Constituent	Tolerance limit
Hydrogen fuel quality (minimum mole fraction)	99.97 %
Total non-hydrogen gases	300 µmol / mol
Water	5 µmol / mol
Total hydrocarbons except methane (C1 basis)	2 µmol / mol
Methane (CH_4)	100 µmol / mol
Oxygen (O_2)	5 µmol / mol
Helium (He)	300 µmol / mol
Nitrogen (N_2)	300 µmol / mol
Argon (Ar)	300 µmol / mol
Carbon dioxide (CO_2)	2 µmol / mol
Carbon monoxide (CO)	0.2 µmol / mol
Total sulfur compounds (S1 equivalent)	0.004 µmol / mol
Formaldehyde (HCHO)	0.2 µmol / mol
Formic acid (HCOOH)	0.2 µmol / mol
Ammonia (NH_3)	0.1 µmol / mol
Halogenated compounds (halogen ion eq.)	0.05 µmol / mol
Maximum particulate concentration	1 mg /kg

Analytical methods: Smart Chemistry

Analyte	ASTM	Technique	Pre-concentration
THC (C1), HCHO, C-X	D7892	GC-MS	Cryo/TD/Cryo
He	D1946	GC-TCD	
N_2, Ar, O_2, H_2O, CO_2	D7649	GC-MS	
CO	D1946	GC-TCD	Cryo
HCO_2H, NH_3, HCl, HBr, Cl_2	WK34574(v1)	GC-ELCD	Cryo/TD/Cryo
Total sulfur	D7652	GC-SCD	Cryo/Cryo

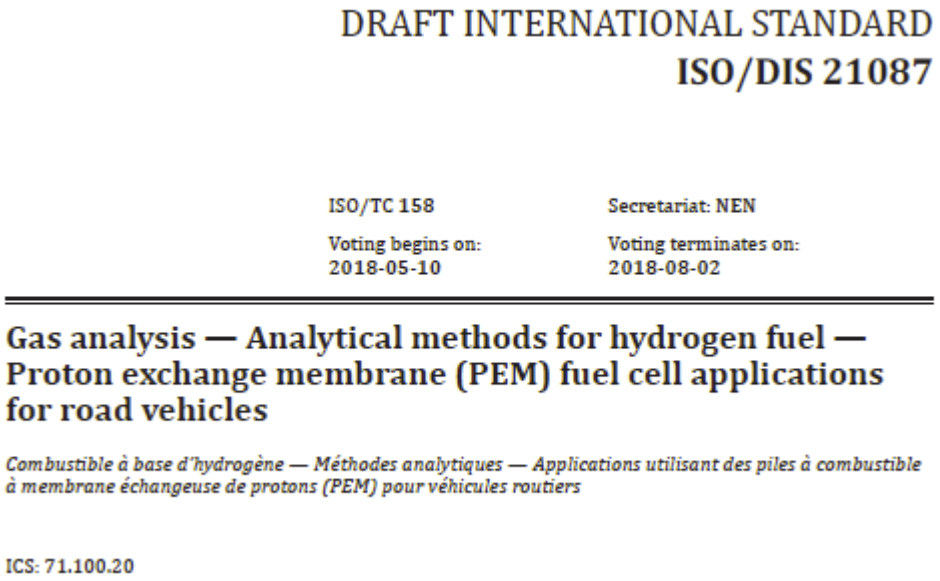
Analytical methods: NPL

Analyte	ASTM	Technique	Pre-concentration
Ar, N_2, O_2		GC-PDHID	None
He		GC-TCD	None
CO, CO_2, CH_4, HCHO, THC		GC-FID	None
H_2O		CRDS	None
Total halogenated compounds	(D7892)	TD-GC-MS	Thermal desorption
Total sulfur	*	GC-SCD	None
Formic acid		FTIR	None
Ammonia		UV	

* Downey ML. Et al., https://doi.org/10.1016/j.chroma.2014.11.076

Analytical metods

- ISO 14687 gives normative reference to ISO 21087
  - Validation of method
    - Selectivity
    - LOD/LOQ
    - Working range
    - Trueness
    - Precision
    - Uncertainty
    - Ruggedness
  - Fit for purpose
  - Sampling strategy
  - Sampling vessels



DRAFT INTERNATIONAL STANDARD
ISO/DIS 21087

ISO/TC 158 | Secretariat: NEN

Voting begins on: 2018-05-10 | Voting terminates on: 2018-08-02

Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles

Combustible à base d'hydrogène — Méthodes analytiques — Applications utilisant des piles à combustible à membrane échangeuse de protons (PEM) pour véhicules routiers

ICS: 71.100.20

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Results from HyCoRA 2014-2017

- 28 gas samples collected from HRS in Europe
- 13 particulate samples
- Analyzed in compliance with SAE J2719 by Smart Chemistry (US)
- 1st campaign: Feedstock diversity
- 2nd campaign: Newly commissioned HRS
- 3nd campaign: No strategy (close to Norway)
  - Samples analyzed by Smart Chemistry, NPL, and SINTEF

1st campaign: 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

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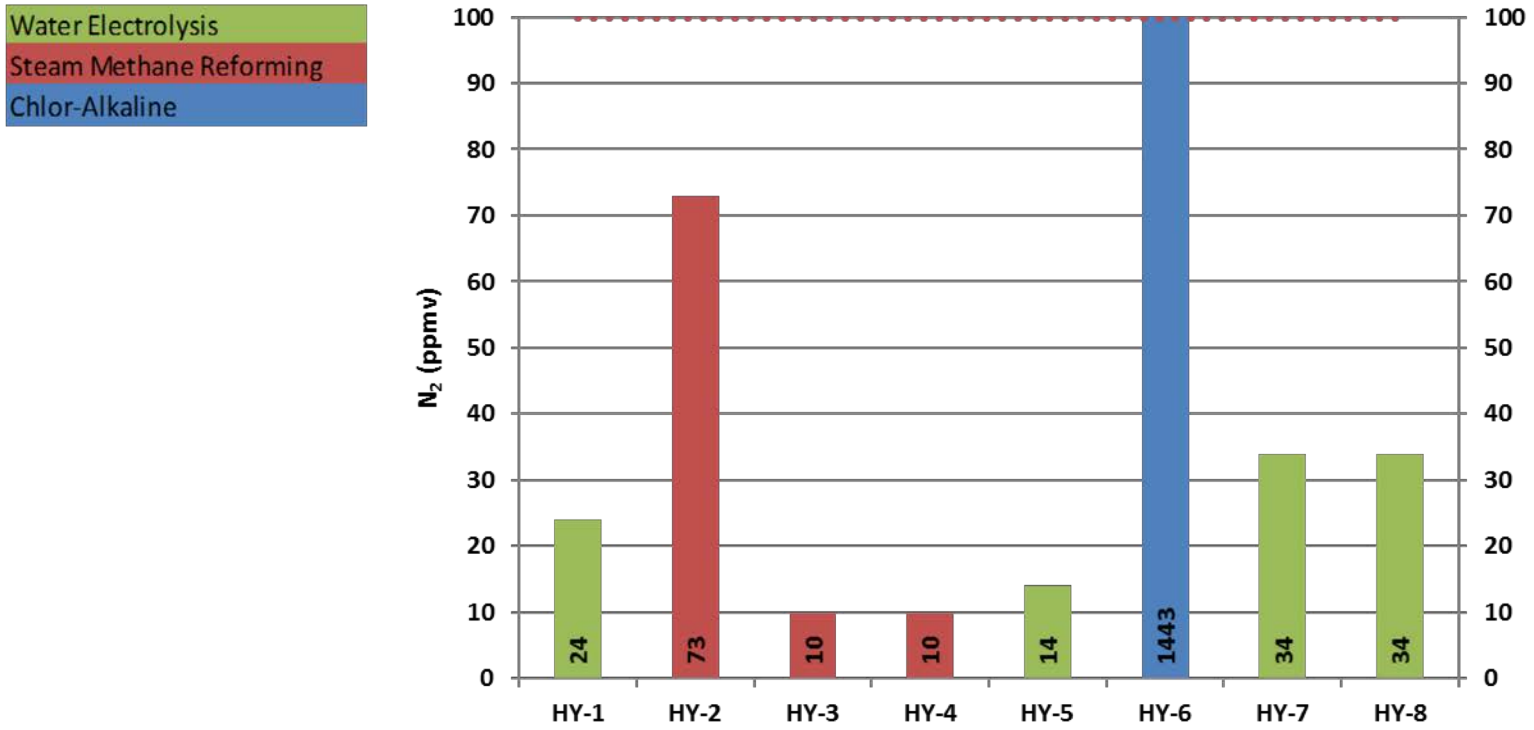
1st campaign: N_2 fuel dilution



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

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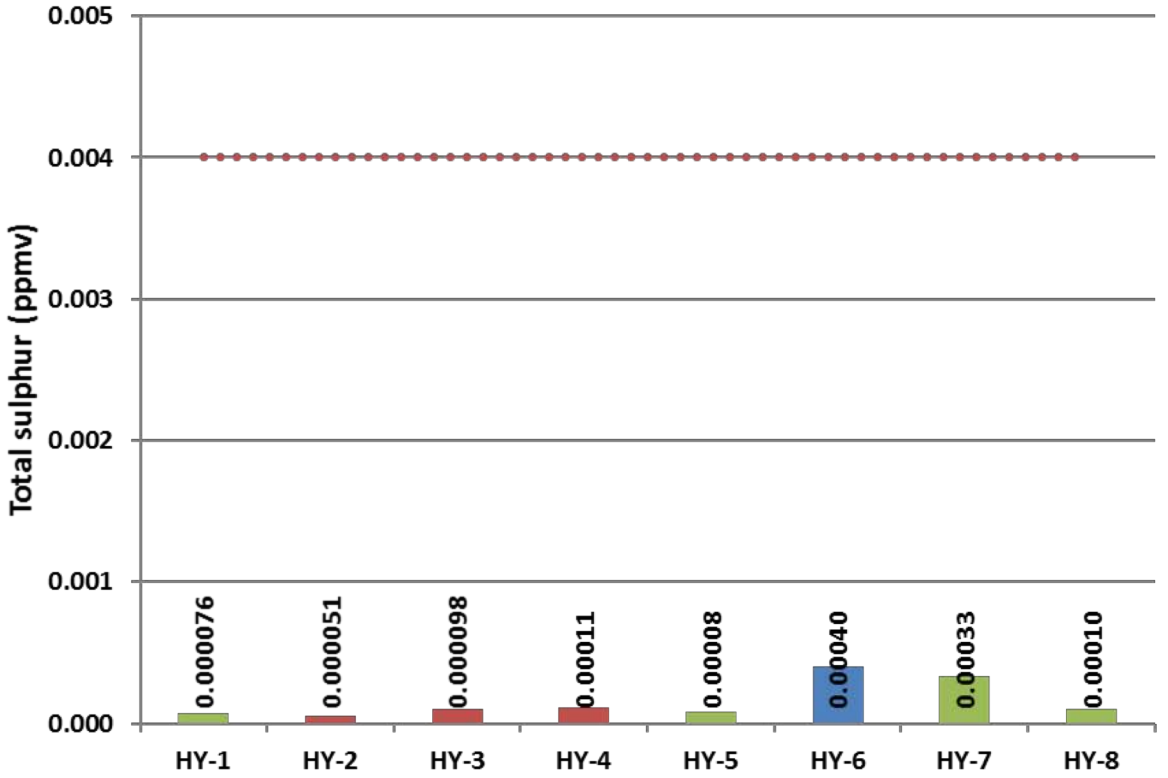
1st campaign: sulfur distribution



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_2S	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
CS2	frac	0.38	0.33	0.17	0.50	0.43	0.25	0.42	0.23

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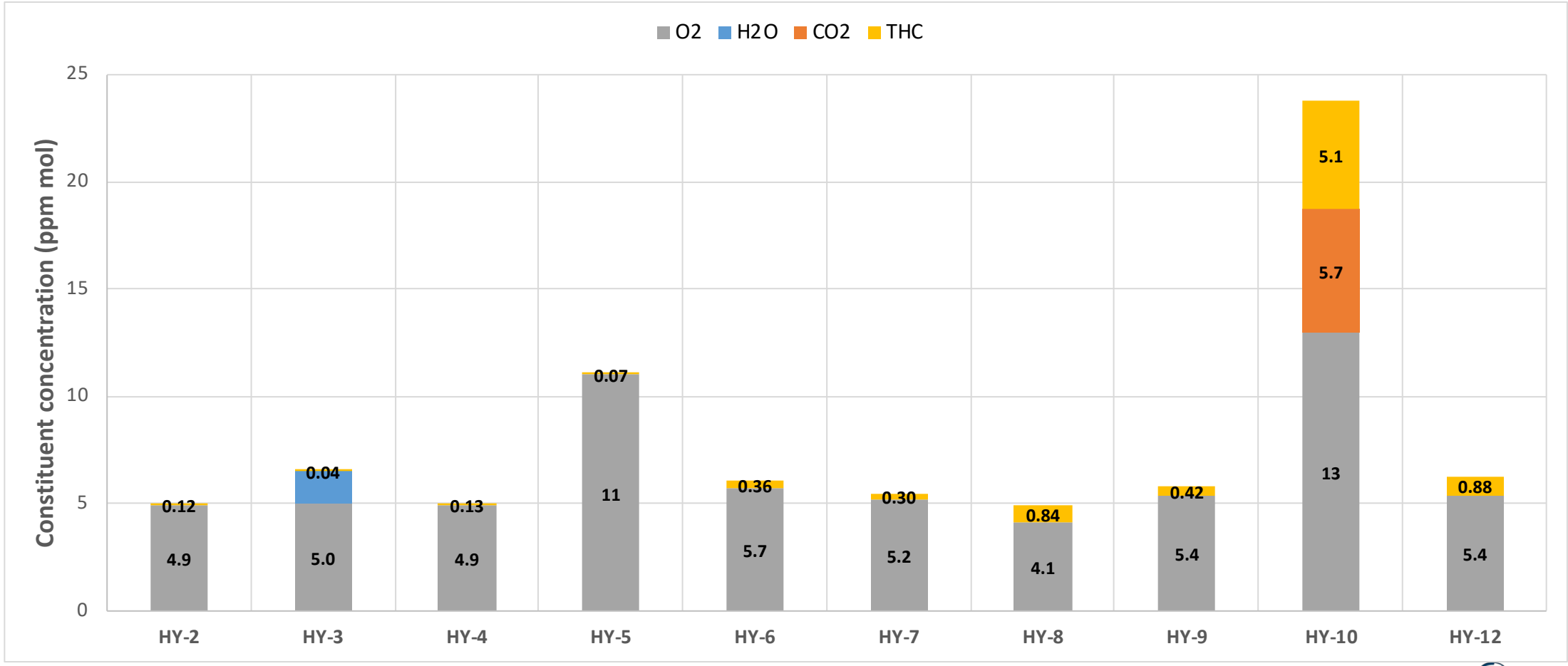
2nd campaign: commissioning

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**

2nd campaign: oxygen



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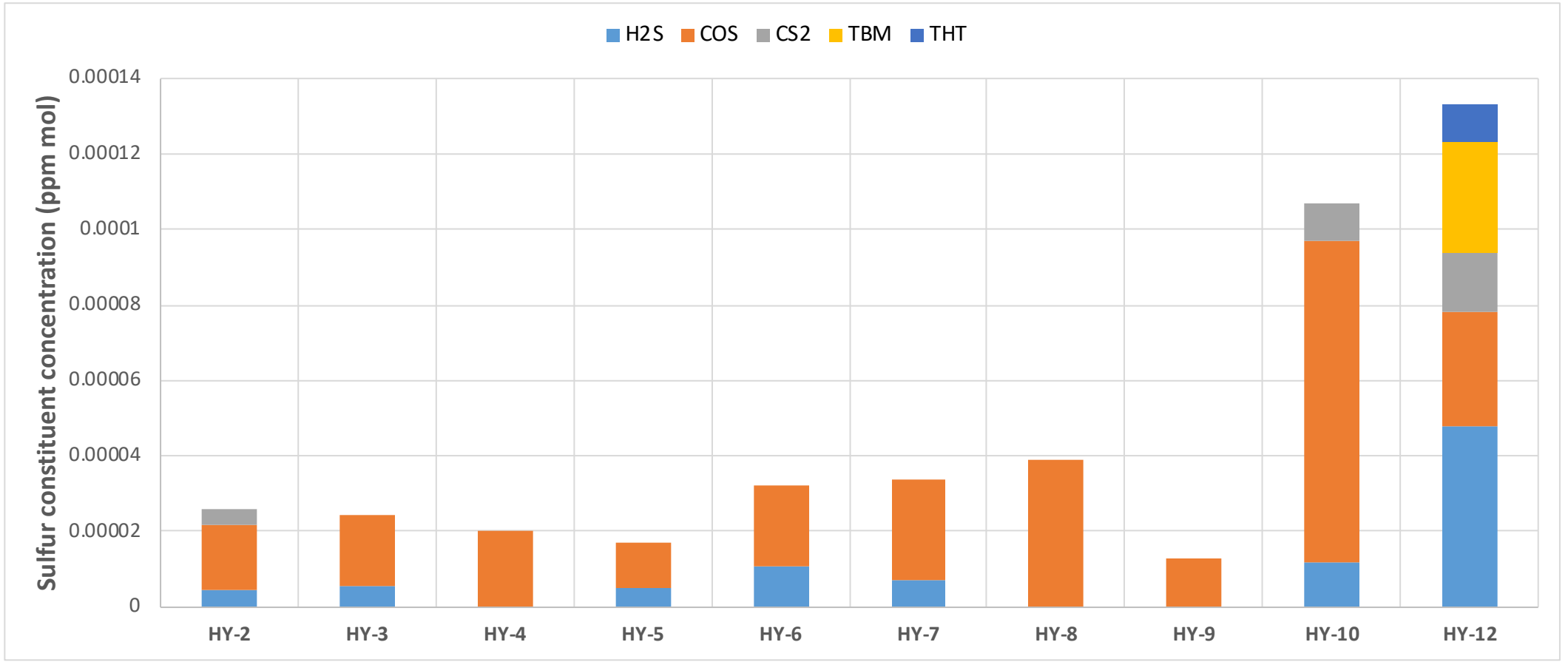
2nd campaign: sulfur



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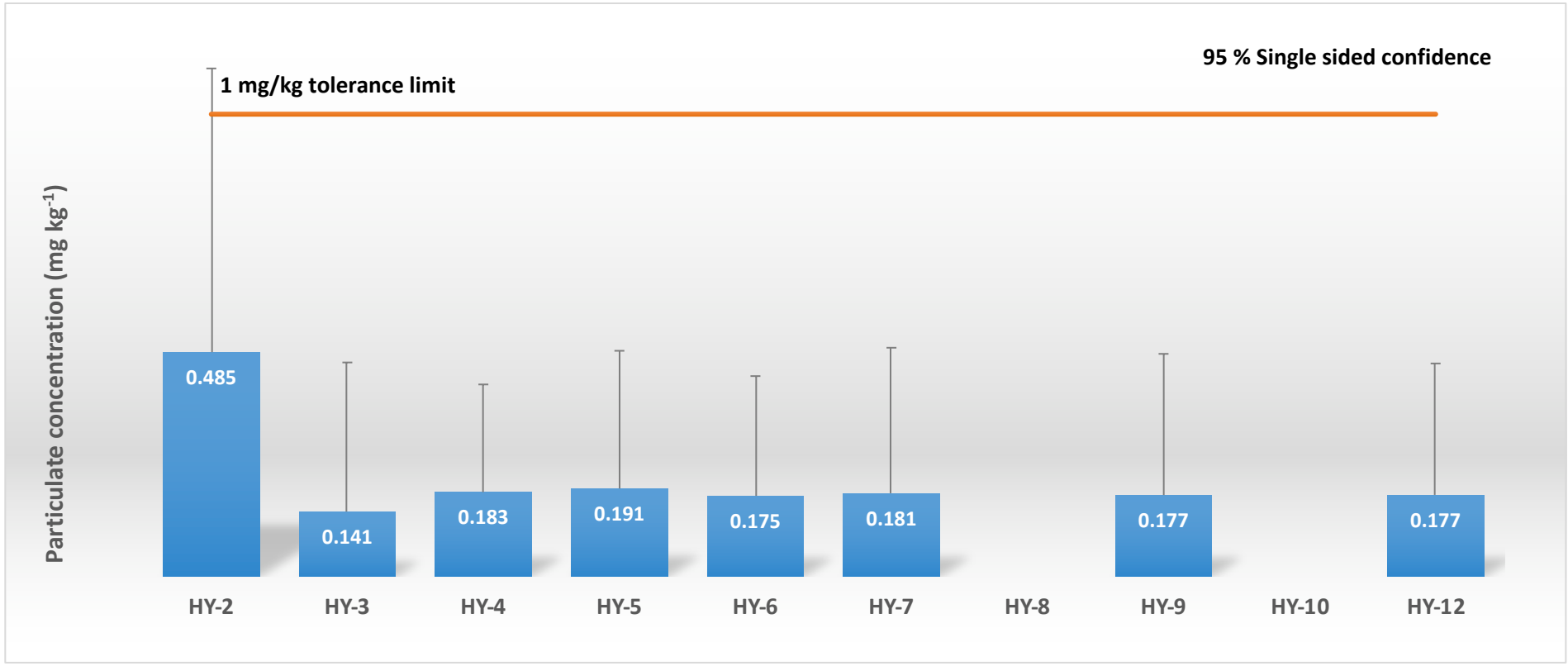
2nd campaign: Particulates



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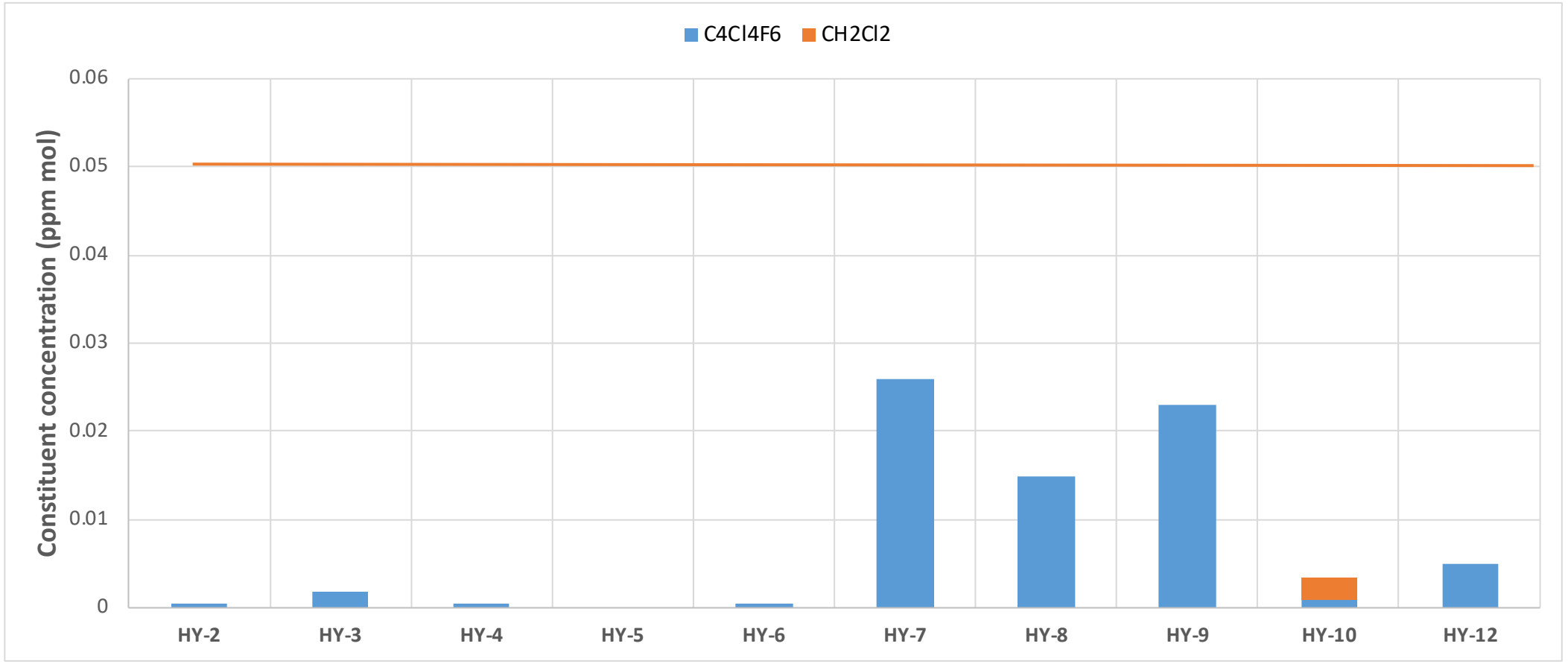
2nd campaign: halogen compounds



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3rd campaign: Scandinavian

	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**	

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3rd campaign: laboratory comaprison

	#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

Sample carry-over?

- No indications

	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

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Conclusions

- Good sampling strategy
  - Need FCEV coordination
- 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

Acknowledgements

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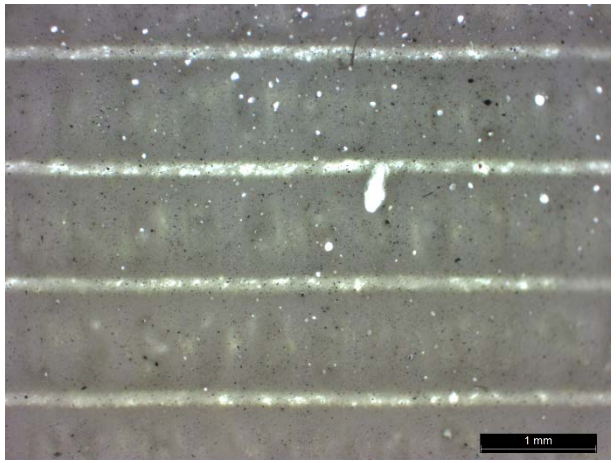
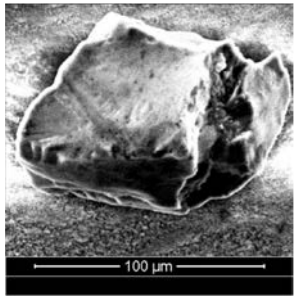
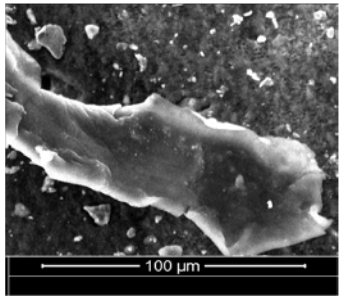
Results: particulates

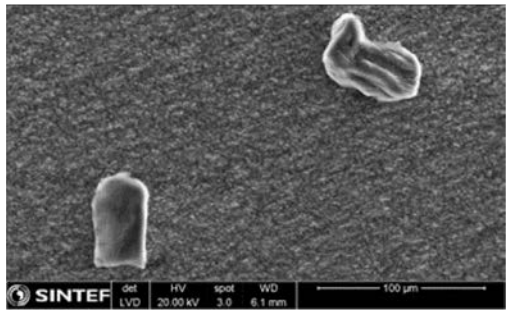
Filter	Total	Stainless steel	Ni-P	Other metals	Oxides	Organic particles	Organic residues
HY-2	medium	+	+	+	+	+	+
HY-3	low	-	-	-	+	++	-
HY-4	medium	+	++	+	+	++	++
HY-5	low	-	-	+	+	++	-
HY-6	medium	+	++	+	-	++	++
HY-7	low	+	-	+	-	++	-
HY-8	low	-	-	-	+	+	-
HY-9	low	-	++	-	+	-	+
HY-10	low	++	+	-	+	+	-
HY-12	high	+	++	-	+	+	-

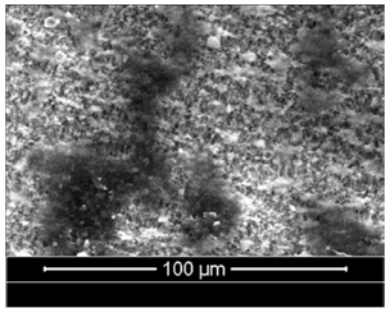


0.2 µm PTFE filter penetration









SINTEF

Uncertainty

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										