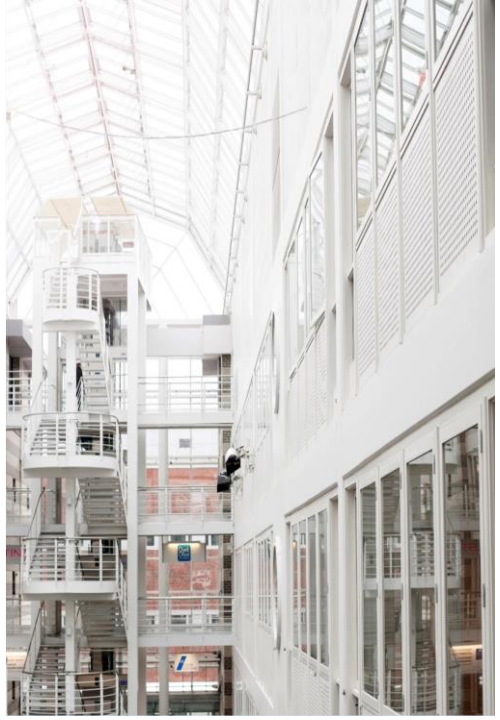
15NRM03 HYDROGEN - METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS

WP2 - ANALYTICAL METHODS



Karine Arrhenius / Oliver Büker

Joined Final meeting and Stakeholder Advisory Board meeting, 21st May 2019

Research Institutes of Sweden

Bioscience and Materials

Chemistry, Materials and Surfaces

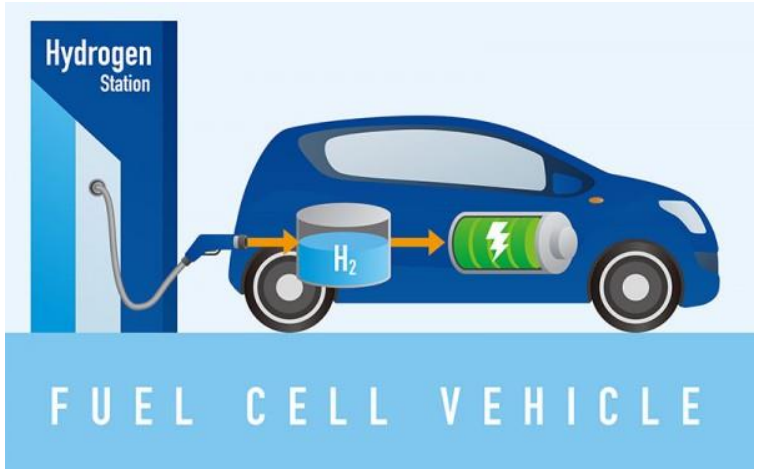
WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

? Proposing optimised analytical protocols (including fit-for-purpose analytical methods)

Discussing the presence of other potentially harmful impurities not yet specified

! Identify the challenges in implementing ISO 14687-2 in routine laboratory/analysis

= Groundwork for potential revision of the standard



WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Deliverables

D3 “Assessment report of the multi-component analyser with optimised sampling analysis that meet the required detection limits as per business plans ISO/TC 197 and CEN/TC 268” – Task 2.2

D4 “Recommendations on optimised analytical protocols including fit-for-purpose analytical methods that enable the implementation of ISO 14687-2” – Task 2.3

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

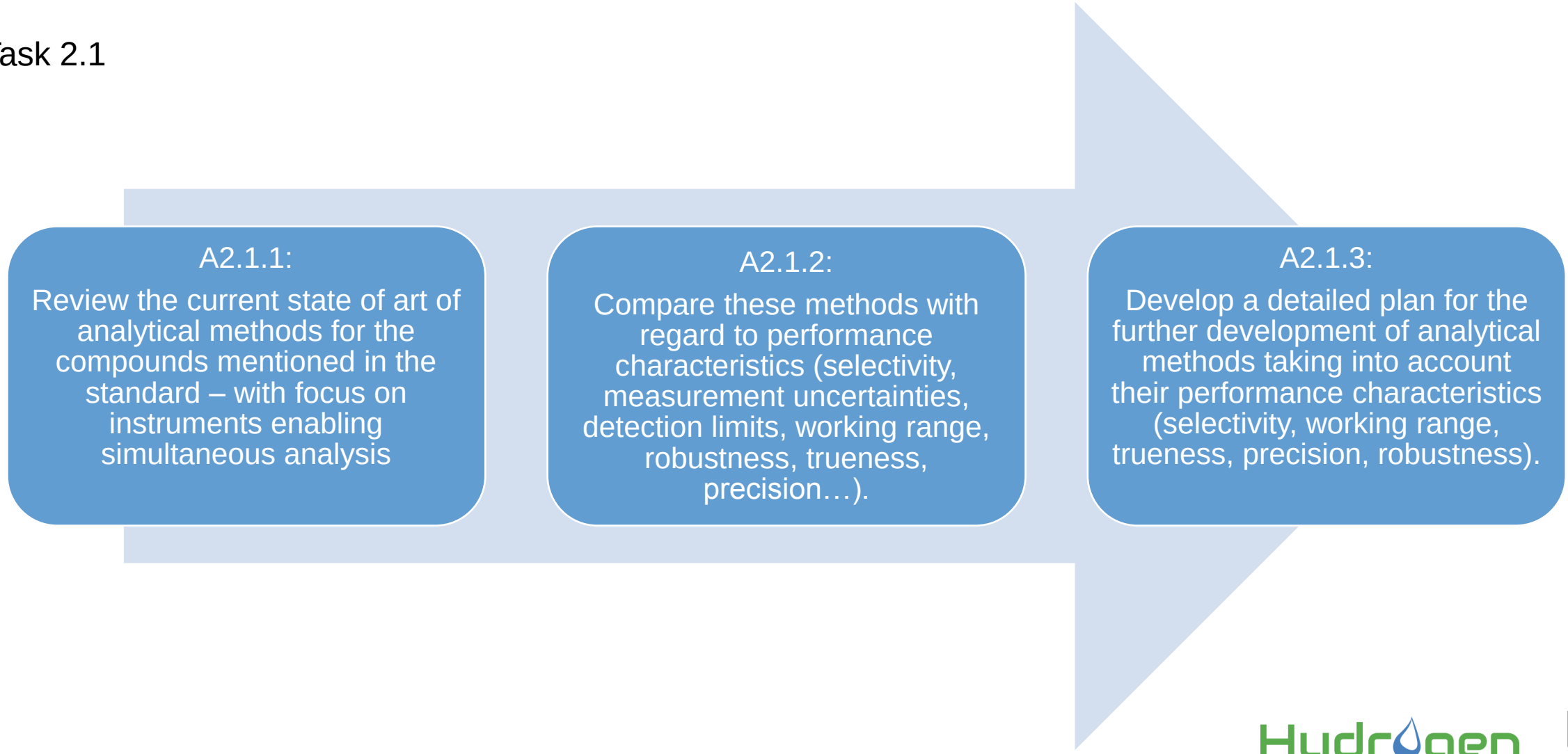
Task 2.1: Literature review of impurity analysis methods (LNE, NPL, RISE, VSL) – Jun 16 to March 18

Task 2.2: Methods development (NPL, RISE, VSL,CEM) Aug 16 to Nov 18

Task 2.3: Analytical procedures (NPL, RISE, VSL,CEM) Dec 18 to May 19

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.1



WP2 — A2.1.3 – Plan for the further development of analytical methods

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
OFCEAS	H2O									Under evaluation by RISE
	O2									
	CO									
	CO2									
	CH2O									
	CH2O2									
	NH3									
	H2S									To be validated, RISE (16ENG01)
	CH4									
	HCl									
	HBr									
CRDS	H2O							ASTM D7941-14		NPL in house methods
	O2							ASTM D7941-14		
	CO2							ASTM D7941-14		
	CO							ASTM D7941-14		
	CO									VSL in house methods
	CH2O2									VSL in house methods
	NH3							ASTM D7941-14		VSL in house methods
	CH4							ASTM D7941-14		VSL in house methods
	HCl									VSL in house methods
	HBr									

ASTM published standards are validated for precision and bias by undergoing an inter-laboratory study program (ILS), in which the standard is tested by independent laboratories.

2016, only one of the H2 standards has undergone an ILS (unfinished): ASTM D7653-10 (FTIR) (NH3, CO2, CO, CH2O, CH2O2, H2O)

WP2 — A2.1.3 – Plan for the further development of analytical methods

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
FTIR	H2O							ASTM D7653-10		
	CO2							ASTM D7653-10		
	CO							ASTM D7653-10		
	CH2O							ASTM D7653-10		VSL in house methods
	CH2O2							ASTM D7653-10		NPL in house methods
	NH3							ASTM D7653-10		NPL in house methods
	CH4							ASTM D7653-10		
GC-TCD	O2									NPL in house methods
	He									NPL in house methods
	N2									NPL in house methods
	Ar									
GC-FID	CH4									Validated by RISE, activity A2.2.3 [2]

ASTM published standards are validated for precision and bias by undergoing an inter-laboratory study program (ILS), in which the standard is tested by independent laboratories.

2016, only one of the H2 standards has undergone an ILS (unfinished): ASTM D7653-10 (FTIR) (NH3, CO2, CO, CH2O, CH2O2, H2O)

WP2 — A2.1.3 – Plan for the further development of analytical methods

Table 2: Identified performance characteristics among LOQ (Limit of Quantification), selectivity, working range, precision, trueness and ruggedness that requires further evaluation

Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
GC-MS	H2O							ASTM D7649-10		
	O2							ASTM D7649-10		
	He							JIS K 0123		
	N2							ASTM D7649-10		
	CO2							ASTM D7649-10		
	Ar							ASTM D7649-10		
	NH3									
	CH2O							ASTM D7892-15		
	Hydrocarbons							ASTM D7892-15		
	Organic sulfur									
	Organic halides							ASTM D7892-15		To be validated (16ENG01)
Dew point hygrometer	H2O							JIS K0225		NPL in house methods
Vibrating quartz crystal analyzer	H2O							JIS K0225		NPL in house methods
Electrochemical sensor	O2							ASTM D7607-11		
GC-PDHID	O2								Rapport NPL [3]	NPL in house methods
	N2									NPL in house methods
	Ar									NPL in house methods
	CO2									
Galvanic cell O2 meter	O2							JIS K0225		
Methanizer GC-FID	CO									VSL and NPL in house

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.1: Literature review of impurity analysis methods (LNE, NPL, RISE, VSL) – Jun-16 to March-18

Task 2.2: Methods development (NPL, RISE, VSL,CEM) Aug-16 to Nov-18

Task 2.3: Analytical procedures (NPL, RISE, VSL,CEM) Dec-18 to May-19

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.2 - Part 1

Methods development and validation for ”total” species – speciation methods

Presence of potentially harmful compounds (if any) detected in real hydrogen samples

A2.2.1:
speciation method based on cryo-GC-SCD for the measurement of sulphur species (NPL)

A2.2.2:
speciation method based on CRDS with OPO as light source for HCl (VSL)

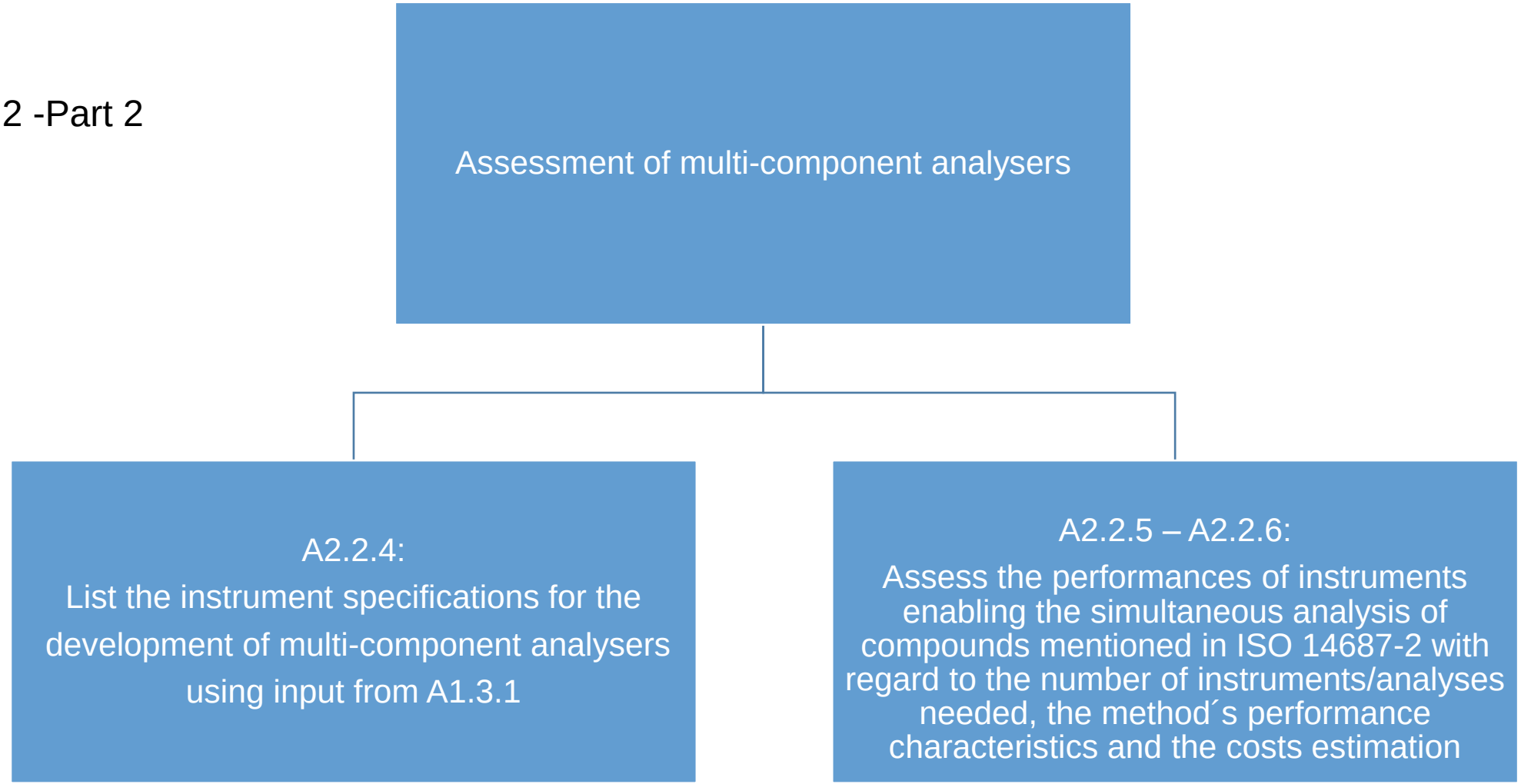
A2.2.3:
speciation method based on gas chromatography (with GC/FID and TD-GC/MS-FID) for the measurement of separate hydrocarbons (RISE)

A2.2.7:
Analysis of all H2 samples collected in WP1 in order to identify and quantify other compounds not yet regulated in ISO14687

”screening” method for volatile organic compounds

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.2 -Part 2



WP2: developing speciation methods for total species (sulfur, halogenated, hydrocarbons – A2.2.1-A2.2.3)

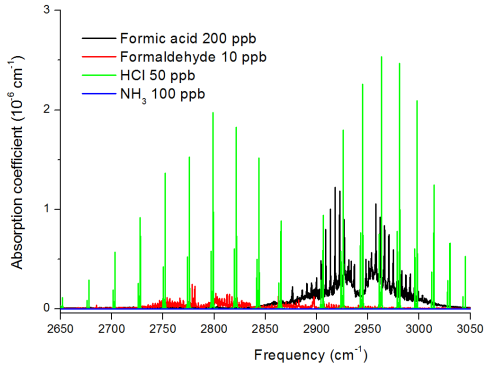
Determination of total species is a real analytical challenge:

- They cover a large number of species
- Quantification mostly based on conversion of compounds into one species (problem with interferences or compounds not efficiently converted)

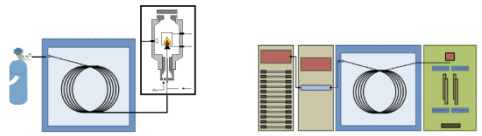
Only a few impurities of a total species group may actually be present in the hydrogen:

- Developing a speciation method allow to measure the actual impurities
- Possibility to suggest to ISO/TC 197 to replace ”total species” with the actual impurities

A2.2.1: cryo-GC-SCD for sulfur species



A2.2.2: CRDS for HCl



A2.2.3: GC-FID + TD-GC-FID/MS for hydrocarbons species

WP2 – A2.2.1 - Development and Validation of speciation method based on cryo-GC-SCD for the measurement of sulphur species

A2.2.1: NPL will develop and validate a speciation method and for the measurement of sulphur species in hydrogen.
Gas standards will be produced by CEM and/or NPL

In ISO 14687: Total sulphur compounds: 0.004 µmol/mol

Existing method:
Non-retaining column, no separation, LOD 1.4 nmol/mol

New method:
Strategy for speciation of pmol/mol: cryo-focussing

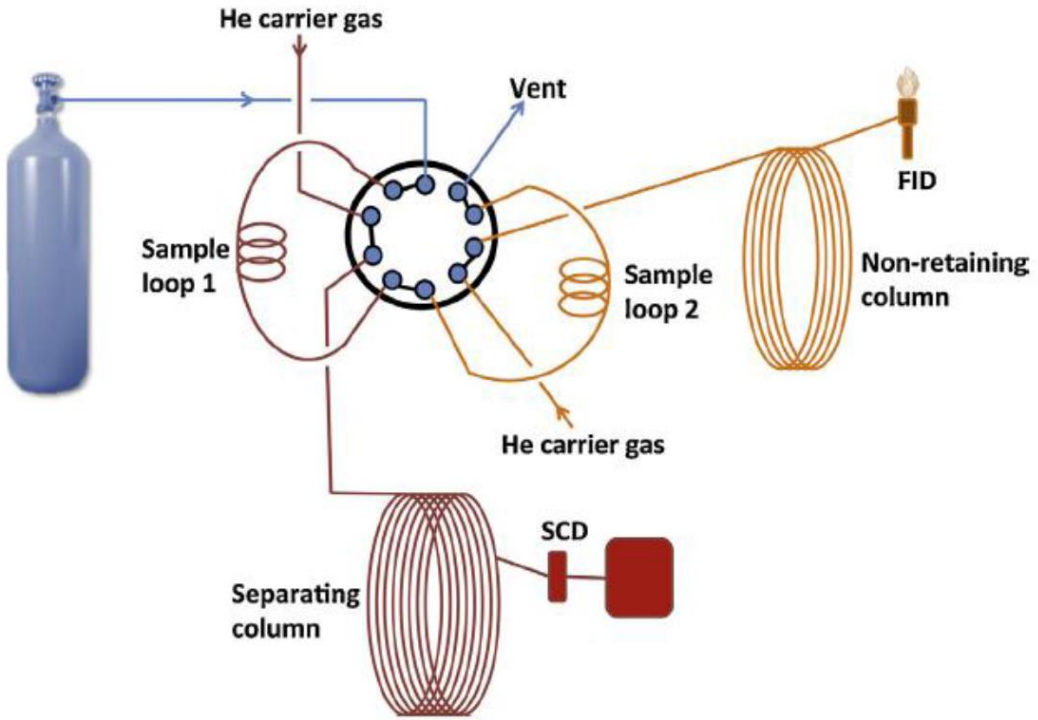


Figure 1: Schematic of the GC-SCD for NPL's total sulphur method

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Hydrogen RISE

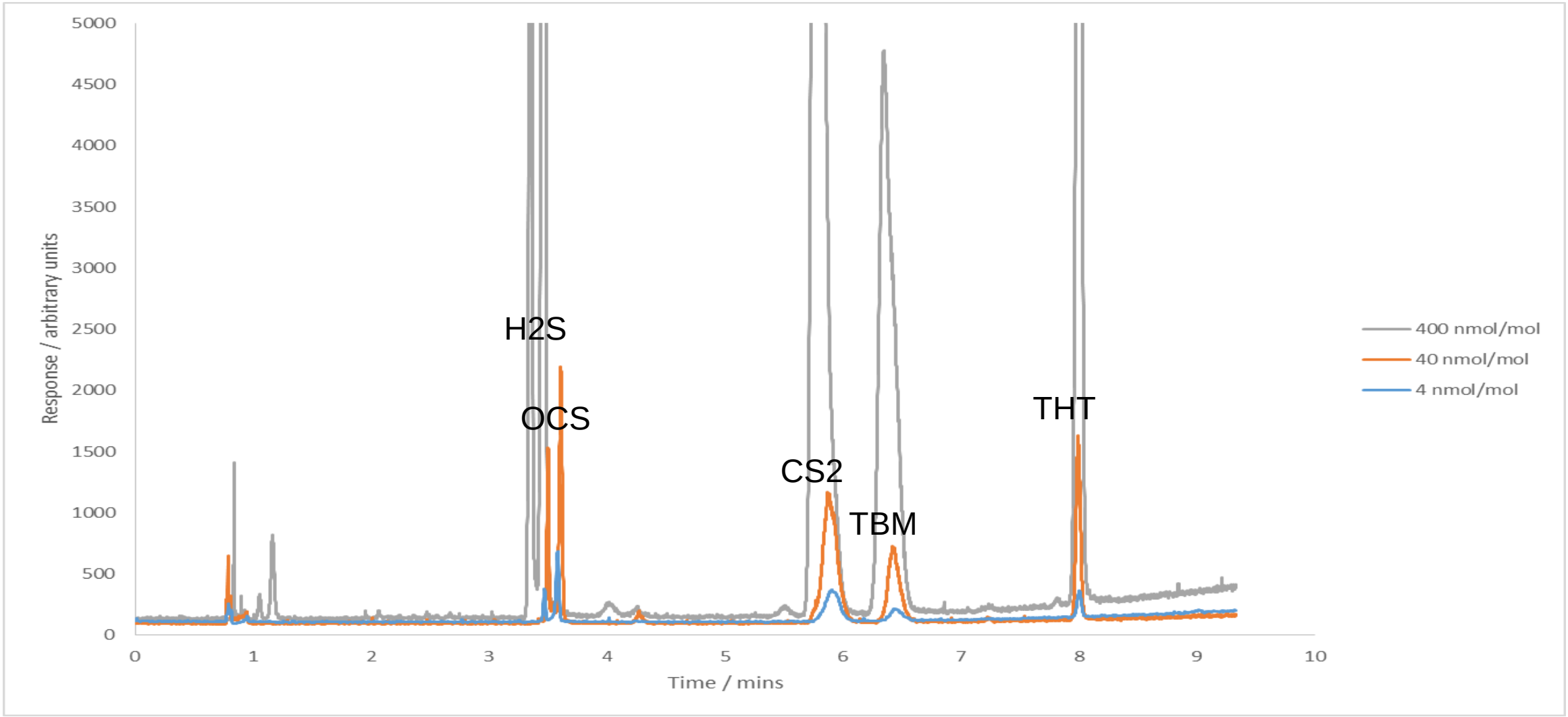
Speciation of sulphur – Cryo-focussing GC-SCD

- **Achievements:**
  - Testing of the cryo-focussing method on sulphur in hydrogen standards
  - Develop new gas standards in hydrogen:
    - Hydrogen sulphide (H_2S)
    - Carbonyl sulphide (OCS)
    - Carbon disulphide (CS_2)
    - 2-methyl-2-propanethiol (TBM)
    - Tetrahydrothiophene (THT)

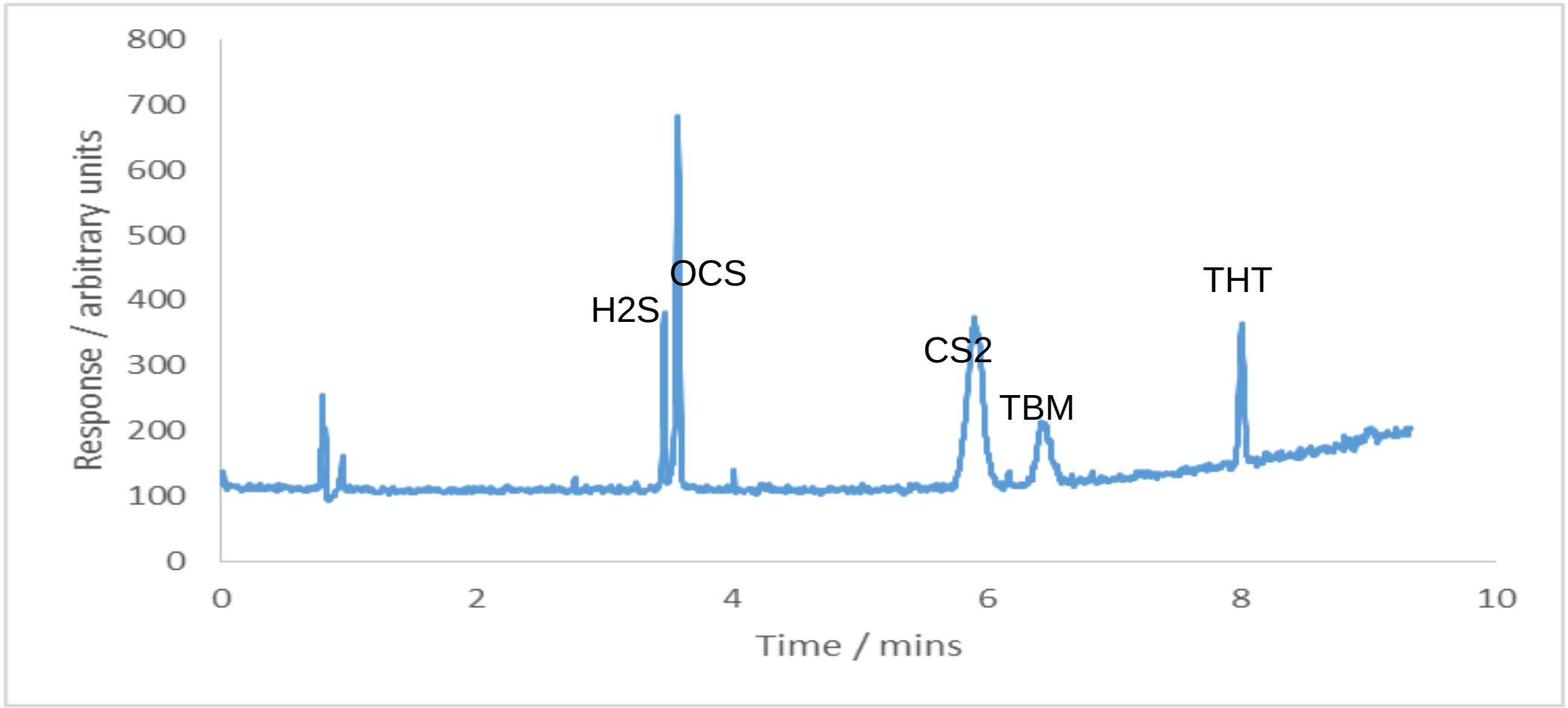
Method development:
Large difference in MW and boiling point

  - Gas standards in hydrogen
    - 400 nmol/mol of H_2S, OCS, CS_2, TBM and THT → Short life time (< 2 weeks)
    - 40 nmol/mol of H_2S, OCS, CS_2, TBM and THT
    - 4 nmol/mol of H_2S, OCS, CS_2, TBM and THT

Results of analysis



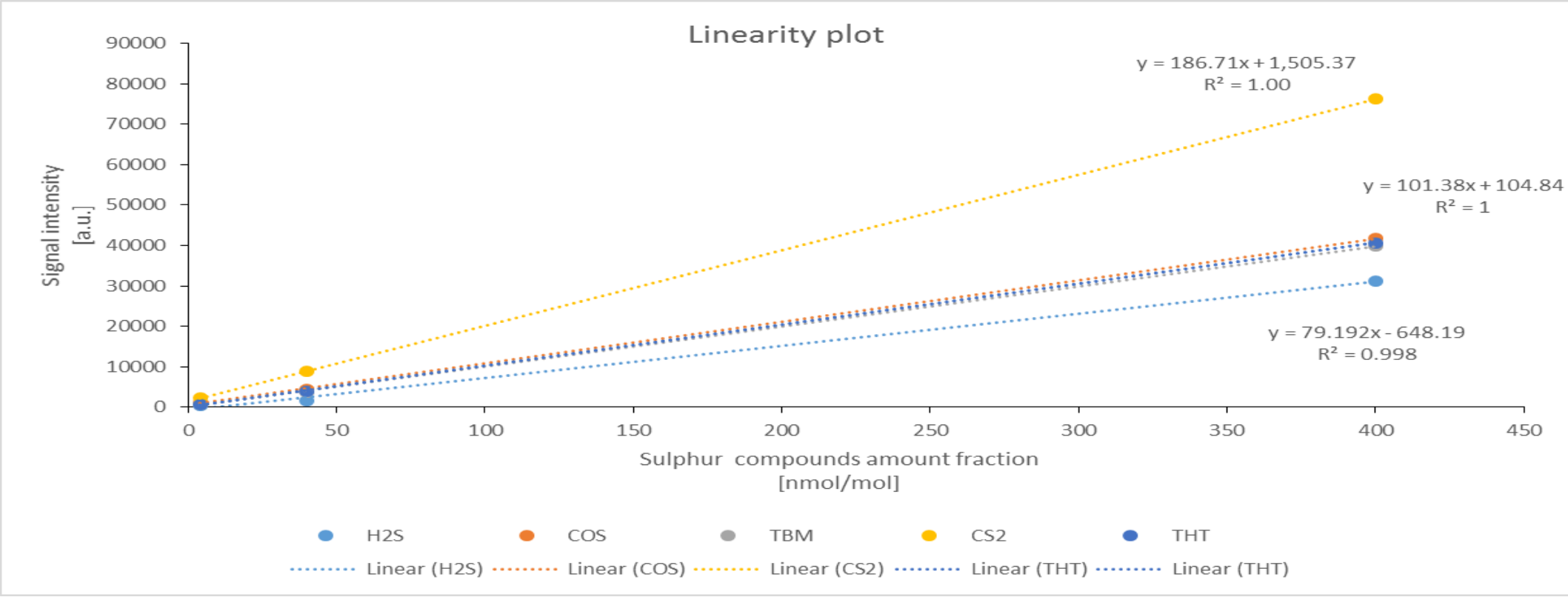
Speciation at 4 nmol/mol



Linearity and repeatability

- Relative Standard Deviation
  - < 13 % for all compounds at 4 nmol/mol
  - < 5 % for all compounds at 40 nmol/mol

- Linearity: good over the range 4 – 400 nmol/mol



Limit of detection and measurement uncertainty

- LOD calculated based on peak height

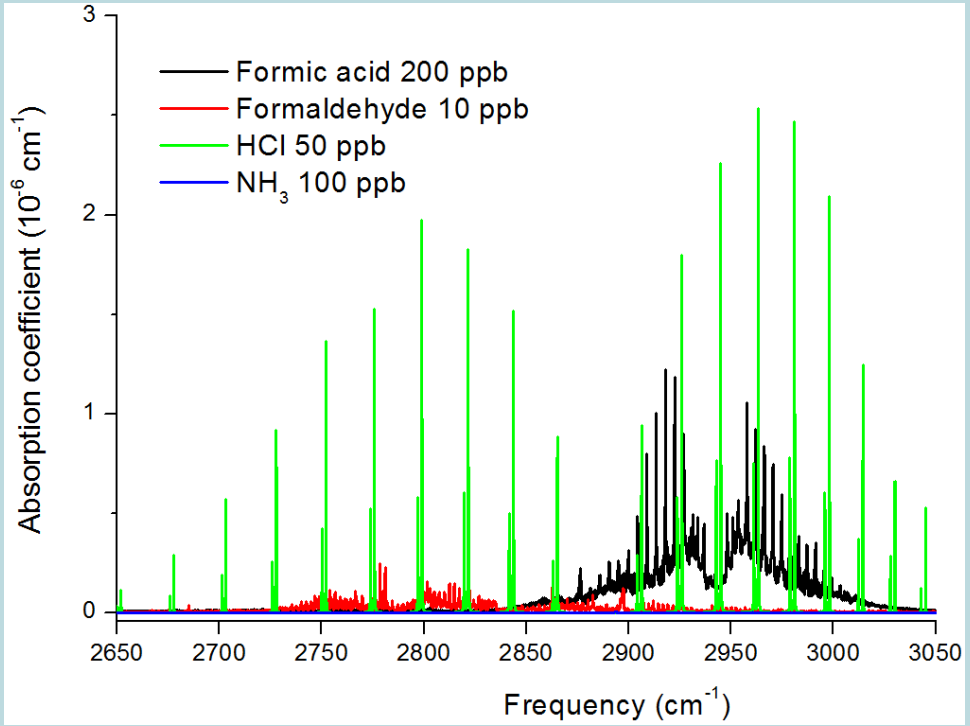
Compound	Concentration (nmol/mol)	Signal Height (µV)	Limit of detection* (pmol/mol)
Hydrogen sulphide	4.2	245.0	514
Carbonyl sulphide	4.3	519.9	248
Carbon disulphide	4.1	301.7	408
2-methyl-2-propanethiol	3.8	94.1	1211
Tetrahydrothiophene	3.6	199.7	541

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

- The expanded uncertainty estimation is 26.96% (incl. a conservative element for trueness which was not assessed

A2.2.2 Speciation method for HCl in H_2

- Many strong lines (2 main isotopes $H^{35}Cl$ and $H^{37}Cl$)
- Lines around 2905 cm^{-1} selected, LoD 1 ppb (in absence of interferences)



Dutch Metrology Institute

VSL

A2.2.2 Speciation method for HCl in H_2

Choice of cell material and sampling lines critical due to high reactivity of HCl (all coated)

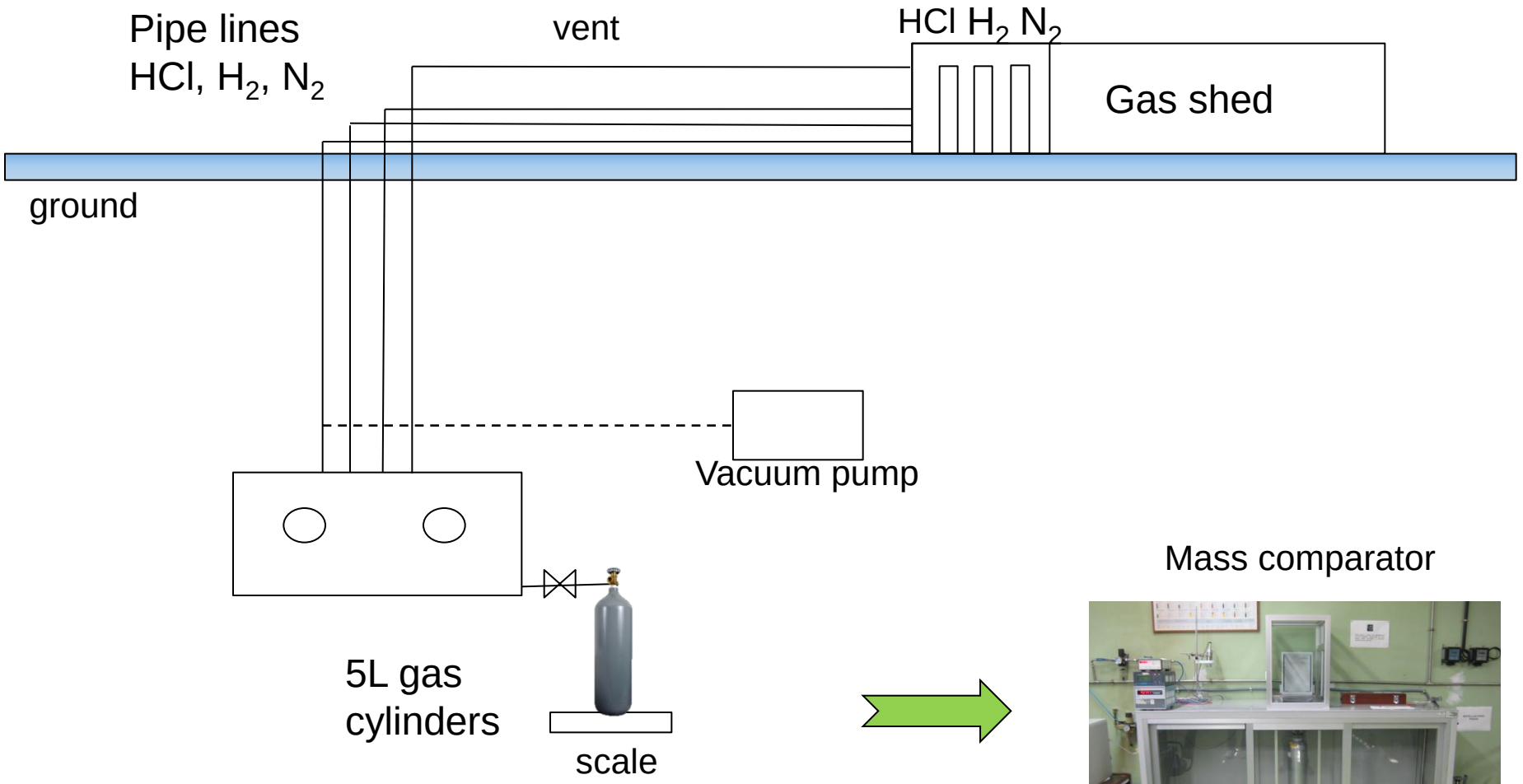
CRDS cell and sampling lines

Currently use certified HCl in N_2 standard and dilute with high purity H_2. Alternative: use of line strength data.

Calibration

Dutch Metrology Institute

VSL

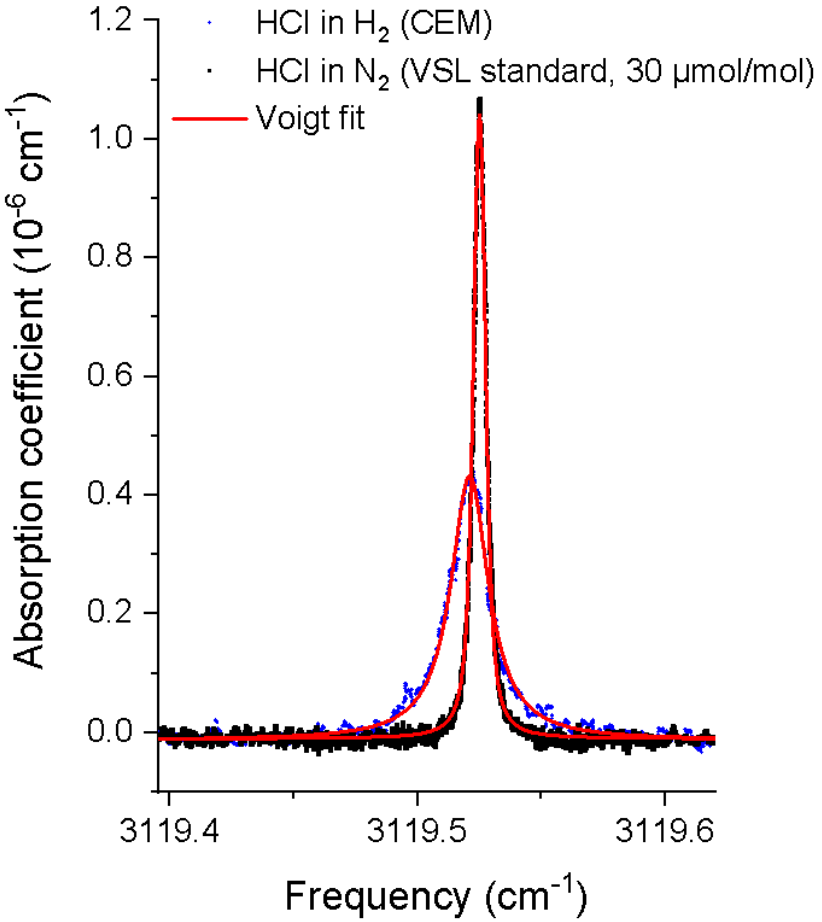


Mass comparator

A2.2.2 CEM mixture (HCl in H_2) measured using CRDS

- Measured on 28-8-2018 using CRDS
- Comparison with HCl standard in N_2 (width of the absorption line different due the matrix)
- Certified amount fraction CEM mixture: 45.5 ± 3 µmol/mol

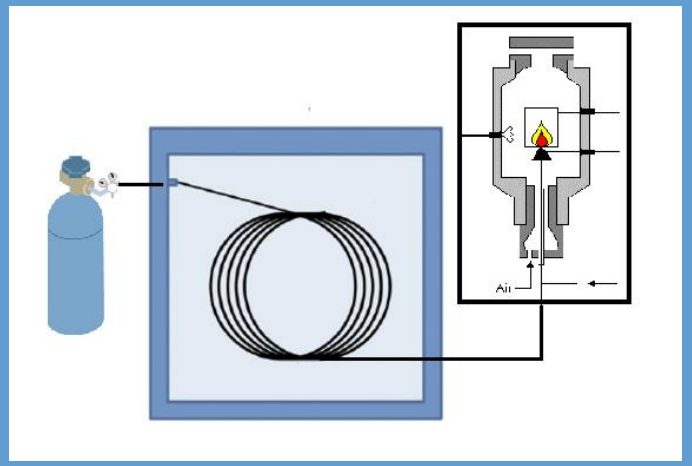
  (nominal 55.2 µmol/mol)



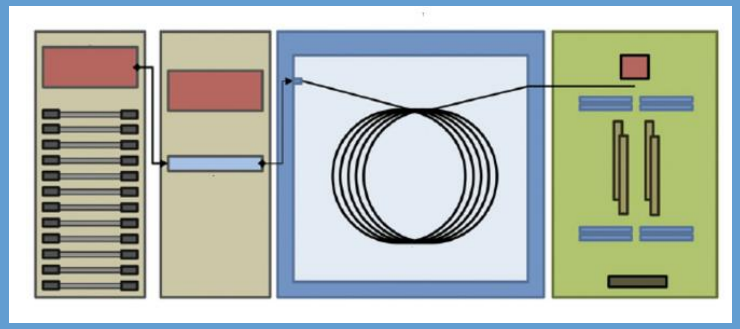
WP2 – A2.2.3 - Development and validation of speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

- Development of a speciation method to quantify hydrocarbons based on the combination of two analytical techniques (GC/FID and TD-GC/FID-MS)
- Measurement uncertainties have been calculated to be around 8-10% for hydrocarbons with GC-FID and around 10-12% for hydrocarbons with TD-GC/FID-MS.
- Limit of detection of 2 µmolC/mol for the “total hydrocarbons” (as required in the standard ISO14687-2) has been shown to be achievable.
- The advantages of this method are that hydrocarbons as well as oxygenated compounds if present in the hydrogen can be identified either using the mass spectrometer for the TD-GC/FID-MS or the retention time for the GC/FID method.

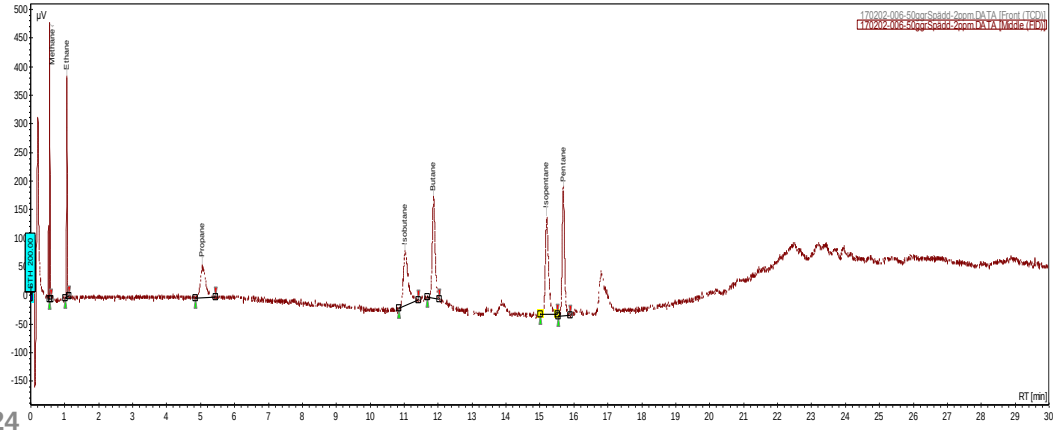
WP2 – A2.2.3 - Development and Validation of speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

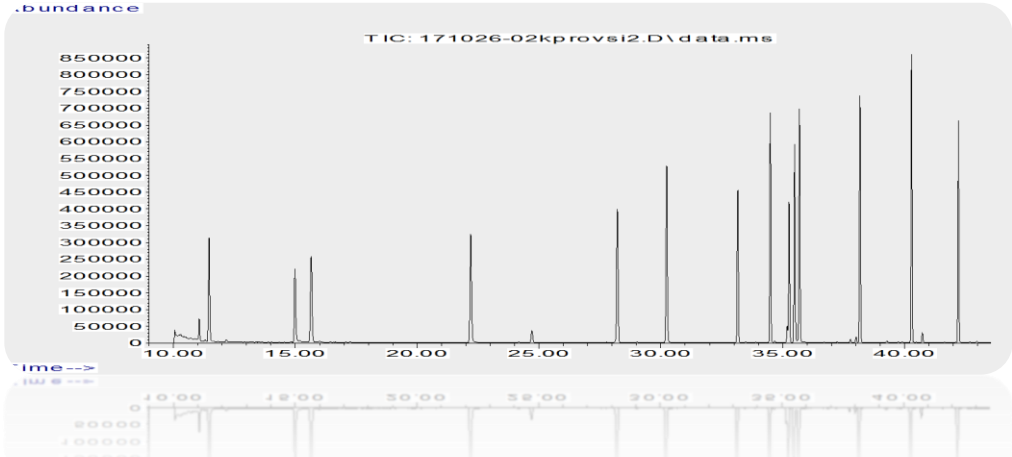


GC-FID

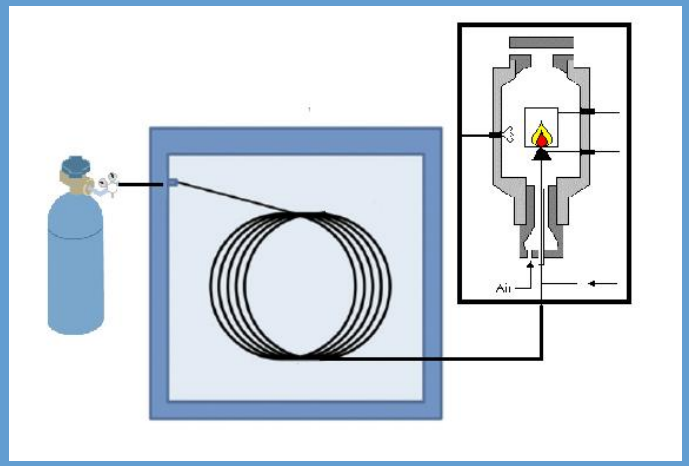


TD-GC-MS

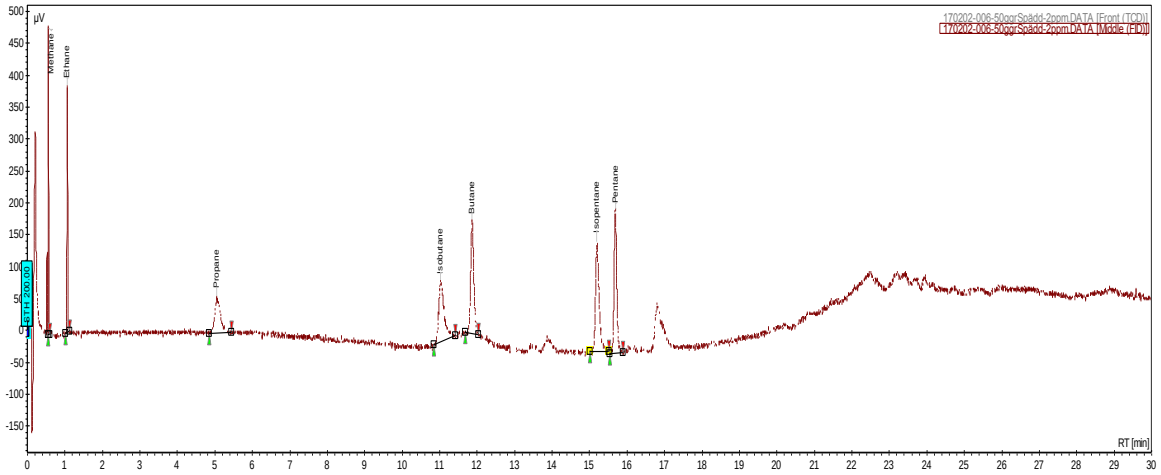




WP2 – A2.2.3 - Development and Validation of speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

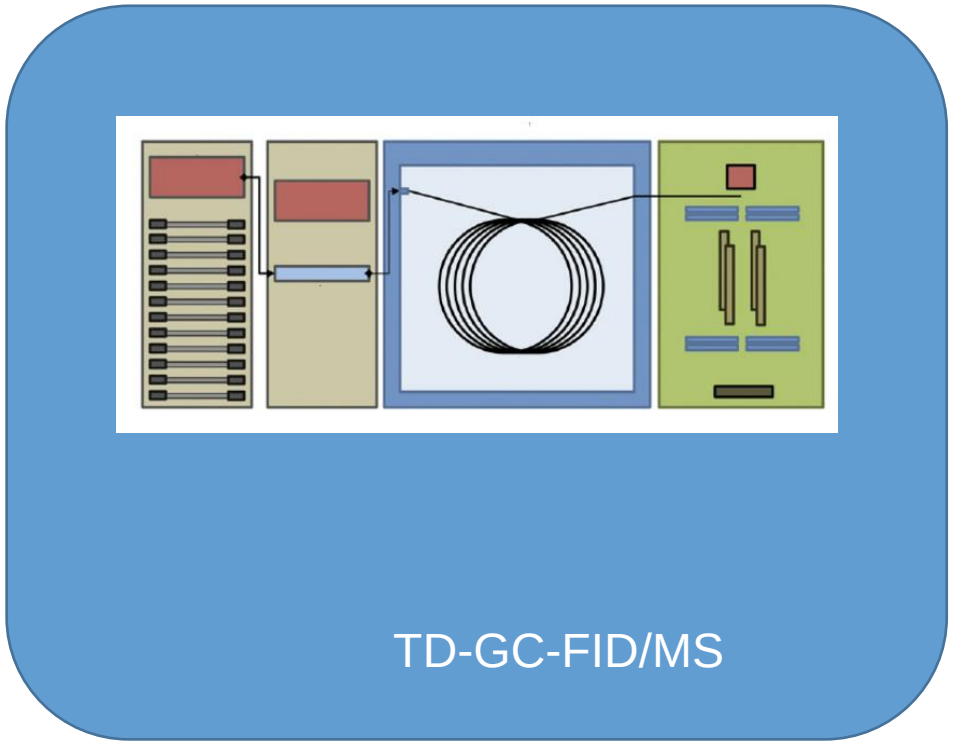


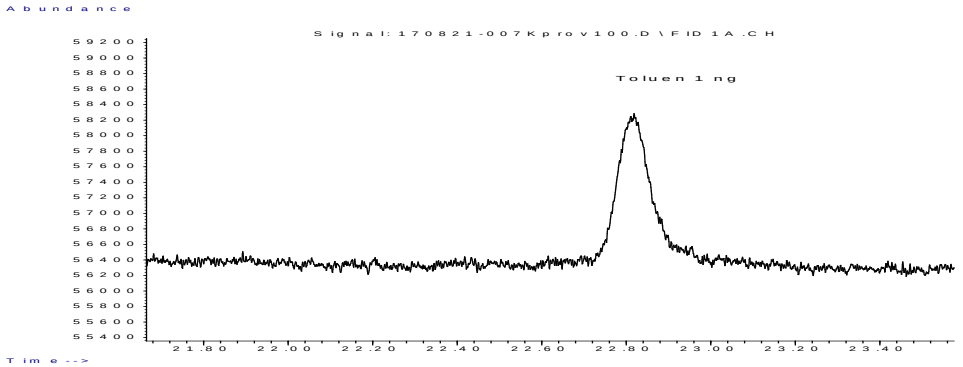
GC-FID



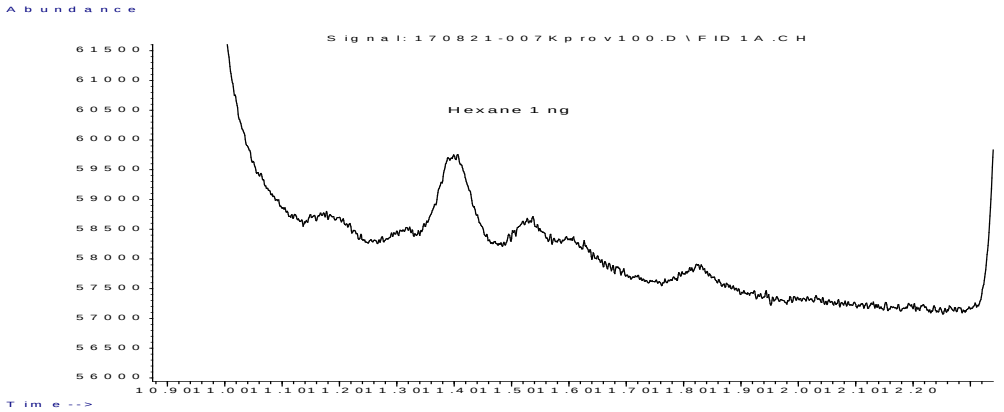
Compounds	S/N	LOD µmol/mol (S/N = 2)	LOD µmolC/mol (S/N = 2)
Methane	490	0,04	0,04
Ethane	400	0,05	0,10
propane	150	0,10	0,30
Isobutane	200	0,09	0,38
Butane	220	0,09	0,37
Isopentane	240	0,08	0,46
Pentane	490	0,04	0,39
Total hydrocarbons		0,55	2,04

WP2 – A2.2.3 - Development and Validation of speciation method based on gas chromatography for the measurement of separate hydrocarbons in hydrogen

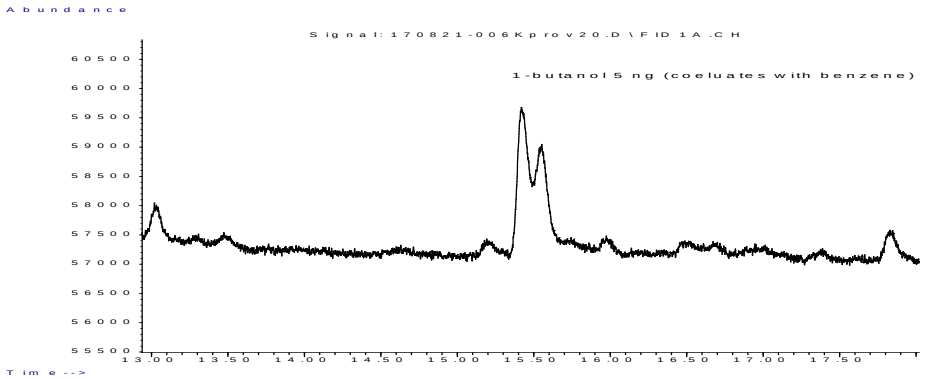




Toluene 1 ng



Hexane 1 ng



1-butanol 5 ng

Compounds	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

WP2 – A2.2.4 – List of instrument specifications for the development of multi-component analysers using input from A1.3.1

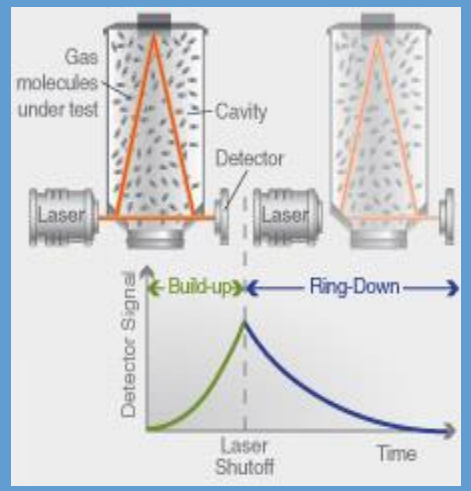
- Performing the 13 analyses (gaseous compounds) required in ISO 14687-2 to assess hydrogen quality require multiple analysis techniques mostly due to challenging detection limits to reach.

- Some instrument manufacturers now offer the possibility to use multi-component analyzers in order to reduce the number of analyses totally required – instruments need to be designed based on the **clients´specifications**

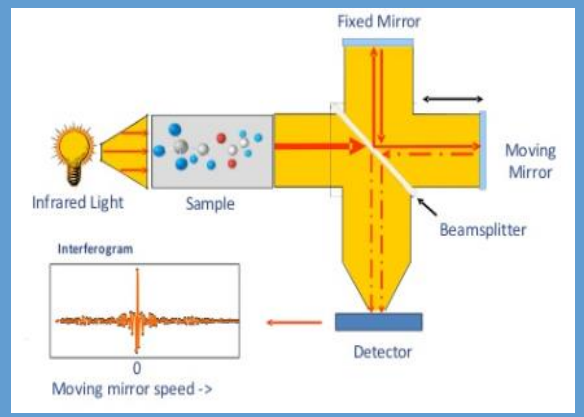
- Clients (for ex. labs) may base the specifications on different factors: taking into other instruments already available at the laboratory or focusing on impurities based on probability of presence or/and impact of impurities of fuel cell system.

- The clients will need to decide on requirements for characteristic performances, costs and possibly other specific requirements (response time, volume the gas needed, possibility to work with different gas matrices)

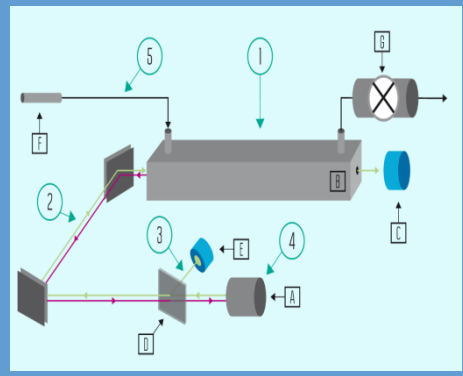
WP2 – A2.2.4 – List of instrument specifications for the development of multi-component analysers using input from A1.3.1



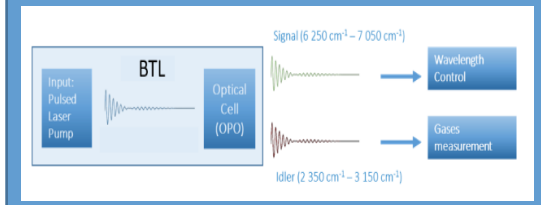
CRDS
Tiger Optics



FTIR
MKS



OFCEAS
AP2E



BTL
Blue Industry and Science

WP2 – A2.2.5 – Assessment of the performances of instruments enabling the simultaneous analysis of compounds mentioned in ISO 14687-2

In this report, the performances of 4 multi-components instruments were assessed by:

- Consulting providers to discuss specifications and performances:
  AP2E for Proceas, Tiger Optics for CRDS, MKS instruments for FTIR, Blue Industry and Science for X-FLR

- Reviewing the available literature about these instruments:
  FCTO (Fuel cell Technologies Office) report from 2016, published results from H2moves.eu project, an article “optical sensor for multi-species impurity monitoring in hydrogen fuel from 2012, EURAMET 1220 international comparability on hydrogen purity from 2017

- Shared experiences from users currently using these techniques:
  NPL for CRDS
  SINTEF for FTIR
  RISE for OFCEAS

WP2 – A2.2.5 – Assessment of the performances of instruments enabling the simultaneous analysis of compounds mentioned in ISO 14687-2

Table 2: Information provided by gas analyzers

	CRDS	FTIR	OFCEAS	X-FLR
Water	Instrument 1	Instrument 1	Instrument 1	
Oxygen	Instrument 4		Instrument 2	Need dev.
Carbon dioxide	Instrument 1	Instrument 1	Instrument 2	
Carbon monoxide	Instrument 1	Instrument 1	Instrument 1	Need dev.
Formaldehyde	Instrument 3	Instrument 1	Instrument 1	
Formic acid		Instrument 1	Instrument 1	
Ammonia	Instrument 2	Instrument 1	Instrument 1	Need dev.
Helium				
Total nitrogen and argon				
Total hydrocarbons		Methane, ethane…		
Methane	Instrument 1	Instrument 1	Instrument 1	yes
Total sulfur compounds				
Hydrogen sulfide			Instrument 1	Need dev.
Total halogenated compounds				
Hydrogen chloride	Instrument 5		Instrument 2	Yes
Hydrogen bromide				yes
Number of instruments required	4 (5 with HCl)		2 racks 19inch 4U and external ump	All in one instrument
Combined price	170 -185 k€	80 – 100 k€	~160 -180 k €	70-90 k€
Instruments connection	In parallel		Total sample consumption 20 l/h at atmospheric pressure Connection Swagelock ¼inch Analysers should be in series	Digital signal RS 232 Gas ports Swagelock 1/8
Contact	Tiger Optics, Florian Adler	MKS and a Swedish distributor (ROWACO)	AP2E Etienne Smith	Blue Industry and Science, Olivier Le Mauguen
Volume/flow and pressure of gas needed	12 l/h	30-60 l/h	20 l/h	< 100 ml total, Low pressure

In this report, we consider analytical techniques that have the capacity to distinguish between the various components present and generate **direct** evidence of their presence and concentration. For this reason, GC which is also a multi-components analytical method has not been selected here as it requires a first step of separation before the detection. However, it is clear that GC-methods are promising methods for analysing impurities in hydrogen

WP2 – A2.2.4 – List of instrument specifications for the development of multi-component analysers using input from A1.3.1

According to criteria listed in ISO21087 – hydrogen fuel – analytical methods

Parameters	Criteria
Detection limit / quantification limit	LOQ + uLOQ (k=2) < threshold value
Working range	The higher value of the working range shall be at least equal to 2 times the threshold value
Selectivity (normal)	Interferences versus ISO 14687 composition
Selectivity (extrem)	Interference versus critical situation observed in real situation
Precision	Precision of the method shall be determined at least at concentrations close to the threshold value Precision for this concentration shall be small enough to have a relative standard measurement uncertainty below 10 % of the concentration (except for sulfur compounds)
Trueness	The bias of the method shall be determined at concentrations close to the threshold value This bias shall be small enough to have a relative standard uncertainty below 10 % of the concentration (except for sulfur compounds)
Measurement uncertainties	The concentration, close to the threshold value, should be measured using the developed analytical method. The relative combined uncertainty for that concentration should be below 10 % relative (except for sulfur compounds)

WP2 – A2.2.5 – Assessment of the performances of instruments enabling the simultaneous analysis of compounds mentioned in ISO 14687-2

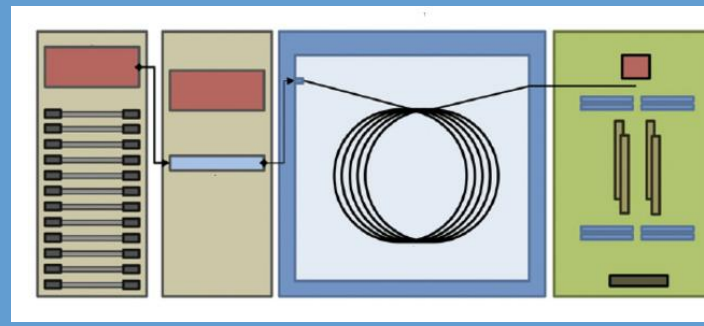
- Using multi-component analysers is a promising way to reduce the number of analyses needed to assess the quality of hydrogen according to ISO14687-2 mostly due to the flexibility with these instruments

- These instruments are often designed based on the client´s requirements; one of which is the selection of compounds to be analysed. In this way, every lab is free to select the compounds that cannot yet be analysed using other instruments available at the laboratory or focused on a priority list of impurities

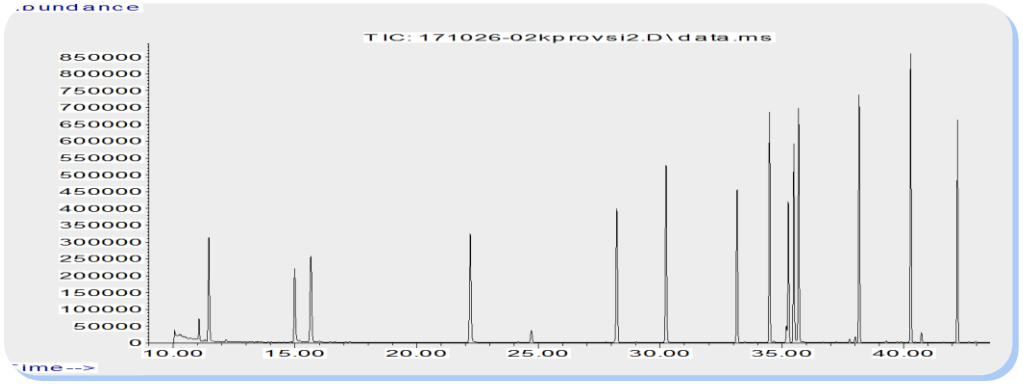
- However, the lack of a proper validation of these instruments has been pointed out in the report A2.1.3 of this project. It is therefore important that external laboratories for example at NMI performed a complete validation of the instruments

- Validation for some parameters on some of the instruments named in this report are planned to be performed in activities of the EMPIR MetroHyVe project.

WP2 – A2.2.7 – Analyze of data produced in WP1 sampling campaigns to assess the presence of potentially harmful compounds (if any) detected in real hydrogen samples



TD-GC-MS



Each sample from A1.1.2, A1.1.4, A1.1.6 has been analyzed with TD-GC-MS after transfer to a Tenax tubes:

- Delivery time sometimes > 3 weeks: risk for adsorption on the walls of the vessel
- Vessel´s material, some sulfinert-treated, some stainless steel: risk for adsorption on the walls of the vessels

Identified compounds: cyclohexane (30-50 nmol/mol), propylene glycol (from 30 up to 300 nmol/mol), cyclohexanone (around 1000 nmol/mol in on sample) and cyclohexanone cyclic trimethylene acetal (around 100 nmol/mol).
The propylene glycol can originate from liquid leak detector solution (introduced during the sampling procedure?). Propylene glycol was the only compound that was found in two distinct samples.

HCl < 8 nmol/mol in all samples

Additional studies may be required to replicate the results after having carefully selected cylinder´s material and determine the significance and the origin of the compounds found. The transport time should be minimized.

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.1: Literature review of impurity analysis methods (LNE, NPL, RISE, VSL) – Jun-16 to March-18

Task 2.2: Methods development (NPL, RISE, VSL,CEM) Aug-16 to Nov-18

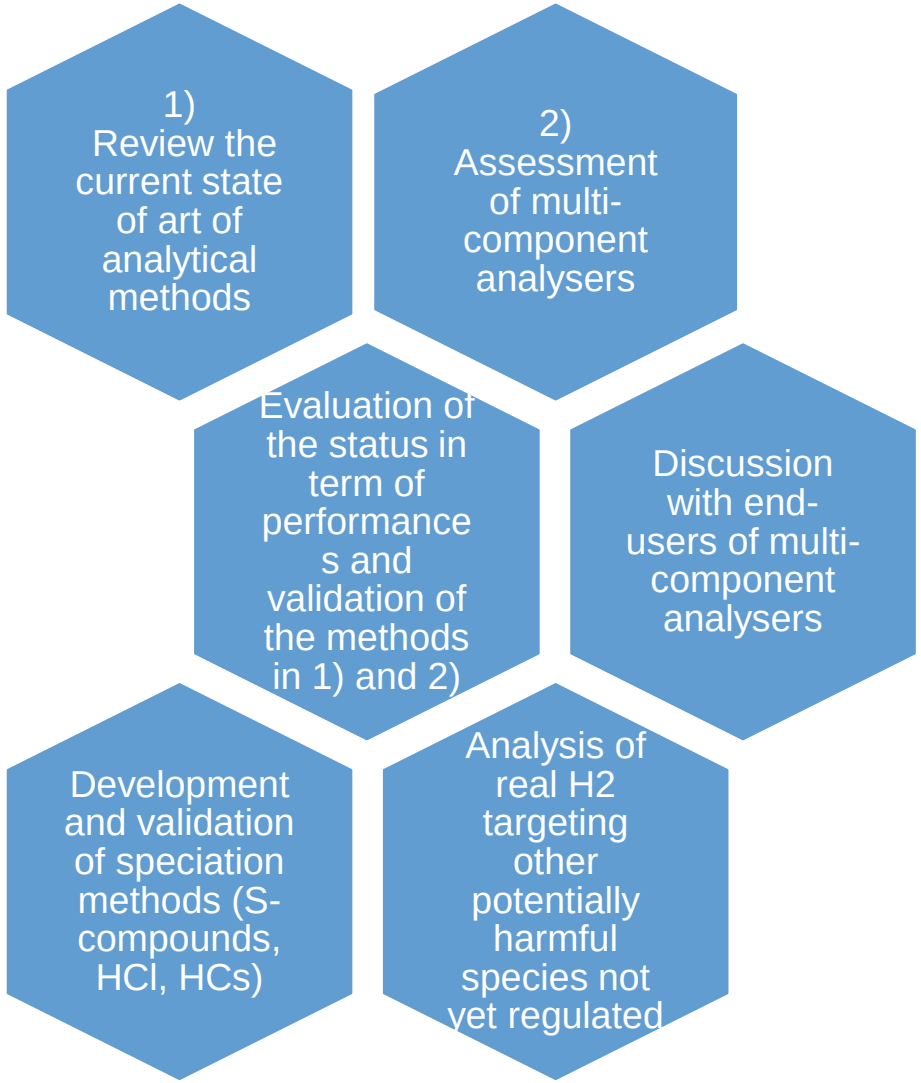
Task 2.3: Analytical procedures (NPL, RISE, VSL,CEM) Dec-18 to May-19

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Activity number	Activity description	Partners	Timeline
A2.3.1	Using input from A1.3.1 and A2.2.2 to A2.2.7, RISE with support from NPL, VSL and CEM will propose optimised analytical protocols enabling the implementation of ISO 14687-2.	**RISE**, CEM, NPL, VSL	Dec-18 – Apr-19
A2.3.2	Once the protocols has been reviewed and agreed by the consortium RISE on behalf of CEM, VSL and NPL will send the coordinator D4 “Recommendations on optimised analytical protocols including fit-for-purpose analytical methods that enable the implementation of ISO 14687-2”. The coordinator will then submit deliverable D4 to EURAMET and ISO/TC 197 and CEN/TC 268.	**RISE**, CEM, NPL, VSL	May-19

WP2 – Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Task 2.3



D4 “Recommendations on optimised analytical protocols including fit-for-purpose analytical Methods”

WP2 – Outcomes and conclusions

Outcomes:

- Literature review of the analytical methods currently available for the impurities to be analysed in ISO 14687
- Evaluation of the status of these methods in term of performance characteristics and validation data
- Assessment of multi-component analysers (FTIR, OFCEAS, CRDS, BLT) through discussion with providers, end-users and literature study
- Develop and validate 3 speciation methods (S-compounds, HCl and hydrocarbons)
- Analyse of real H2 sample using speciation method developed for hydrocarbons (= screening VOC method)
- No harmful compounds not yet regulated in ISO14687 have been identified in 20 H2 samples analysed with a VOC screening method (at ppb levels)

Conclusions:

- Need for complete validation of many proposed methods as required in ISO21087
- Need for certified reference materials to validate the methods (and possibly intercomparison studies)
- Need to optimise the number of methods needed to lower operational costs (using fit-for-purpose multi-component analysers or combining/coupling instruments)

WP2 - Dissimination

Reports (incl. deliverables D3 and D4) available on the project website:

15NRM03_WP2_A211_LNE_NPL_RISE_VSL
15NRM03_WP2_A213_RISE_VSL_NPL
15NRM03_WP2_A221_NPL
15NRM03_WP2_A222_VSL
15NRM03_WP2_A223_RISE
15NRM03_WP2_A224_RISE_NPL_VSL_LNE
15NRM03_WP2_A231_RISE_ LNE_NPL_VSL_CEM

International Workshop at R&D center, Air Liquide: Presentations "analytical methods review for hydrogen quality control according to ISO standards" and "Analytical method development for the most challenging impurities" – 7-8th November 2018 – France

Poster presentation at Gas Analysis 2019: "Performances of available analytical methods to control the purity of hydrogen according to ISO14687-2" – 18-20th June 2019 – Netherlands

Presentation at The International Congress of Metrology (CIM) 2019: "Validated analytical techniques for ensuring H2 quality in full compliance with ISO 14 687" – 24-26th September 2019 – France

15NRM03 HYDROGEN - METROLOGY FOR SUSTAINABLE HYDROGEN ENERGY APPLICATIONS

WP2 - ANALYTICAL METHODS

Thank you!

Research Institutes of Sweden
Bioscience and Materials

Chemistry, Materials and Surfaces