Hydrogen

VSL

Dutch Metrology Institute

Analytical method development for the most challenging impurities

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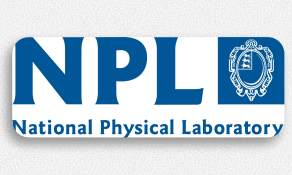


The challenge: H_2 purity analysis

Limits in ISO 14687-2 range from 300 µmol/mol down to 4 nmol/mol.

H_2 purity analysis: a real challenge

Formic acid	Total hydrocarbons	Ammonia	Total sulphur	Formaldehyde	Total halogenates

✓ **Suitable materials**

-sample cylinders
-sampling lines, reducers, flow meters
-analyzer

✓ **Highly sensitive analyzer**

✓ **Reference materials & calibration**

Current state-of-art for analytical methods

Sources:	Analytical methods:
• ASTM standards • JIS standards • NMI methods • Contacts with instruments providers	• Gas chromatographic methods (GC-TCD, GC-MS…) • Optical methods (FTIR, CRDS…) • Other (Dew point analyzer…) • Injection method: jet pulse injection, thermal desorption, pre-concentration device

Reports available at http://projects.lne.eu/jrp-hydrogen/tools-publications/

Capabilities analytical methods

OK
Partial

Analytical technique ↓	Impurity →											
	H2O	Total hydrocarbons	O2	Helium	Nitrogen & Argon	CO2	CO	Total sulphur	Formaldehyde	Formic acid	Ammonia	Total halogenated compounds
Dew point analyzer												
Vibrating quartz crystal analyzer												
CRDS		CH4										HCl
GC-MS												
GC-MS with jet pulse injection												
FTIR												
OFCEAS		CH4						H2S				HCl
FID												
GC-FID												
Methane GC-FID												
ECD												
GC-TCD												
GC-PDHID												
GC-SCD with concentrator												
GC-SCD without pre-concentration												
DNPH-HPLC-UV												
IC with concentrator												
IC-CD												
HPLC-CD												
CIC												
GC-ELCD												
TD-GC-MS								organic				
Galvanic cell O2 meter												
ICP-MS												No F- compounds

Comparison of methods based on performance characteristics

H_2O limit ISO 14687:
5 µmol/mol

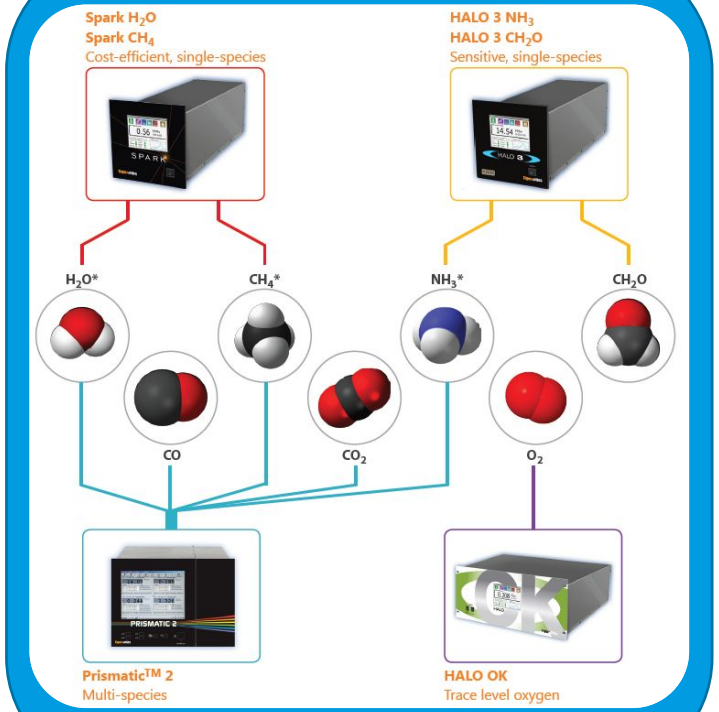
Methods	Working range	Detection limit (µmol/mol)	Selectivity	Repeatability	Linearity	Robustness	Accuracy	Precision	Measurement uncertainties
Dew point hygrometer	1 - 250 µmol/mol	1	good	-	-	-	-	-	-
Vibrating quartz crystal analyzer	2 - 250 µmol/mol	2	good	-	-	-	-	-	-
CRDS	-	Low range: 0.0008	High	0.0001 µmol/mol at 0.00044 µmol/mol	linearity coeff >0.995 over 4 magnitudes of concentration	-	-	-	-
CRDS	ex: 0.006-1750 µmol/mol	High range: 0.0042	high	0.0052 µmol/mol at 0.0015 µmol/mol	-	-	-	-	-
GC-MS with jet pulse injection	-	at least 4 µmol/mol		1.6 at 5.1 µmol/mol	-	-	-	-	-
OFCEAS	adaptable / 0-10 µmol/mol	lod 3σ 60seconds 0.001 µmol/mol	high	<1%	linearity coeff >0.999 linear on 4 to 5 decades of concentration	high	< 0.01 µmol/mol	1% relative or 2 LOD (which is worst).	0.005 µmol/mol
OFCEAS	adaptable / 0-100 µmol/mol	Expected lod 3σ 60seconds 0,01 µmol/mol	high	< 1%	linearity coeff >0.999 linear on 4 to 5 decades of concentration	high	Expected < 0.1 µmol/mol	1% relative or 2 LOD (which is worst).	expected < 0.05
FTIR	-	0.12-0.3	high	-	-	-	-	-	-

Comparison of methods based on performance characteristics

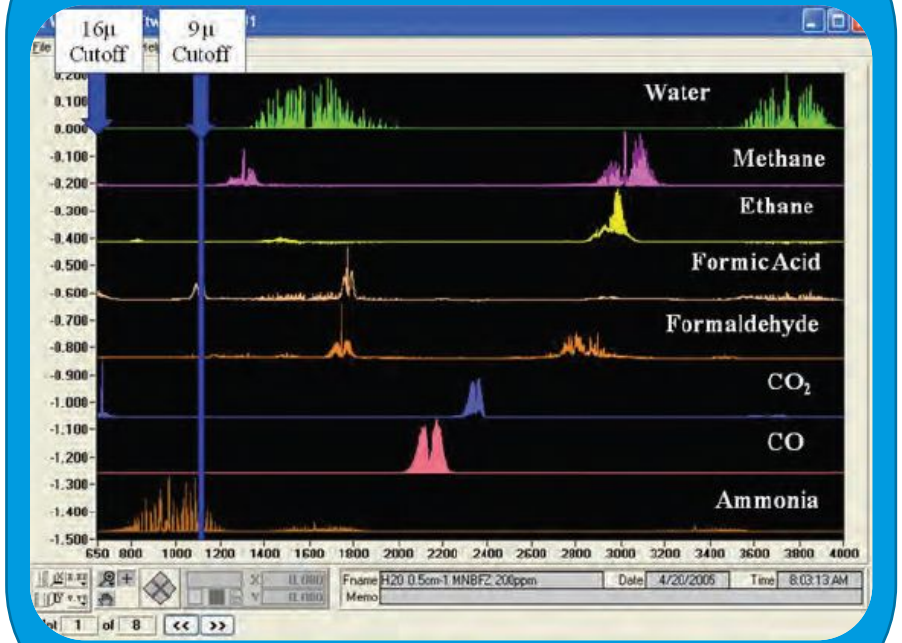
H_2O for ISO 14687-2

Parameter / Methods	Volume needed	Pressure required	Other impurities which can be analyzed	Response time	Standards	Cost estimate
Dew point hygrometer	0.5 L/min for 30 min minimum (stabilisation may take longer)	adaptable close to atm		Direct reading but long stabilisation time	JIS K0225	
Vibrating quartz crystal analyzer	0.33 L/min for 20 min	adaptable close to atm		direct reading but long stabilisation time	JIS K0225	
CRDS	100 ml/min @ 15 min = 1.5 liter		4 impurities (ex: CO, CO_2, H_2O, CH_4 or NH_3)	10-15 minutes	D7941/D7941M -14	4-species: 50-65 k€, single species: 40 k€
GC-MS with jet pulse injection			CO_2, Ar, N_2, O_2		ASTM D7649-10	
OFCEAS	-standard flow 13 l/h, volume needed <1 l -special option fuel cell exhaust with test flow <2 l/h	adaptable 2 bara is great	HCHO, HCOOH, NH_3 ppb level range to be confirmed on the same laser	< 1 minute	Information from AP2E	50 k€, combination of gases possible in 1 analyzer
FTIR			NH_3, CO, CO_2, formaldehyde, formic acid, methane		ASTM D7653-10	80 k€ for MKS multigas 2031 LN2

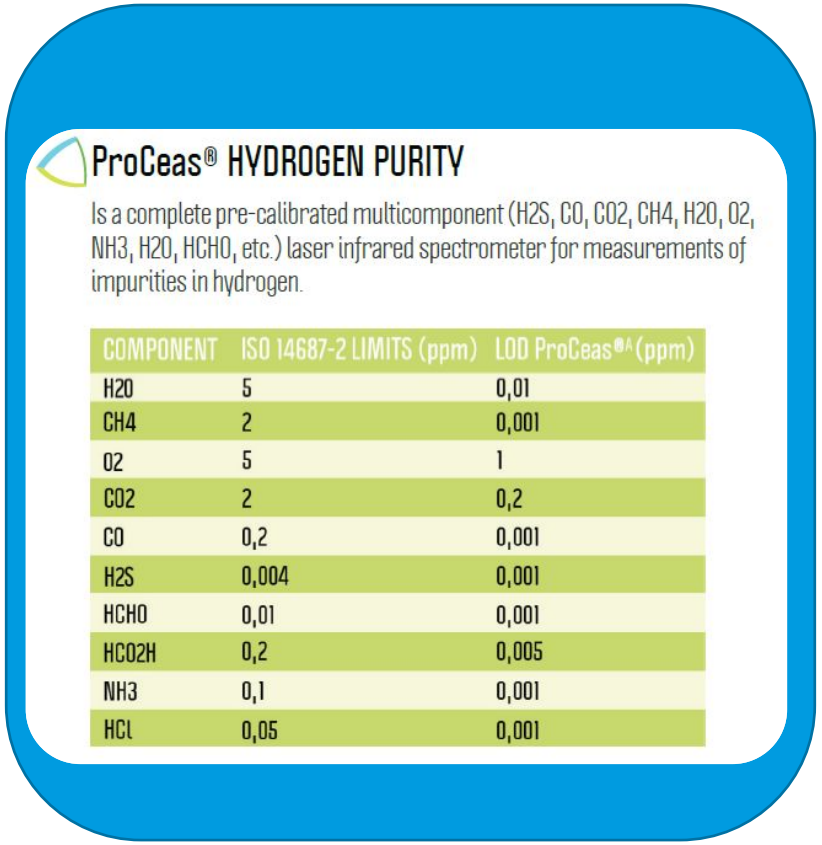
Multi-component analysers



CRDS
Tiger Optics

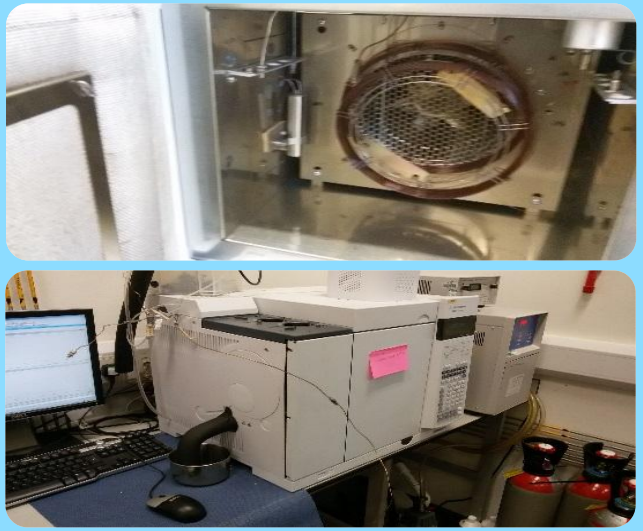


FTIR
MKS



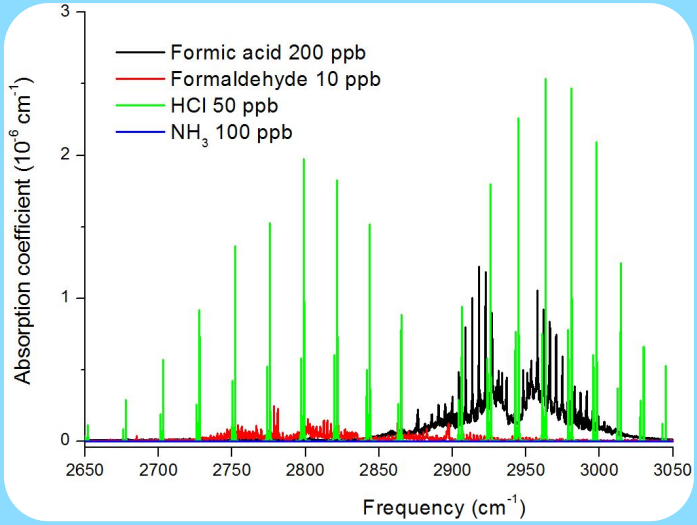
OFCEAS
AP2E

Method development by Hydrogen project partners



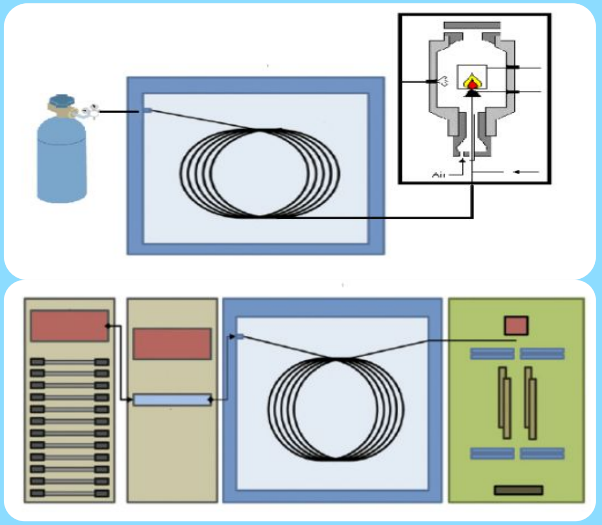
NPL: GC-SCD & cryo-focussing

Hydrogen sulphide (H_2S)
Carbonyl sulphide (OCS)
Carbon disulphide (CS_2)
2-methyl-2-propanethiol (TBM)
Tetrahydrothiophene (THT)



VSL: CRDS

Hydrogen chloride (HCl)
HCl in H_2 standard from CEM



RISE: GC-FID + TD-GC/FID-MS

Linear alkanes: C1 to C18
+ oxygenated compounds:
1-butanol…

Speciation of sulphur – Cryo-focussing GC-SCD

LoD GC-SCD ~ low nmol/mol for sulphur compounds

- **Strategy for speciation of pmol/mol: cryo-focussing**
  - enhanced sensitivity & selectivity: Improving chromatography
  - larger volume of gas sampled: improving limit of detection
  - Pre-concentration of analyte before separation: increased signal

Achievements

Method development

- Testing of the cryo-focussing method on sulphur in H_2 standards

Gas standard development

- Develop new gas standards in hydrogen:

Hydrogen sulphide (H_2S)
Carbonyl sulphide (OCS)
Carbon disulphide (CS_2)
2-methyl-2-propanethiol (TBM)
Tetrahydrothiophene (THT)

Large difference in MW & boiling point

Gas standards in H_2 of H_2S, OCS, CS_2, TBM & THT

Short life time (< 2 weeks)

400 nmol/mol
40 nmol/mol
4 nmol/mol

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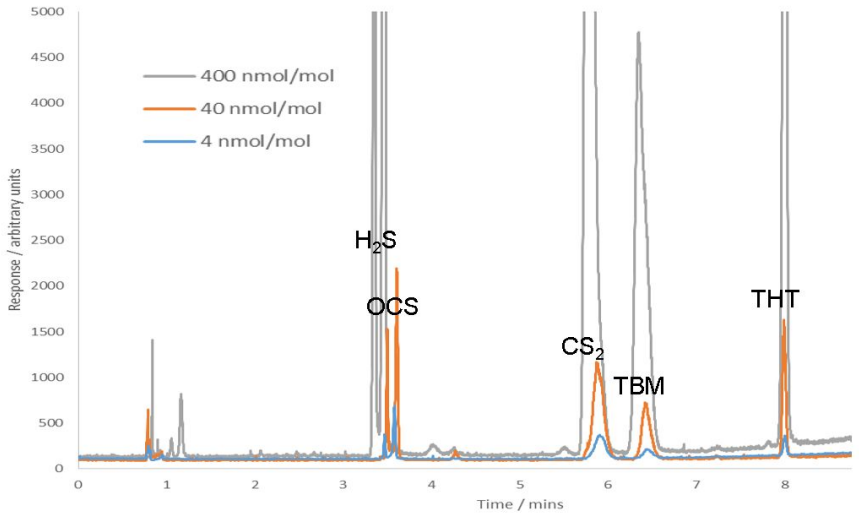
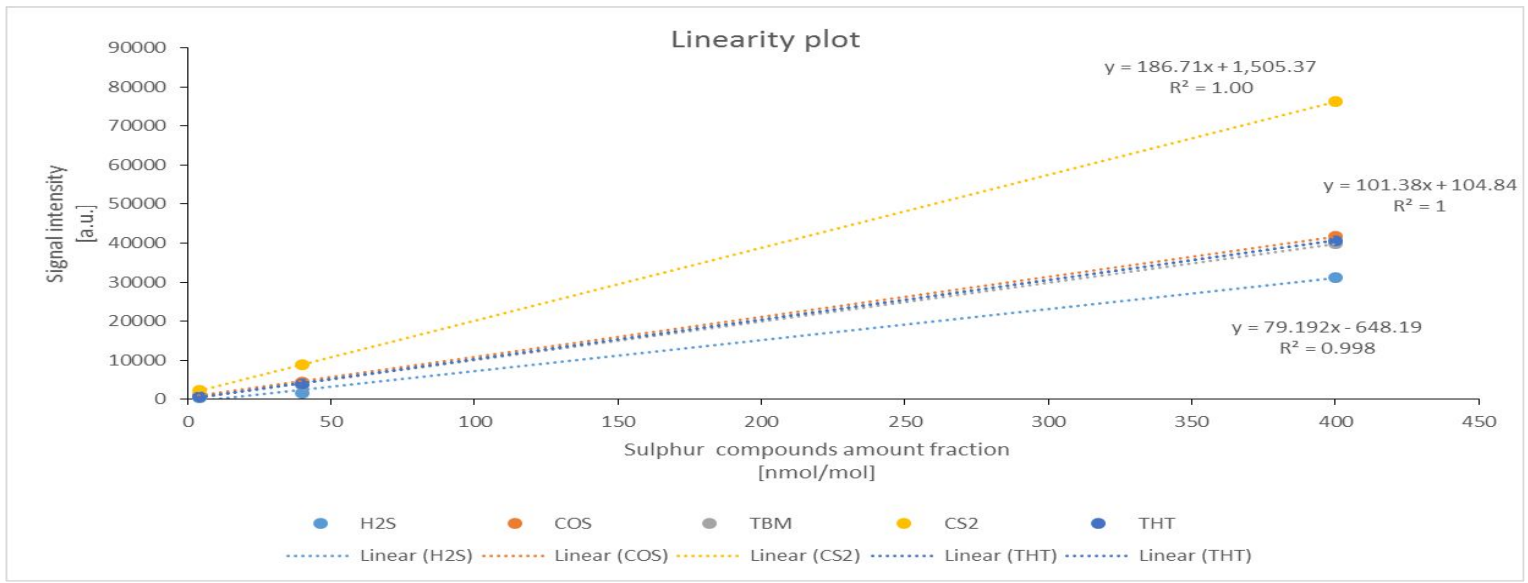
Linearity and repeatability



<u>Rel. standard deviation</u>

<13 % for all compounds at 4 nmol/mol

<5 % for all compounds at 40 nmol/mol



<u>Linearity</u>

Good over the range

4 – 400 nmol/mol

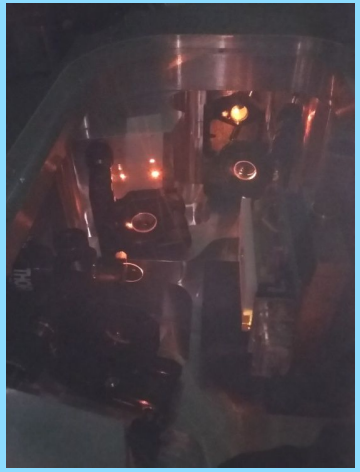
Limit of detection

- LOD calculated based on peak height:

Compound	Concentration (nmol/mol)	Signal Height (µV)	Limit of detection* (pmol/mol)
Hydrogen sulphide	4.2	245.0	514
Carbonyl sulphide	4.3	519.9	248
Carbon disulphide	4.1	301.7	408
2-methyl-2-propanethiol	3.8	94.1	1211
Tetrahydrothiophene	3.6	199.7	541

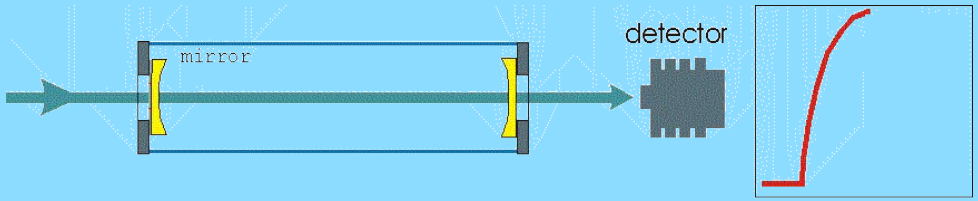
**LoD's calculated using average noise height value of 10 µV*

Speciation method for HCl in H_2: CRDS



- Operating range λ =2.3-5.1 µm
- Power up to 3 Watt
- Line width ≤ 0.001 nm

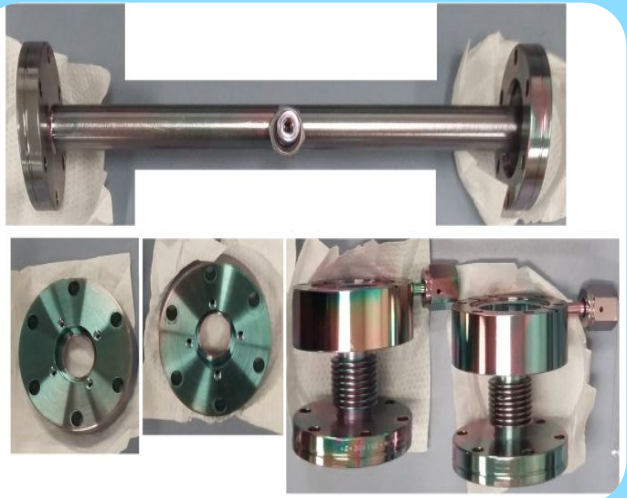
Optical parametric oscillator (OPO)



- 1-5 km effective path length
- Coated cell to reduce adsorption of the impurities

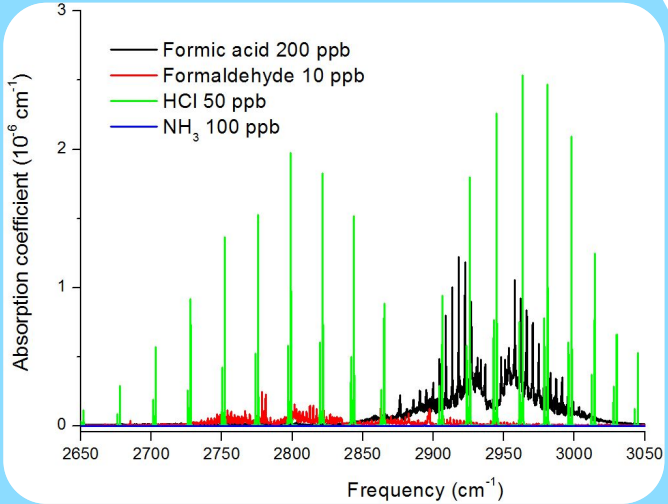
Cavity Ring Down Spectroscopy (CRDS)

Speciation method for HCl in H_2



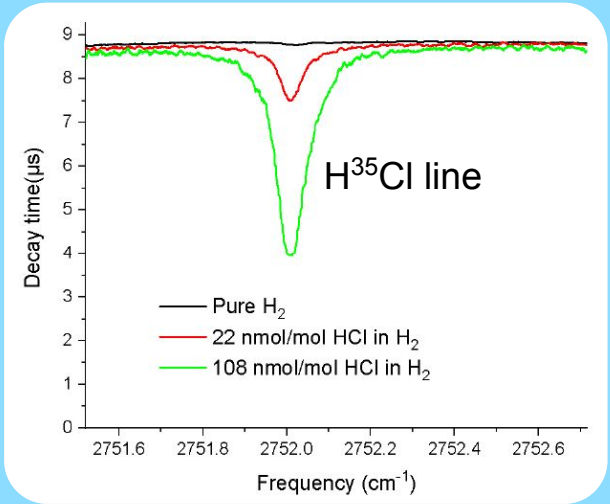
Choice of cell material & sampling line critical due to high reactivity of HCl (polymers, Dursan or SilcoNert 2000 coated)

CRDS cell & sampling lines



- Small hydrocarbons
- HCl, HF
- CH_2O, CH_2O_2
- NH_3, H_2O
- CO_2, CO

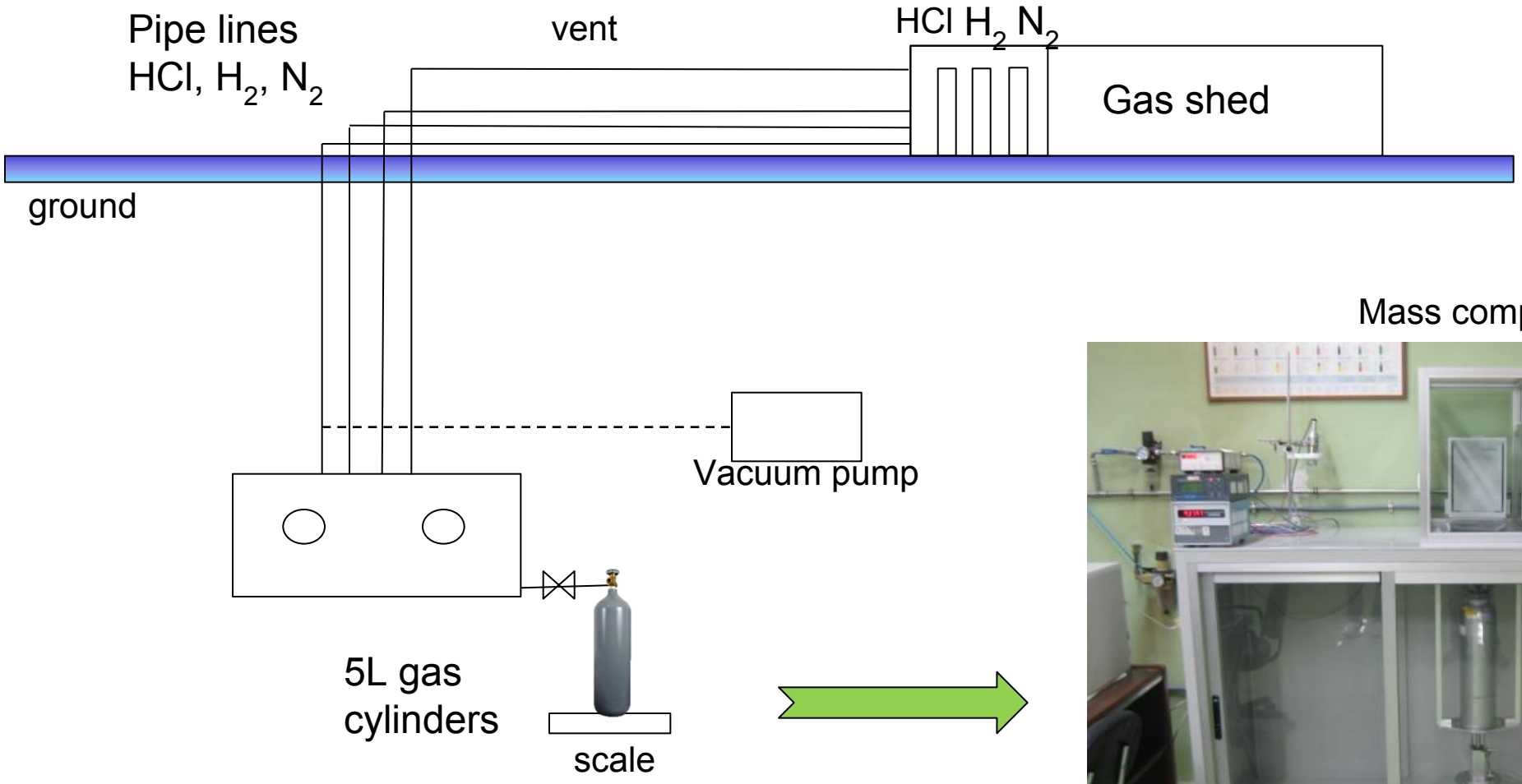
Detectable compounds



System suitable for low nmol/mol up to µmol/mol range. Calibration using gravimetric standards and permeation.

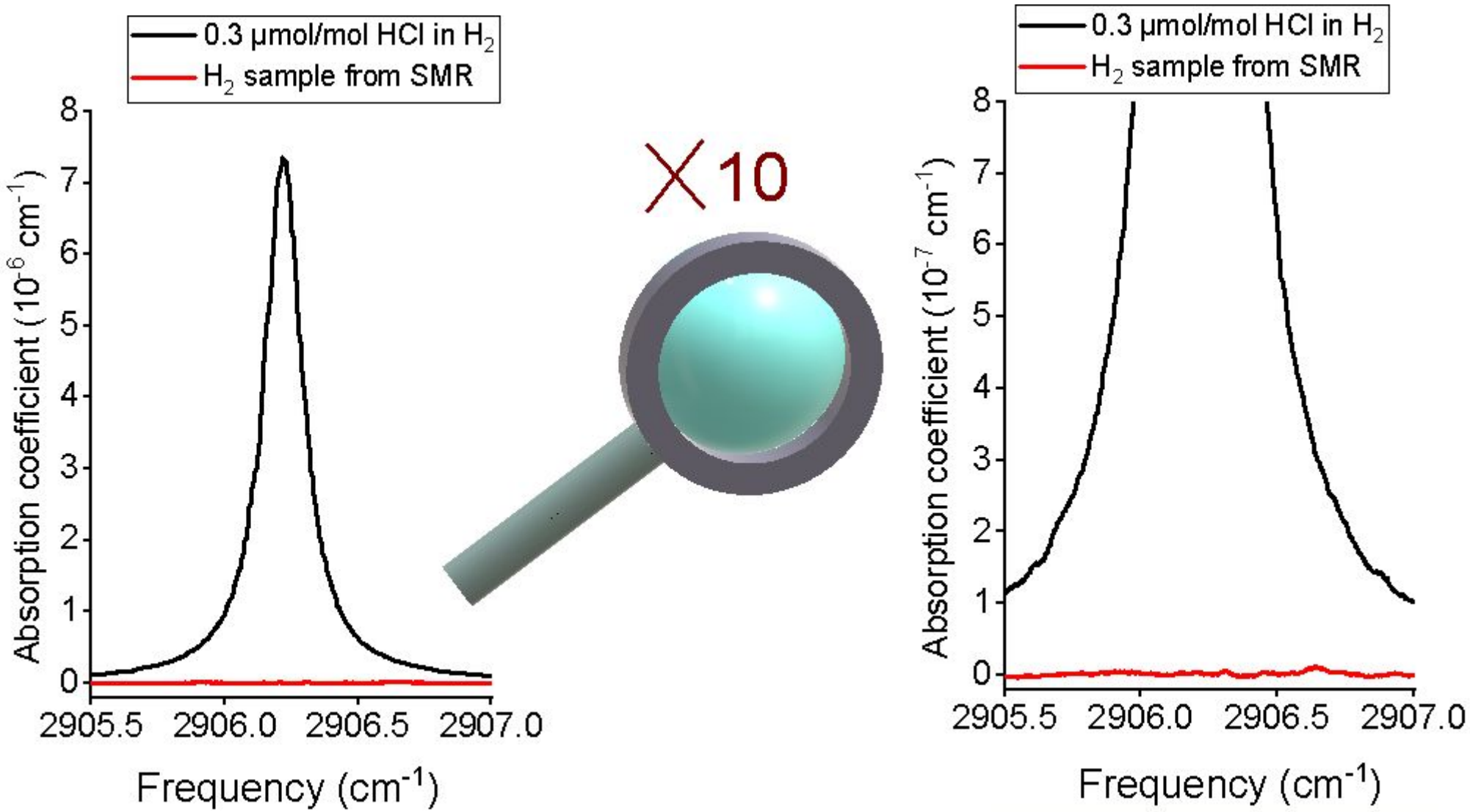
Calibration

Preparation of HCl in H_2 gas standard

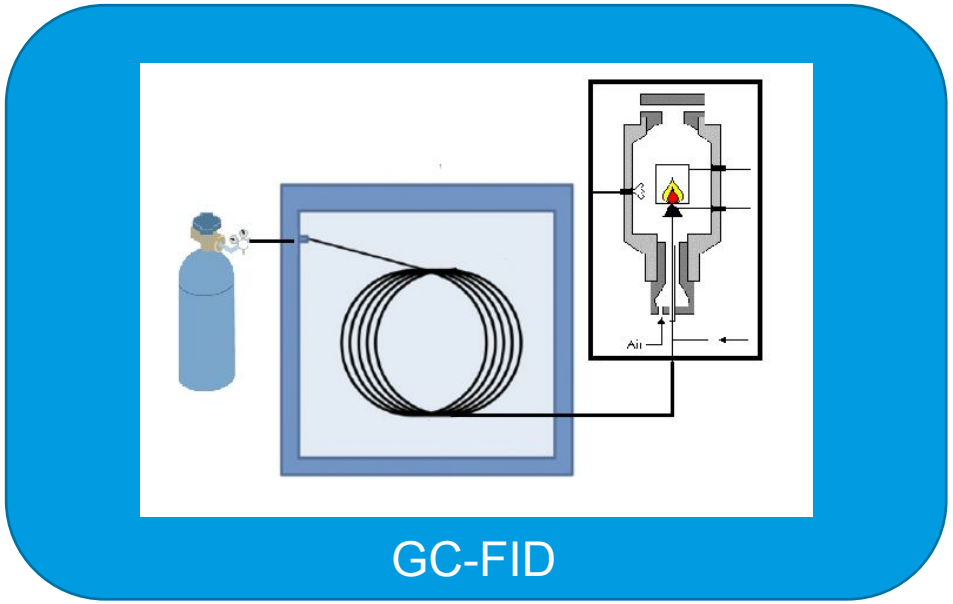


Mass comparator

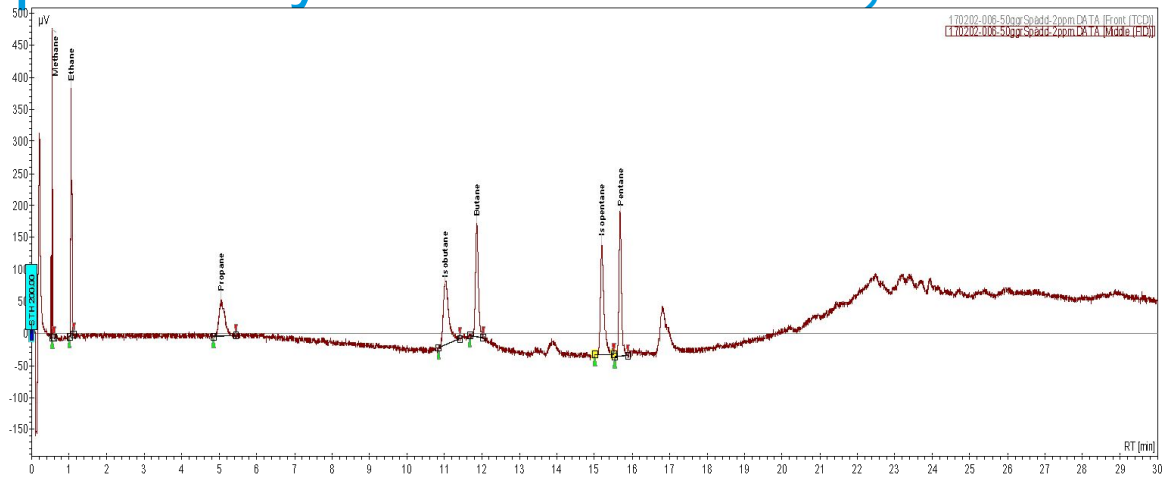
Speciation method for HCl in H_2



Development & validation of speciation method based on GC for the measurement of separate hydrocarbons in H_2



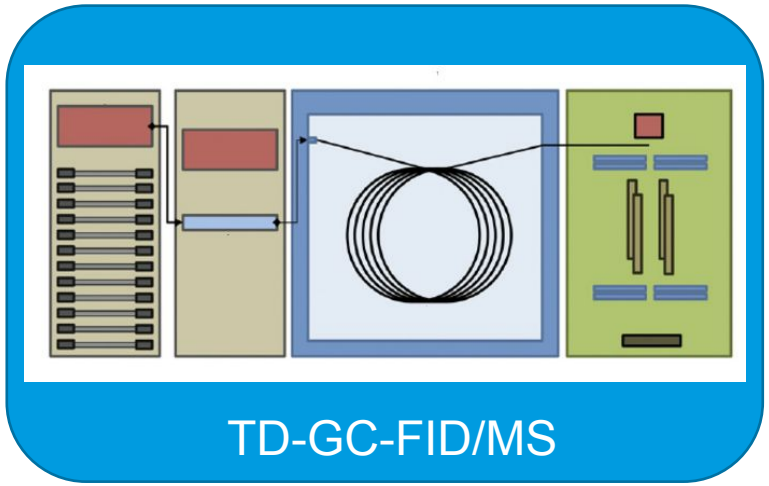
GC-FID



Compounds	S/N	LOD µmol/mol (S/N = 2)	LOD µmolC/mol (S/N = 2)
Methane	490	0,04	0,04
Ethane	400	0,05	0,10
propane	150	0,10	0,30
Isobutane	200	0,09	0,38
Butane	220	0,09	0,37
Isopentane	240	0,08	0,46
Pentane	490	0,04	0,39
Total hydrocarbons		0,55	2,04

Measurement uncertainty ~8-10% for hydrocarbons with GC-FID

Development and validation of speciation method based on GC for the measurement of separate hydrocarbons in H_2



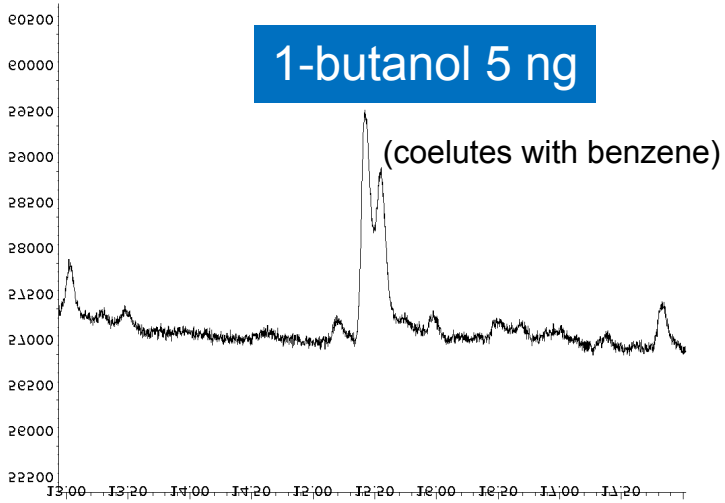
TD-GC-FID/MS

Achievements

- LoD of 2 µmolC/mol for “total hydrocarbons” (ISO14687-2) has been shown to be achievable.
- Advantages method: both hydrocarbons and oxygenated compounds can be identified either using the mass spectrometer (TD-GC/FID-MS) or retention time (GC/FID).

Measurement uncertainty 10-12% for hydrocarbons with TD-GC/FID-MS

Compound	ng of compound on Tenax TA	nmol/mol equivalent for 100 ml sample	nC	LOD µmolC/mol
Hexane	2	5,7	6	0,03
Decane	1	1,7	10	0,17
Octadecane	4	3,9	18	0,69
Toluene	1	2,7	7	0,19



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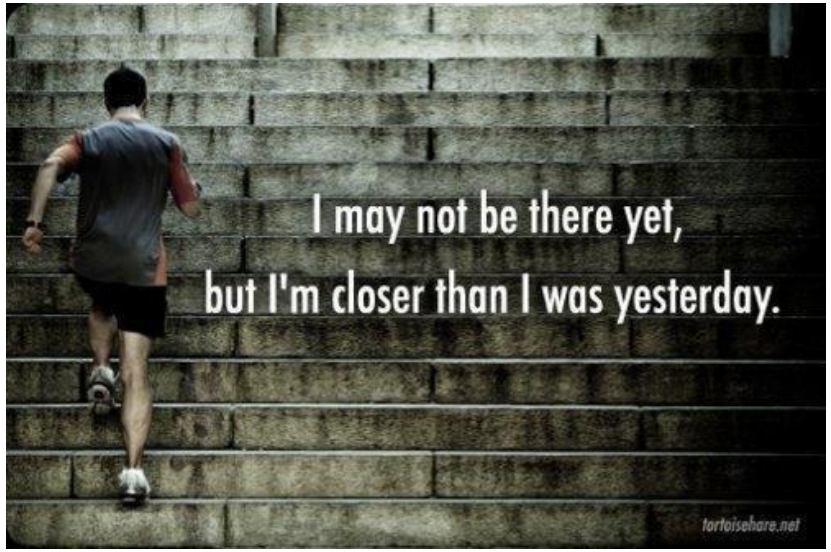
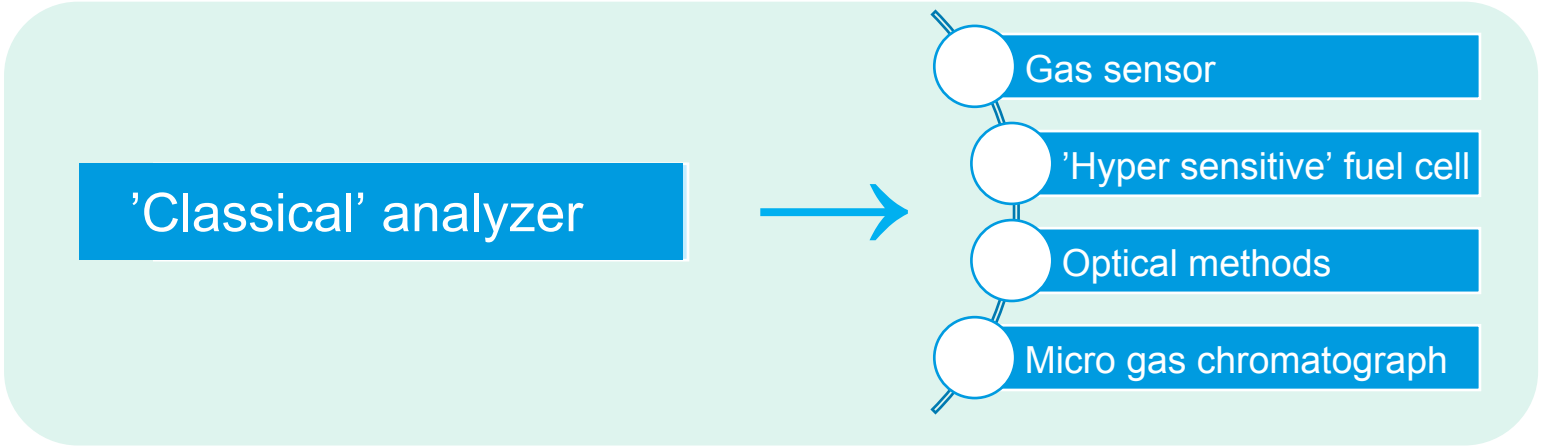


Getting closer but....

....more practical (=cheaper, smaller, easier to use, multi-component) analytical solutions are needed.




THANK YOU!
CONTACT: SPERSIJN@VSL.NL

Instrument specifications for the development of multi-component analysers using input from risk assessment

Probability of impurity presence	Steam methane reforming with PSA	Chlor-alkali process (membrane cell process)	PEM water electrolysis process with TSA
Frequent	CO	O_2	None identified
Possible	N_2	None identified	None identified
Rare	CH_4, H_2O and Ar	N_2 and H_2O	N_2, O_2 and H_2O
Very rare	CH_2O	CO_2	CO_2
Unlikely	He, CO, O_2, CH_2O_2, NH_3, sulphur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, sulphur compounds, hydrocarbons compounds, halogenated compounds	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, sulphur compounds, hydrocarbons compounds, halogenated compounds

Component \ Method	CRDS	FTIR	OFCEAS
Water	Instrument 1	Instrument 1	Instrument 1
Oxygen	Instrument 4		Instrument 2
Carbon dioxide	Instrument 1	Instrument 1	Instrument 2
Carbon monoxide	Instrument 1	Instrument 1	Instrument 1
Formaldehyde	Instrument 3	Instrument 1	Instrument 1
Formic Acid		Instrument 1	Instrument 1
Ammonia	Instrument 2	Instrument 1	Instrument 1
Helium			
Total N_2 and Ar			
Total hydrocarbons		Methane, Ethane	
Methane	Instrument 1	Instrument 1	Instrument 1
Total sulfur compounds			
Hydrogen sulfide			Instrument 1
Total halogenated compounds			
Hydrogen chloride	Instrument 5		Instrument 2
Nr of instruments required	4 (5 with HCl)	1	2 racks 19 inch 4U & external pumps
Combine price	170-185 k€	80-100 k€	160-180 k€
Instrument connection	In parallel		In series