ISO TC197 WG27/WG28

Metrology research for hydrogen standardisation: a cross-cutting approach

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

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

Discussing the presence of other potentially harmful impurities not yet specified

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

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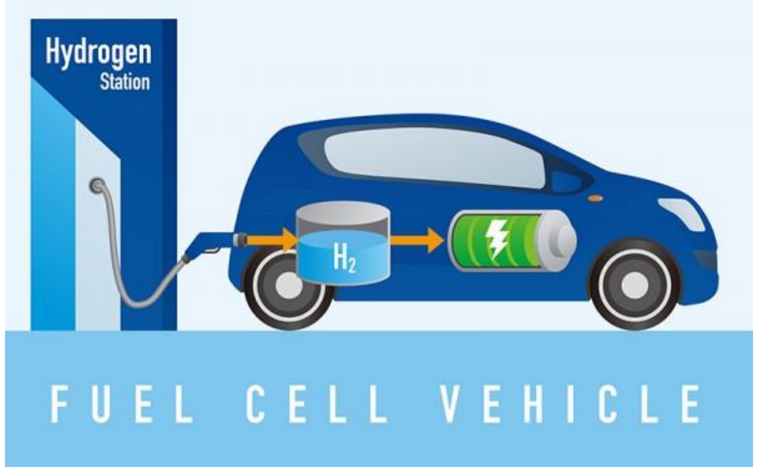
Groundwork for potential revision of the standard



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

- Literature review of impurity analysis methods
- Methods development
- Analytical procedures and multi-components analyser
- Investigation beyond ISO 14687-2

Literature review for hydrogen quality

Analytical technique	Impurity												
	H_2O	C_nH_m	O_2	He	N_2 / Ar	CO_2	CO	R-S	HCHO	HCOOH	NH_3	THC	
	Water	Total hydrocarbons	Oxygen	Helium	Nitrogen and Argon	Carbon dioxide	Carbon monoxide	Total sulphur	Formaldehyde	Formic acid	Ammonia	Total halogenated compounds	
Dew point analyzer													
Vibrating quartz crystal analyzer													
CRDS		CH_4											7 (9)
GC-MS									X			X	
GC-MS with jet pulse injection													
FTIR													6 (7)
OFCEAS	A		A			A	A	H_2S A	A	A	A		7 (10)
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 cpds	

Can be updated during the project

Sources

- ASTM standards
- JIS standards
- NMI methods: NPL, (RISE)
- Some contacts with instruments providers

Comparison of methods based on performance characteristics

Water Limit ISO 14687	5 µmol/mol

Methods	Working range	Detection limit (µmol/mol)	Selectivity	Repeatability	Linearity	Robustness	Accuracy
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		0.8					
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
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
FTIR		0.12-0.3	high				

Comparison of methods based on performance characteristics

Water Limit ISO 14687	5 µmol/mol

Methods	Precision	Measurement uncertainties	Volume needed	Pressure required	Sampling Vessels	Other impurities analysable with this method	Response time	Standards	Cost estimations
Dew point hygrometer			0.5 L/min for 30 min minimum (stabilisation may take longer)	adaptable close to atm	Compatible		Direct reading but long stabilisation time	JIS K0225	
Vibrating quartz crystal analyzer			0.33 L/min for 20 min	adaptable close to atm	Compatible		direct reading but long stabilisation time	JIS K0225	
CRDS							2-3 minutes	D7941/D7941M-14	
CRDS			100 ml/min @ 15 min = 1.5 liter			4 impurities (ex: CO, CO2, H2O, CH4 or NH3)	10-15 minutes	D7941/D7941M-14	4-species: 50 to 65 K€, single species: 40 K€
GC-MS									
GC-MS with jet pulse injection						CO2, Ar, N2, O2		ASTM D7649-10	
OFCEAS	1% relative or 2 LOD (which is worst).	0.005 µmol/mol	in standard flow13l/h ; volume needed <1l special solution for fuel cell exhaust test flow < 2l/h	adaptable 2 bara is great	compatible	configuration dependend (several laser on the same system can be set)	< 1 minute	Information from AP2E	35K€ but combination of gas possible in 1 analyzer
OFCEAS	1% relative or 2 LOD (which is worst).	expected < 0.05	in standard flow13l/h ; volume needed <1l special solution for fuel cell exhaust test flow < 2l/h	adaptable 2 bara is great	compatible	HCHO, HCOOH, NH3 ppb level range to be confirmed on the same laser	< 1 minute	Information from AP2E	50K€ but combination of gas possible in 1 analyzer
FTIR						NH3, CO, CO2, formaldehyde, formic acid, methane		ASTM D7653-10	80 K€ for MKS multigas 2031 LN2

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 I ndependent laboratories.

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

Plan for the further development of analytical methods

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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.

Plan for the further development of analytical methods

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Methods	Compounds	LOD	Selectivity	Working range	Precision	Trueness	Ruggedness	Standardised methods	Methods information in public domain	In-house methods
GC-MS	H_2O							ASTM D7649-10		
	O_2							ASTM D7649-10		
	He							JIS K 0123		
	N_2							ASTM D7649-10		
	CO_2							ASTM D7649-10		
	Ar							ASTM D7649-10		
	NH_3									
	CH_2O							ASTM D7892-15		
	Hydrocarbons							ASTM D7892-15		
	Organic sulfur									
	Organic halides							ASTM D7892-15		To be validated (16ENG01)
Dew point hygrometer	H_2O							JIS K0225		NPL in house methods
Vibrating quartz crystal analyzer	H_2O							JIS K0225		NPL in house methods
Electrochemical sensor	O_2							ASTM D7607-11		
GC-PDHID	O_2								Rapport NPL [3]	NPL in house methods
	N_2									NPL in house methods
	Ar									NPL in house methods
	CO_2									
Galvanic cell O_2 meter	O_2							JIS K0225		
Methanizer GC-FID	CO									VSL and NPL in house

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

- Literature review of impurity analysis methods
- Methods development
- Analytical procedures and multi-components analyser
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Validated analytical methods to fulfill ISO 14687-2 impurity specifications

- <u>Development of analytical and speciation methods for challenging impurities</u>
  - ✓ Total species determination is a real analytical challenge for metrology consideration
    → keeping high level of sensitivity, measuring ranges and measurement uncertainty
  - ✓ Can cover a large number of species for halogenated, hydrocarbons and sulphur compounds
  - ✓ The identification of all species is almost impossible in routine analysis
- <u>Performance assessment of multi-component analysers</u>
  - ✓ Not turnkey solutions commercially available
  - ✓ Need to be designed based on the clients' specifications
  - ✓ Specifications and performances in terms of sensitivity, selectivity, reproducibility need to be assessed

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

Groundwork for potential revision of the standard

Hydrogen RISE

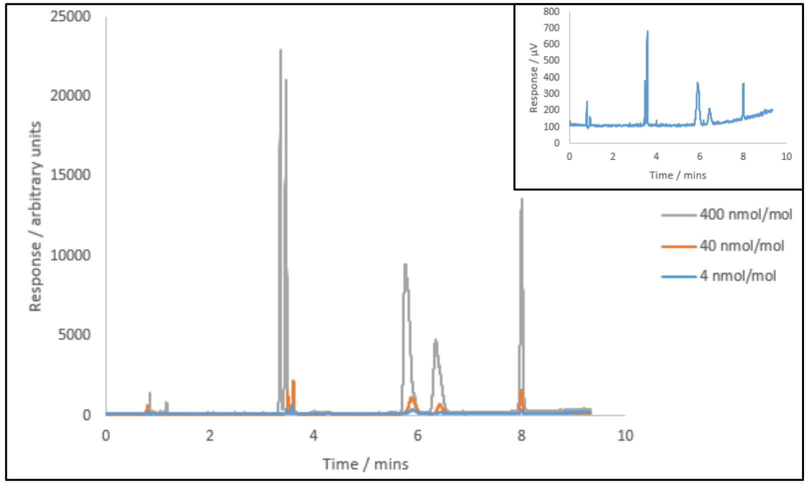
Analytical methods for performing hydrogen purity testing to enable the full implementation of the revised ISO 14687-2 standard

Development of analytical and speciation methods for total sulphur compounds

NPL developed and validated a speciation method based on cryo-focussed GC coupled with SCD **for the measurement of sulphur species**

Compounds (for hydrogen minimum 99.97% mol)	ISO 14687-2 threshold [µmol/mol]
Total sulphur compounds	0.004

Exceeding this limit could cause degradation of Pt in FC system



- Cryo-focussing system concentrates sample prior to separation – **increased sensitivity**
- Distinguish different sulphur-containing compounds below 4 nmol/mol
- Individual compounds can be identified and quantified. Effects on fuel cell assessed

Qualification of the instrument for selectivity, limit of detection, linearity, precision and robustness has validated the method

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

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

Development of analytical and speciation methods for total halogenated compounds

VSL developed and validated a speciation method based on Cavity Ring Down Spectrometry operating in the mid-infrared **for the measurement of halogenated species**

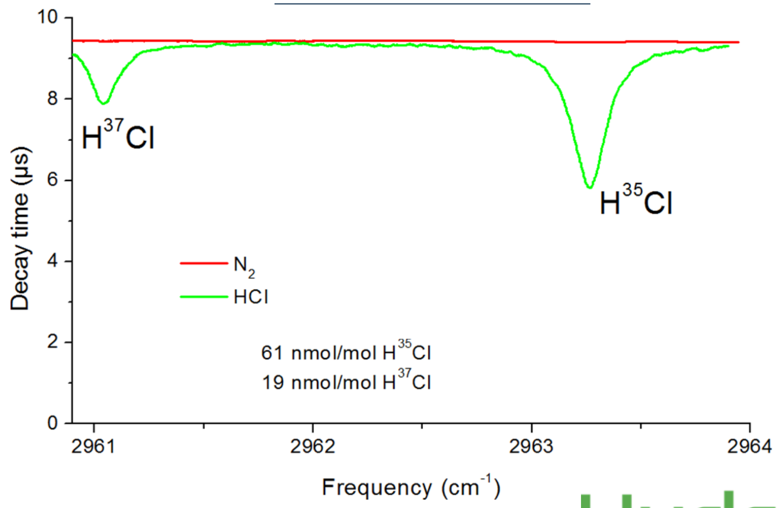
Compounds (for hydrogen minimum 99.97% mol)	ISO 14687-2 threshold [µmol/mol]
Total halogenated compounds	0.05

→ Exceeding this limit could cause irreversible damage of PEMFC

- Operating range λ =2.3 - 5.1 µm
- Sampling system: coated materials to reduce surface interaction
- Instrument can also detect formaldehyde, formic acid & ammonia

- Measurement of the main isotopes
- LoD down to sub nmol/mol using strongest HCl absorption line

HCl measurement



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

Development of analytical and speciation methods for total hydrocarbons

RISE developed and validated a speciation method based on the combination of two analytical techniques: GC/FID and TD-GC/FID-MS **for the measurement of separate hydrocarbons in hydrogen**

Compounds (for hydrogen minimum 99.97% mol)	ISO 14687-2 threshold [µmol/mol]
Methane CH_4	2
Non CH_4 hydrocarbons	2

→ Exceeding this limit for alkenes and aromatics could degrade the FC system

Method	Hydrocarbons		Limit of Detection
GC/FID	CH_4 and other hydrocarbons including oxygenated organic species as alcohols, ketones… with relatively low boiling point (BP < 70°C)	HC with BP comprised between 40-50°C and 100°C can be analysed by both methods	0.55 µmol mol^{-1} for total hydrocarbons to be measured with GC/FID method
TD-GC-FID/MS	Other compounds with BP > 70°C		≤ 0.69 µmolC mol^{-1} for hydrocarbons to be measured

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Analytical procedures and multi-components analyser

Performance assessment of multi-component analysers

- Not turnkey solutions commercially available
- Need to be designed based on the clients' specifications
- Specifications and performances need to be assessed as sensitivity, selectivity, reproducibility

Methods are being compared in terms of:

- ✓ Nature and number of analysed compounds
- ✓ Limit of Detection
- ✓ Uncertainty measurement
- ✓ Number of instruments required
- ✓ Connection
- ✓ Volume/flow and pressure of gas needed
- ✓ Costs

Method under study

OFCEAS

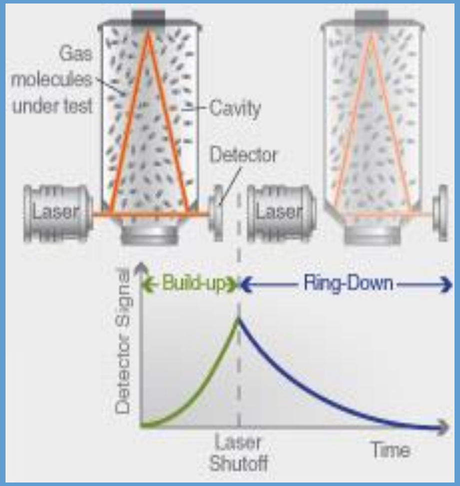
FTIR

BTL

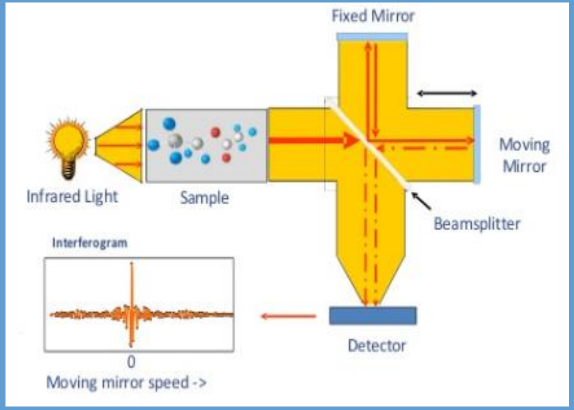
CRDS

Hydrogen RISE

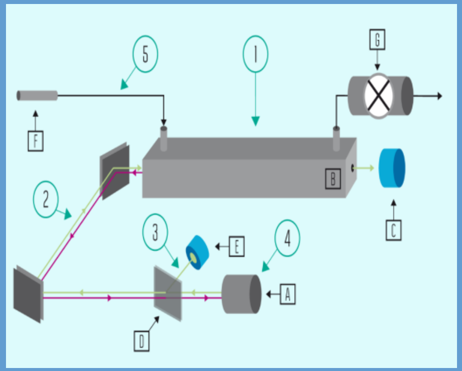
List of instrument specifications for the development of multi-component analysers



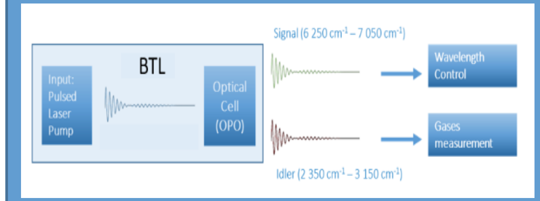
CRDS
Tiger Optics



FTIR
MKS



OFCEAS
AP2E



BTL
Blue Industry and Science

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

In table 5, the criteria and requirements discussed in the section above are summarized.

	Criteria	Requirements / Action / evidences
Simultaneous analysis of several compounds	List of compounds analysed	compare to priority lists
Specifications related to method performances		
Detection limit/quantification limit	LOQ + uLOQ (k=2) < ISO 14687	Verify detection limit with analysis of PRM
Working range	Preferably 10 * ISO 14687 (at least 2* ISO 14687)	Provide linearity plot
Selectivity (normal)	Interferences versus ISO 14687 composition	Literature or experiments If possible use PRM cocktail at ISO 14687 level
Selectivity (extrem)	Interference versus critical situation observed in real situation	Literature / Technical evidences
Precision	< 10 % rel at ISO level	use of PRM at ISO threshold
Trueness	< 10 % rel at ISO level	use of PRM at ISO threshold
Measurement uncertainties	< 20 % rel at ISO level < 50% CH2O and Sulphur	Provide calculation and equation including at least uC = $\sqrt{u(Rw)2+u(bias)2}$

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

In table 5, the criteria and requirements discussed in the section above are summarized.

	Criteria	Requirements / Action / evidences
Costs		
Capital costs	Equipment price	Check equipment price versus number of analysis and length life < 1 € / kg H2 produced
Operational costs	Number of calibration / year	Estimate operational cost and maintenance / year < 1 € / kg H2 produced (customer requirements)
Personal, training and third party maintenance support costs	Personal time requirement / year / maintenance	Cost estimation and target < < 1 € / kg H2 produced (customer requirements)
Other requirements		
Response time	Stabilisation time at ISO threshold	< 30 min for stabilisation
Calibration using other matrices than hydrogen	Which standards can be used	evidence of equivalence between PRM in hydrogen and other matrices
Volume of gas needed HRS Buffer low pressure	flow and time: 5 L/min and 30 min stabilisation 0.5L/min and 60 min stabilisation < 0.5L/min and 30 min stabilisation	Evidence of flow and stabilisation
Use at pressure	Effect of pressure on the system if offered	Demonstrate measurement with PRM at high pressure and no bias

*PRM: Primary reference materials

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

Hydrogen RISE

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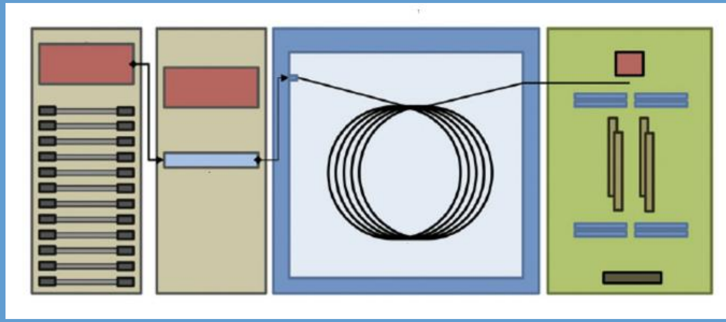
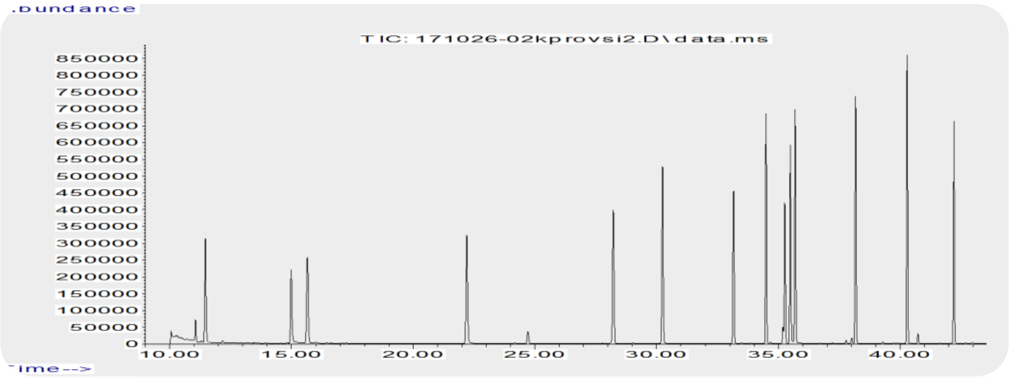
Analyze of data produced in WP1 sampling campaigns to assess the presence of potentially harmful compounds (if any) detected in real hydrogen samples



TD-GC-MS



sampling campaign at hydrogen production point (> 15 samples)
→ 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
- Difficulty to obtain a real blank: some compounds found in the first samples now appear to be "background compounds" (nonanal, siloxanes)

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