

Metrology for sustainable hydrogen energy applications

JRP EMPIR 15NRM03 HYDROGEN

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

Task 2.2: Methods development

Deliverable D3

Assessment report of a multi-component analyser with optimised sampling analysis that meets the required detection limits as per business plans ISO/TC 197 and CEN/TC 268

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Summary

For routine laboratory/analysis, performing the whole set of analysis required by ISO14687-2 is currently extremely challenging. Traceability of the measurements, trueness and detection limits are some of the critical points. As a large number of components need to be quantified, it is not possible to analyse all the components using a single method; on the contrary, many methods are required. Moreover, a number of these compounds are unstable and/or reactive which implies that extreme care has to be taken during analysis to ensure that these compounds do not adsorb to sampling lines and other analytical equipment.

The latest developed multi-component instruments have the potential to meet the required detection limits according to ISO14687-2. These instruments need to be designed based on the client's specifications (number of compounds to be analysed simultaneously, the analytical measuring range...). In this report, the performances of 3 multi-components instruments were assessed by:

- Consulting providers to discuss specifications and performances
- Reviewing the available literature about these instruments
- Shared experiences from users currently using these techniques

Table of contents

Summary	2
Table of contents	3
1 Introduction	4
2 Short description of the analytical methods	5
2.1 Fourier Transform Infrared Spectroscopy (FTIR)	5
2.2 Cavity Ring Down Spectroscopy (CRDS)	6
2.3 Optical feedback cavity enhanced absorption spectroscopy OFCEAS	7
2.4 Gas analyzer based on broadly tunable laser BTL	8
3 Performances assessment of multi-components analysers	9
3.1 Information from providers	9
3.2 Literature survey	10
3.3 Discussion with users	11
3.3.1 OFCEAS	11
3.3.2 FTIR	12
3.3.3 CRDS	13
4 References	14

1 Introduction

Work package 2 (WP2) of the *HYDROGEN* project aims at proposing optimised analytical protocols (including fit-for-purpose analytical methods) for performing hydrogen purity testing and at assessing multi-component analysers that enable the implementation of the ISO 14687-2:2012 standard [1].

The characteristics for the fuel specification that are listed in Table 1 in the standard, include today three “total species”: Total hydrocarbons (Methane basis), Total sulfur compound (H₂S basis) and total halogenated compounds (Halogenate ion basis) as well as 10 individual compounds - water, oxygen, helium, nitrogen, argon, carbon dioxide, carbon monoxide, formaldehyde, formic acid, ammonia, methane. Finally, particles content also needs to be assessed.

In the first activity of this WP, a literature review of the current state of art of analytical methods for all the compounds to be analysed was performed. The last table of this report is presented below (Table 1):

Table 1: Agreement between the impurity to be analysed and the techniques following the ISO requirements (green: ≤ the spec., orange: partially feasible, red: > spec., “X” specifies the need for a pre-concentration, A: from application notes of a multi-gas analyser).

		Impurity											
		H ₂ O	C _n H _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
Analytical technique	Dew point analyzer	Green											
	Vibrating quartz crystal analyzer	Green											
	CRDS	Green	CH ₄ (Orange)	Green			Green	Green			Green		THC (Orange)
	GC-MS	Green	Green		He (Orange)					X (Green)		NH ₃ (Red)	X (Green)
	GC-MS with jet pulse injection	Green		Green		N ₂ / Ar (Orange)	CO ₂ (Orange)						
	FTIR	Green	Green				Green	Green		A (Green)	Green		THC (Orange)
	OFCEAS	A (Green)		A (Green)			A (Green)	A (Green)	H ₂ S (Orange), A (Green)	A (Green)	A (Green)	A (Green)	
	FID		Green										
	GC-FID		Green										
	Methane GC-FID		Green				Green			Green			
	ECD			Green									
	GC-TCD			Green	He (Orange)		CO ₂ (Orange)	Green					
	GC-PDHID			Green		Green	Green	Green		THC (Orange)			
	GC-SCD with concentrator							Green					
	GC-SCD without pre-concentration							Green					
	DNPH-HPLC-UV									Green			
IC with concentrator										Green			
IC-CD								THC (Orange)				THC (Orange)	

The sample is bombarded with infrared radiation produced by the source. When the frequency of the IR radiation matches the natural frequency of the bond, the amplitude of the vibration increases, and the infrared is absorbed.

The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. One beam is transmitted by the splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and the moving mirrors reflect the radiation back to the beam splitter. Half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source.

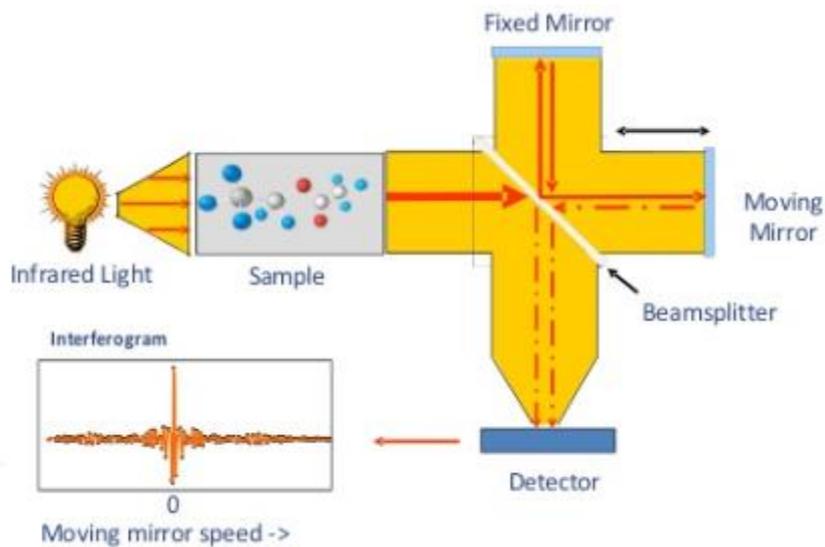


Figure 1: FTIR principle

2.2 Cavity Ring Down Spectroscopy (CRDS)

Cavity Ring Down Spectroscopy (CRDS) is based on the measurement of the decay rate of the light intensity leaking out of a high finesse cavity rather than the change of intensity due to the absorption (Figure 2).

In CRDS, the beam from a single-frequency laser diode enters a cavity defined by 2 or 3 high reflectivity mirrors. When the laser is on, the cavity quickly fills with circulating laser light. A fast photodetector senses the small amount of light leaking through one of the mirrors to produce a signal that is directly proportional to the intensity in the cavity.

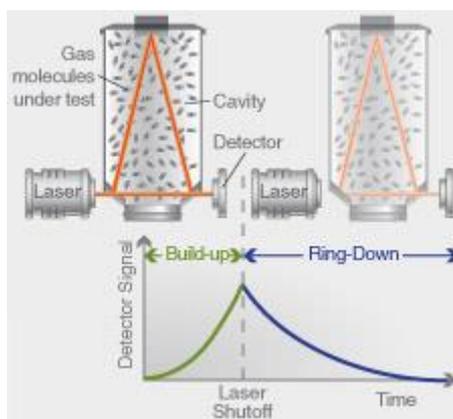


Figure 2: CRDS principle

When the photodetector signal reaches a threshold level, the continuous wave (CW) laser is abruptly turned off. The light already within the cavity continues to bounce between the mirrors, but because the mirrors have slightly less than 100% reflectivity (but typically >99.995% in the near-infrared), the light intensity inside the cavity steadily leaks out and decays to zero in an exponential fashion. This decay, or "ring down", is measured in real-time by the photodetector, and the amount of time it takes for the ring down to happen is determined solely by the reflectivity of the mirrors (for an empty cavity).

If a gas species that absorbs the laser light is introduced into the cavity, a second loss mechanism within the cavity (absorption) is now introduced. This accelerates the ring down time compared to a cavity without any additional absorption due to a targeted gas species. The final concentration data is derived from the difference between these ring down times and is therefore independent of laser intensity fluctuations or absolute laser power.

This produces precise, quantitative measurements that account for any intra-cavity loss that may be changing over time, and it allows the discrimination of loss due to absorption from losses due to the cavity mirrors.

2.3 Optical feedback cavity enhanced absorption spectroscopy OFCEAS

The intensity transmitted by the cavity is measured continuously.

OFCEAS (Figure 3) relies on direct intensity measurement rather than the estimate of a ring-down time. A varying current is applied to the temperature controlled laser source, enabling the tuning of the laser to the frequencies of resonance modes of the cavity. Cavity-enhanced absorption spectroscopy (CEAS) relies on a continuous coupling of laser light to the cavity, which requires the laser frequency to be actively locked to one of the cavity modes. In OFCEAS, this is accomplished by optical feedback to the laser. The laser coupling is arranged so as to permit a restrained return of the resonant intracavity field back to the laser while avoiding a reappearance of light directly reflected from the cavity input mirror. The feedback phenomenon increases the purity of the laser source.

The optical cavity serves to trap the light so that it passes through the sample gas multiple times as it is reflected by the cavity mirrors. The resulting effective path length is very long.

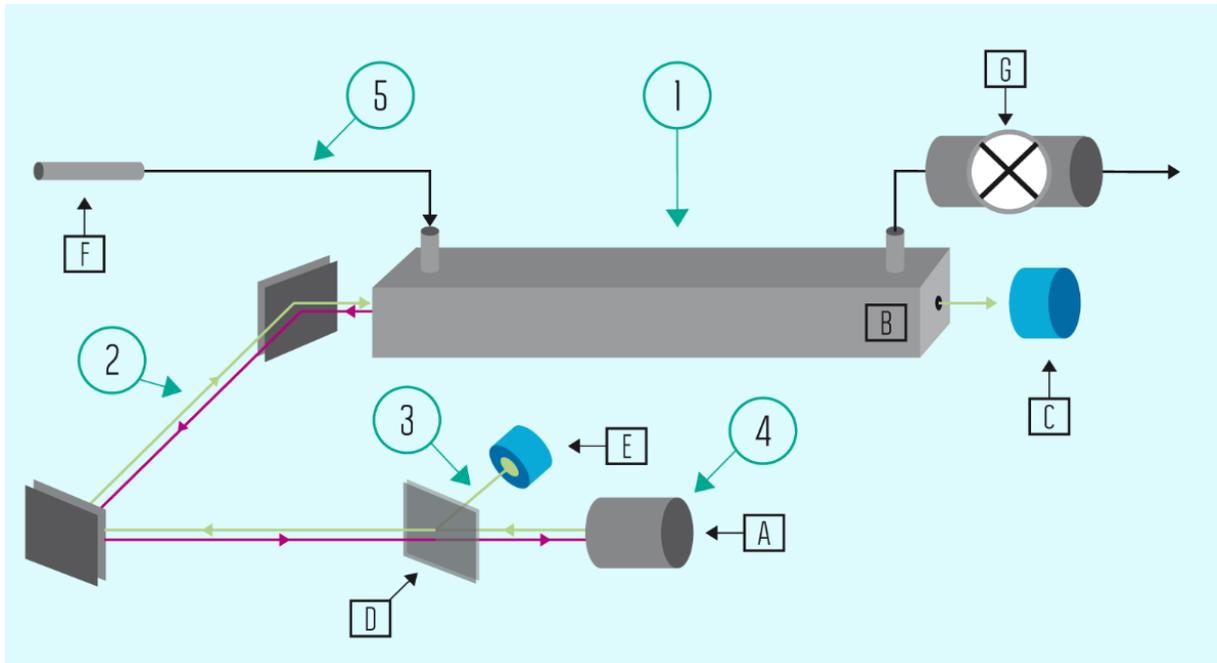


Figure 3: Schematic of a OFCEAS instrument (A: scanning laser, B: gas cell, C, E: detector, D: beam splitter and associated optics, F: Sampling probe, G: pump)

2.4 Gas analyzer based on broadly tunable laser BTL

The broadly tunable laser (Figure 4) is actually not a laser but an optical parametric oscillator (OPO). In the OPO cavity, light from a pump laser is converted in a non-linear crystal into two beams with a longer wavelength known as signal and idler. The wavelengths of the output beams are tuned by controlling certain parameters of the system (crystal temperature and crystal poling period). The gas sample is pumped into the measurement cell, which is temperature-controlled at 50°C. The laser emits a beam into the measurement cell (typically the idler is used for this as it has a wavelength in the mid-infrared range while the signal is in the near-infrared range where gases absorb much weaker). The gas molecules in the sample absorb part of the energy of the beam in a way directly related to their nature and quantity.

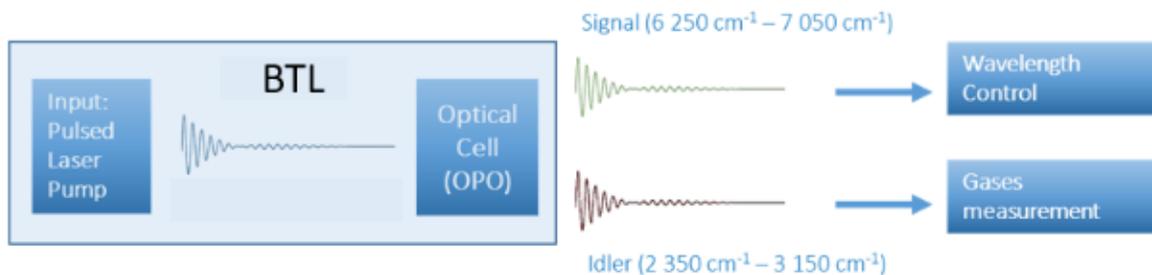


Figure 4: BTL principle

3 Performances assessment of multi-components analysers

3.1 Information from providers

Providers of instruments have been contacted: for FTIR MKS (USA), for OFCEAS AP2E (FR), for CRDS Tiger Optics (USA), for BTL Blue Industry and Science (FR). Discussions to assess which impurities that can be measured by their systems (simultaneous analysis) have led to the table 2 which also includes an estimation of the price. The color green indicates that according to the instrument's providers, the compound can be quantified at limits of quantification equal or better than the maximum limits required in ISO14687-2. Most of the time, the required working range is adaptable and specified by the client. To require a large working range may impact on the limit of quantification.

Some statements for the repeatability are available, as for CRDS where it has been calculated for levels close to the limits of detection (ex. for water: 0.0001 $\mu\text{mol/mol}$ at 0.00044 $\mu\text{mol/mol}$) or for OFCEAS (provided repeatability <1%). However, these statements cannot easily be compared to the repeatability calculated with other methods. Repeatability shall be assessed by users.

These are information provided by instrument's provider which would need to be assessed by independent users.

Table 2: Information provided by gas analyzers

	CRDS	FTIR	OFCEAS	BTL
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	Instrument 1	Instrument 1	Instrument 1	
Ethane		Instrument 1		
Total sulfur compounds				
Hydrogen sulfide			Instrument 1	Need dev.
Total halogenated compounds				
Hydrogen chloride	Instrument 5		Instrument 2	
Hydrogen bromide				
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 1/4inch	Digital signal RS 232 Gas ports Swagelock 1/8

			Analysers should be in series	
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

Green: detection limit required in ISO14687-2 achievable

Red: not possible with the analytical technique

Orange: only some compounds of a family can be analysed at required detection limit

For more information:

<https://www.ap2e.com/en/application-notes/h2-purity-control/>

<https://www.mksinst.com/Docs/r/OnLineHydrogenPurityAnalysis-AppNote.pdf>

<http://www.tigeroptics.com/markets-applications/applications/hydrogen-fuel-cells.html>

<http://www.blueindustryandscience.com/broadly-tunable-gas-analyzers/blue-gas-analyzers-for-oem/>

3.2 Literature survey

Sources of information published regarding the performances of multi-components analysers are peer-reviewed articles and reports (i.e. technical, research).

Analytical methods for hydrogen fuel quality are constantly being developed and validated through different initiatives and projects mainly in Europe, Japan and USA. Each survey related to this subject would then need periodical updates.

Progresses [3] in developing an international consensus on hydrogen fuel quality specifications have been reported in a FCTO (Fuel cell Technologies Office) report [4] from 2016. In this report, the methods discussed are the methods/procedures developed by ASTM. Under ASTM procedures, 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. At the time the report was prepared, only one of the standards has undergone an ILS and it is still in revision almost two years after initiation. This standard is ASTM D7653-10 [5] where ammonia, carbon dioxide, carbon monoxide, formaldehyde, formic acid and water are analyzed by FTIR. The report from this ILS will give a good basis to evaluate the performances of FTIR for simultaneous analysis of 6 impurities listed in ISO14687-2. The standard ASTM D7941/D7941M-14 [6] using CRDS is not mentioned in the FCTO report from 2016.

Tripathi et al. [7] developed an optical sensor for multi-species impurity monitoring in hydrogen fuel. They tested a laser-induced breakdown spectroscopy (LIBS) based optical sensor to detect nitrogen, argon, oxygen and helium in hydrogen. The limits of detection were estimated to be 80 ppm for nitrogen, 97 ppm for argon, 10 ppm for oxygen (above threshold limit proposed in ISO14687-2) and 25 ppm for helium. According to the authors, the sensor is field deployable and can be modified to monitor other impurities.

A study on the applicability of FTIR for hydrogen quality assessment has been done by SINTEF during the project H2moves.eu Scandinavia. Results are presented in the report for deliverable D7.4 [8]. The study was performed in real samples so limited to the species found in these samples. Results obtained by CO, CO₂ and hydrocarbons have been verified using other analytical methods and results

are in good agreement even if the concentration of CO was found slightly different (11 to 21 ppb with FTIR and 1 to 5 ppb with GC-PDHID – gas chromatography – pulsed discharge helium ionization detector).

Recently, an inter-comparison on hydrogen purity analysis has been performed by National Metrology Institutes (NMIs) [9]. H₂S and CO were analysed using different analytical techniques including CRDS (CO) and OFCEAS (H₂S). For both techniques and both compounds, the reported values were in agreement with the consensus values within uncertainty statements.

3.3 Discussion with users

3.3.1 OFCEAS

RISE (Sweden) has recently (2017) acquired two OFCEAS (AP2E, FR) coupled together in series to measure O₂, CO, CO₂, H₂S and H₂O. The instruments are pre-calibrated and work with different matrices: hydrogen, helium and nitrogen.

The instrument was first tested using gas standards with known amounts of targeted compounds. The concentration in the gas standards were well above the detection limits. The first tests show that the instrument has no bias and good repeatability as it can be seen in the figure 5.

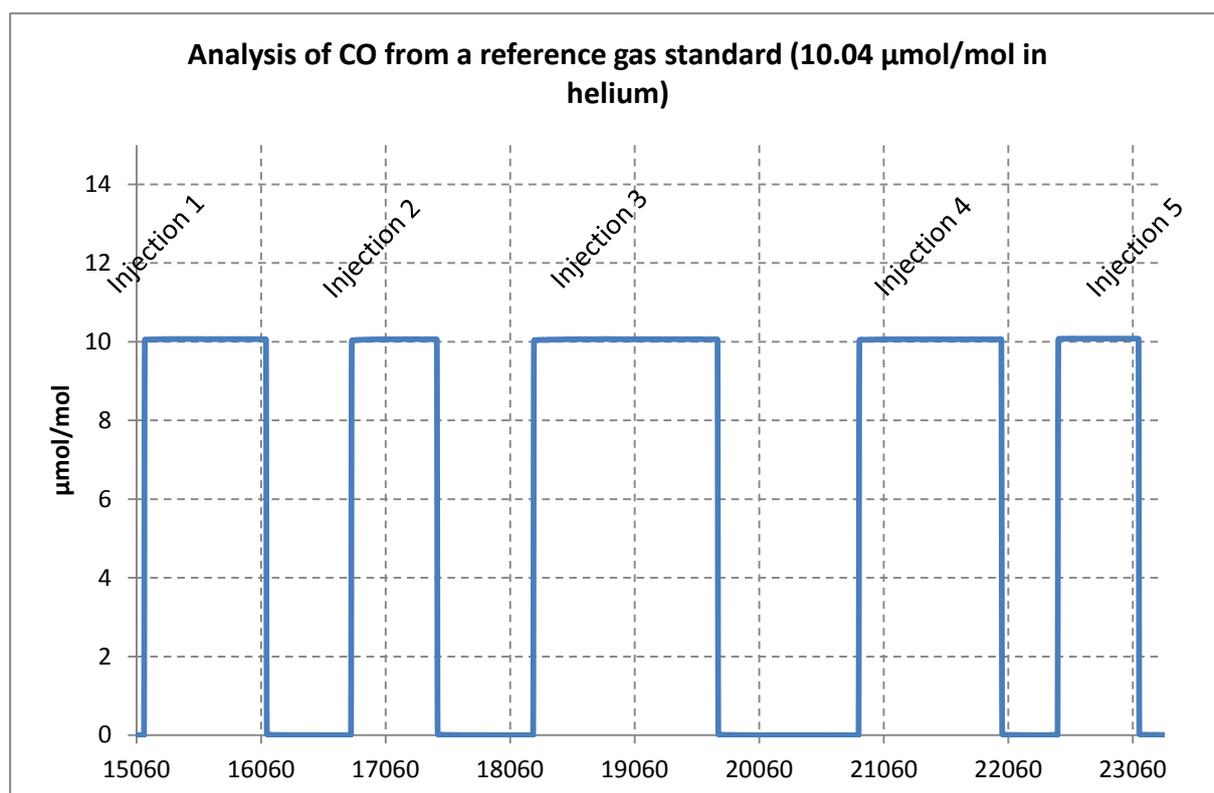


Figure 5: CO analysed with OFCEAS, 5 consecutive injections

The instrument has so far been used on 4 hydrogen samples provided during the activity A1.1.4, (electrolysis process analytical campaign). In 2 samples, the level of impurities was under the detection limits of the instrument. But for 2 samples, H₂O, CO₂, O₂ were at levels well above the detection limits. Results obtained were compared with results obtained at other NMIs using other analytical methods (ex for water: quartz crystal microbalance and CO₂, methanizer GC-FID). Results

were in agreement for H₂O and O₂. However, some inconsistency was observed for the measurement of CO₂. In one occasion, the OFCEAS instrument measured around 34 µmol/mol while the results reported by other institutes were around 4-5 µmol/mol. No explanation for the discrepancy has been found yet.

It is however too soon to report more extensively the experiences collected when using these instruments. More tests need be performed in order to evaluate if the instrument is user-friendly and to assess the performances of the instrument incl. measurement uncertainties, time of analysis... In the project MetroHyVe (16ENG01), this method will be validated for H₂O, CO₂, CO, H₂S and O₂.

3.3.2 FTIR

SINTEF (Norway) has through the H2Moves Scandinavia project [8] documented the application of Long Path FTIR spectroscopy to hydrogen fuel quality control (Deliverable 7.4). By application of a 35 meter thermostat able cell, a quantification limit for CO at 5 ppbv was demonstrated. Elevated temperatures were used in order to prevent condensation and/or adsorption of gases to cell walls and mirrors. This has been shown to be necessary especially when analyzing sticky gases like SO₂. A FTIR spectrometer with the 35 m cell mounted is illustrated in Figure 6.



Figure 6: 35 m cell mounted on Bruker Vertex 70 (left) and Bruker IFS 66v/S operated under vacuum (right). Pictures taken with permission from [10].

For strongly absorbing greenhouse gases like perfluorocarbons, SINTEF has documented quantification limits down to 100 pptv. FTIR has signatures for HCl and HBr. SINTEF investigated the presence of HCl in production samples from a chlor-alkali plant upstream the gas drying step that is expected to remove halogens with the water. With Cl₂ being transparent to the instrument, HCl was not detected in the gas. The presence of water in the spectra limited the detection limit to about 40 ppbv. For total halogenate assessment, this was not satisfactory for the 50 ppbv tolerance.

FTIR is a very versatile multicomponent analyser in dilute solutions. Since H₂ fuel quality tolerance is 99.97 % and most of the 0.03 % impurities are transparent for the analyzer, interference problems are limited. The main absorbers in the mid-infrared range are H₂O, CO₂ and SO₂. At low levels, the interference problem is also limited.

The main limitation for FTIR spectroscopy is the lack of signature for homonuclear species like O₂, N₂, H₂, Ar and He in the mid-IR spectral range. Due to the low molar absorptivity of H₂S, the application of FTIR to the total sulfur inventory would require a light path in the range of several kilometers.

Due to the high volume of the sample cell in the case of long path instruments (11 L in the case illustrated in Figure 6), a large sample volume is required. Calibration can be done using calibration gases and dynamic dilution. For FTIR it is also possible to simulate spectra for a broad range of analytes and in this way obtain quantification with fairly good analytical performance. The supplier of the FTIR instruments usually provides a library of common analytes over the most typical concentration ranges.

For FTIR it is common to apply multivariate analysis in order to handle spectral interference. With PLS modelling, spectral interference can be minimized but also the modelling errors can be used to evaluate the analytical performance.

3.3.3 CRDS

NPL (UK) has used CRDS LaserTrace 3, H₂O module (Tiger Optic, US) for the determination of water in hydrogen. The method developed by NPL was accurate with an expanded uncertainty below 13% (k=2). The instruments performance was checked on daily basis against gravimetric standard of water in hydrogen and was always within the quality assurance threshold. The range tested was from hundreds of nmol/mol to 20 μmol/mol with good linearity in hydrogen matrix. The NPL analytical method using CRDS has been tested on more than 20 different samples and provided reliable results. The large hydrogen flow required (1L/min) and the stabilization time (<1 hour especially for low amount fraction) are the two drawbacks of the CRDS method.

4 Conclusions

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. However, the lack of a proper validation of these instruments has been pointed out in the report A2.1.3 of this project (see table 2, it is therefore important that external laboratories like NMI (National Metrological institutes) performed a complete validation of the instruments using well established procedures and certified reference materials. Several documents are available to guide a laboratory through a method validation including the Eurachem guide "The Fitness for purpose of analytical methods" [11]. ISO TC158 is working on a new standard ISO/DIS 21087 [12] proposing a detailed approach for the validation process. The study performed in this work package demonstrated that there is a need of standardization and method validation for the multi-components analysers commercially available. Reported performance criteria of commercial multi-components analysers are indeed not easily available which makes difficult the selection of analysers for commercial analytical laboratories. Validation for some parameters on some of the instruments named in this report are planned to be performed in activities of the project EMPiR MetroHyVe.

Moreover we strongly support the implementation of ISO/DIS 21087. It will be crucial to guarantee that reliable and accurate results are obtained when controlling if the hydrogen quality is satisfactory as fuel cell electrical vehicles fuel (compliance to ISO 14687-2).

5 References

- [1] ISO 14687-2 Hydrogen Fuel - Product Specification - Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles, 2012.
- [2] http://www.gas2015.org/dynamics/modules/SFIL0100/view.php?fil_id=1123
- [3] DOE reports highlight fuel cell buss economy, hydrogen fuel quality, Fuel Cells Bulletin, 2016, 12, 12
- [4] Hydrogen Fuel Quality Specifications for Polymer Electrolyte Fuel Cells in Road Vehicles, FTCO, U.S. Department of Energy, November 2016
- [5] Standard test method for determination of trace gaseous contaminants in hydrogen fuel by Fourier Transform Infrared (FTIR) Spectroscopy, ASTM D7653-10
- [6] Standard Test Method for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer D7941/D7941M-14
- [7] An optical sensor for multi-species impurity monitoring in hydrogen fuel, M.M. Tripathi, K.E. Eseller, F-Y Yueh, J.P.Singh, Sensors and actuators, 2012, B171-172, 416-422
- [8] Results from H₂-fuel gas quality monitoring at various HRSs in Oslo Area, 2013, T.A. Aarhaug, A.M.C. Ferber, H2moves.eu Scandinavia
- [9] EURAMET 1220 international comparability on hydrogen purity, T. Bacquart, A.M.H. van der Veen, S. Bartlett, H. Ent, J.I.T. van Wijk, M.D. Minarro, R.E. Pearce, P.J. Brewer, R.J.C Brown, A.S. Brown, A. Murugan, NPL Report ENV 16, 2017
- [10] Aarhaug, T.A. and Ferber, A.M.C., Deliverable 7.4 H2Moves Scandinavia
- [11] "The fitness for purpose of analytical methods - A laboratory Guide to Method Validation and related topics (2nd ed. 2014), Eurachem Guide, B. Magnusson, U. Örnemark, ISBN 978-91-87461-59-0
- [12] ISO/DIS 21087 Gas analysis -- Analytical methods for hydrogen fuel -- Proton exchange membrane (PEM) fuel cell applications for road vehicles