METROLOGY for HYDROGEN VEHICLES

REPORT:

A4.3.1: Review and selection of compounds for total measurements (halogenated, sulphur and hydrocarbons)

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This report was written as part of activity A4.3.1 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. The three year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

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1 - Introduction

Among the characteristics for the fuel specification that are listed in Table 1 of the standard ISO 14687-2, three are total species: Total hydrocarbons (Methane basis), Total sulphur compound (H2S basis) and total halogenated compounds (Halogenate ion basis).

Determination of total species is a substantial analytical challenge from a metrological point of view. A total compounds family cover a large number of species with physical properties (molecular weight, polarity, boiling point…) which vary greatly within the family.

Quantification is mostly based on converting all compounds into one species or independent elements (Cl, F, I and Br). Due to large differences in physical properties, it is a real challenge to sample all the compounds of one family into one unique vessel. It then requires the conversion (during analysis) to be equally efficient for all compounds of the family. Interferences from other compounds (not within the family of interest) may also lead to biased results.

Moreover, only a few impurities of a total compounds family may actually be present in the hydrogen. Defining which compounds are the most likely to be present may be done by a speciation method.

Two strategies can then be used for performing hydrogen quality monitoring:

- Defining marker of presence (selecting most abundant species as a marker for halogenated, sulfur or hydrocarbons contamination. If the sample contains significant amounts of the marker then the total species needs to be measured.
- Revision of the ISO standards to focus only on selected compounds from the families. Development of speciation methods would allow measuring what the actual impurities are in the real samples of hydrogen which in turn could enable the replacement of the total species characteristics with the actual impurities in the standard ISO14687-2.

In this report, we have reviewed reports from purity analysis of real samples of hydrogen to select 3 to 5 compounds per family of total halogenated, total sulphur and total hydrocarbons. These compounds will then the target compounds used in the other activities of Task 4.3 (Efficiency of sorbent tubes).

In total 32 hydrogen purity reports from 24 different stations (SRM, chlor-alkaline and electrolysis processes) have been reviewed.

2 - Literature survey

2.1 - Smart Chemistry

Smart Chemistry is a company located in Sacramento, USA performing sampling of particulates and gaseous sample of hydrogen fuel at nozzle of HRS (Hydrogen Refuelling Stations) following ASTM methods for performing analysis of trace impurities in hydrogen fuel. They analyse:

- 12 sulphur compounds (hydrogen sulphide, carbonyl sulphide, methyl mercaptan, ethyl mercaptan, dimethyl sulphide, carbon disulphide, isopropyl mercaptan, Tert-butyl mercaptan, n-propyl mercaptan, n-butyl mercaptan, dimethyl disulphide and tetrahydrothiophene.
- chlorine, hydrogen chloride and hydrogen bromide and 36 organic halides compounds (1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,2-dibromoethane, 1,1-dichloroethane, 1,1-dichloroethene, 1,2,4-trichlorobenzene, 1,2-dichloroethane, 1,2-dichloropropane, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, benzyl chloride, bromodichloromethane, bromoform, bromomethane, carbon tetrachloride, chlorobenzene, chloroethane, chloroform, chloromethane, cis-1,2-dichloroethene, cis-1,3-dichloropropene, dibromochloromethane, dichlorodifluoromethane, 1,1,2.trichloro-1,2,2-trifluoroethane (freon113), 1,2-dichlorotetrafluoroethane (freon114), hexachlorobutadiene, methylene chloride, tetrachloroethene, trans-1,2-dichloroethene, trans-1,3-dichloropropene, trichloroethene, trichlorofluoromethane, vinyl chloride and 1,2,3,4-tetrachlorohexafluorobutane).

- Hydrocarbons from methane to trimetylbenzenes, ketones, alcohols (ethanol, isopropyl alcohol), ester (ethyl acetate) and ether (methyl tert-butyl ether).

Tetrachloethene has been found three times in high concentrations from hydrogen samples provided by operational refuelling stations (personal communication with Professor Jong Pyng Hsu).

2.2 - HyCoRa project

The HyCoRa project was aimed at developing and executing a strategy for cost reduction for hydrogen fuel quality assurance. The project received funding from the European Union´s Seventh Framework Programme for research, technological development and demonstration under grant agreement no 621223. VTT (Finland) was project coordinator while other partners were CEA (France), the European Commission, Protea Limited (UK), SINTEF (Norge) and Powercell Sweden AB (Sweden). The project started April 2014.

In 'Deliverable 3.2 - Measurement of hydrogen quality variation at various HRSs with different fuel feedstock', 8 HRSs located in Norway and Germany were visited in 2014 and purity analysis was performed. The analyses were performed by Smart Chemistry. The results are available at http://hycora.eu/deliverables.htm and are summarised below:

Total hydrocarbons:

Methane, acetone, ethane, ethanol, isopropyl alcohol and propane were detected in quantifiable level of concentration (0.002 µmolC/mol).

Total Sulphur:

Hydrogen sulphide, carbonyl sulphide and carbon disulphide were detected in quantifiable level of concentration (0.02 nmol/mol).

Total halogenated:

1,2,3,4-tetrachlorohexafluorobutane was detected in quantifiable level of concentration (0.001 µmol/mol)

In 'Deliverable 3.3 – Results from the 2nd HRS measurement campaign', 16 HRSs located In Germany, Denmark, Sweden and Norway were visited in 2016 and 2017 during 2 sampling campaigns and purity analysis was performed. At two stations, sampling and analysis were performed two times during the same day or within some weeks' interval. The analyses were performed by Smart Chemistry.

Total hydrocarbons:

Methane, n-butane, isobutane, ethane, octane, decene and propane were detected in quantifiable level of concentration (0.002 µmolC/mol).

Total Sulphur:

Hydrogen sulphide, carbonyl sulphide, tert-butyl mercaptan and tetrahydrothiophene were detected in quantifiable level of concentration (0.02 nmol/mol).

Total halogenated:

1,2,3,4-tetrachlorohexafluorobutane and dichloromethane was detected in quantifiable level of concentration (0.001 µmol/mol)

2.3 - H2moves Scandinavia

The H2moves Scandinavia project aimed to gain customer acceptance for Hydrogen Fuel Cell Electric Vehicles (FCEV) and demonstrate the market readiness of fuel cell vehicles and hydrogen refuelling infrastructure. The Ludwig-Bölkow-Systemtechnik GmbH – LBST was coordinator of the project. Three HRS located in Norway were visited (2012-2013) and purity analysis was performed. The analyses were performed by Smart Chemistry and summary of results are below.

Total hydrocarbons:

Methane, acetone, ethane, heptane and propane were detected in quantifiable level of concentration (0.001 µmolC/mol).

Total Sulphur:

Hydrogen sulphide, carbonyl sulphide and carbon disulphide were detected in quantifiable level of concentration (0.02 nmol/mol).

Total halogenated:

1,1,3,4-tetrachlorohexafluorobutane was detected in quantifiable level of concentration (0.001 µmol/mol).

2.4 - H2Protocol.com

H2Protocol.com was started in June 2015 with the mission to share data to help accelerate the commercialization of hydrogen fuelling. Three sources of data were received, firstly from the H2Moves Scandinavia, then from the California State University, Los Angeles and finally from HyCoRa (coming soon).

Samples of hydrogen were taken at the California State University HRSs at different occasions (April 2014, November 2014, other occasion in 2015 but the files available on the website cannot be opened). The analyses were performed by Smart Chemistry and are summarised below.

Total hydrocarbons:

Methane, cyclohexane and isopropyl alcohol were detected in quantifiable level of concentration (0.001 µmolC/mol).

Total Sulphur:

Hydrogen sulphide, carbonyl sulphide and carbon disulphide were detected in quantifiable level of concentration (0.02 nmol/mol).

Total halogenated:

No halogenated was detected in quantifiable level of concentration (0.001 µmol/mol).

2.5 – National Physical Laboratory (NPL)

NPL has performed hydrogen purity analysis on a number of samples for clients and in some research projects. The results from clients cannot be divulgated but some general observations are summarized below:

Total hydrocarbons:

Methane, ethane, propane, n-butane have been detected in quantifiable level of concentration in some samples (0.001 µmolC/mol).

Total halogenated:

Dichloromethane was detected in quantifiable level of concentration in some samples (0.001 µmol/mol).

1,2,3,4-tetrachlorohexafluorobutane has never been observed (LOD ~ 1 nmol/mol). The same list of halocarbons as the one used at Smart chemistry was investigated, but none of these compounds were found in hydrogen samples above NPL analytical method detection limit (< 5 nmol/mol).

HCl and Cl_2 have not been analysed.

Total sulphur:

No speciation has been performed until now. No samples so far have shown a total sulfur amount fraction above 4 nmol/mol. It can therefore be concluded that no individual sulfur compound has been present above 4 nmol/mol.

3 - Tables of results

In the following tables, all the results are presented and the following colour codes are used:

Green: Found but under specification level

Orange: higher than specification level but not a violation.

Red: found above specification level

For the stations:

Blue: water electrolysis

Yellow: SMR

Purple: Chlor-alkaline

Hydrocarbons	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3 SC2											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
Methane																									
Acetone																									
Ethane																									
Ethanol																									
Isopropyl alcohol																									
Propane																									
Heptane																									
Cyclohexane																									
n-butane																									
Isobutane																									
Octene																									
Decene																									

SC: Sampling campaign

HRS8 and HRS12 in the HyCora project are the same station but two different sampling and analysis (the same day)

CSU H2 HRS1 and HRS2 are the same station

Hydrocarbons	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
Methane										
Acetone										
Ethane										
Ethanol										
Isopropyl alcohol										
Propane										
Heptane										
Cyclohexane										
n-butane										
Isobutane										
Octene										
Decene										

HRS1 and HRS9 are the same station but two different sampling and analysis (within 3 weeks)

Sulfur	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
H2S																									
COS																									
CS2																									
TBM																									
THT																									

H2S: hydrogen sulphide
COS: carbonyl sulphide
CS2: carbon disulphide
TBM: Tert-butyl mercaptan
THT: Tetrahydrothiophene

Sulfur	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
H2S										
COS										
CS2										
TBM										
THT										

Halogenated	HyCoRa D3.2								H2Moves Scandinavian			CSU H2 HRS		HyCoRa D3.3											
HRS	1	2	3	4	5	6	7	8	1	2	3	1	2	1	2	3	4	5	6	7	8=12	9	10	11	12=8
Cl_2																									
HCl																									
HBr																									
C4Cl4F6																									
CH_2Cl_2																									

Cl_2: Chlorine
HCl: Hydrogen Chloride
HBr: Hydrogen Bromide
C4Cl4F6: tetrachlorohexafluorobutane
CH_2Cl_2: dichloromethane

Halogenated	HyCoRa D3.3 SC3									
HRS	1=9	2	3	4	5	6	7	8	9=1	10
Cl_2										
HCl										
HBr										
C4Cl4F6										
CH_2Cl_2										

4 - Processes at the HRS stations

HyCora D3.2, SC1

SMR, compressed: HRS2

SMR, Liquid: HRS3, HRS4

Water-electrolysis, compressed: HRS1, HRS5, HRS7, HRS8

Chlor-alkaline, compressed: HRS6

H2Moves Scandinavia:

Alkaline electrolysis, trucked in: HRS1

Water electrolysis, compressed: HRS2

Chlor-alkaline, compressed: HRS3

HyCora D3.3, SC2

SMR, Compressed: HRS2

SMR, Liquid: HRS3, HRS4, HRS5, HRS6

Water electrolysis, compressed: HRS7, HRS8, HRS9, HRS10, HRS12

HyCoRa D3.3, SC3

Water electrolysis, compressed: HRS1, HRS2, HRS3, HRS5

Water electrolysis, trucked in: HRS6, HRS7, HRS8, HRS9, HRS10

Chlor-alkaline, compressed: HRS4

CSU H2 HRS

Not specified

NPL

Not specified

5 - Summary of results

Results are then summarized in the following table:

Total hydrocarbons

N =number of samples	SMR		Water electrolysis		Chlor-Alkaline		Total
	Under specification	Above specification	Under specification	Above specification	Under specification	Above specification	
Methane	6	0	18	1 *	2	1*	28
Acetone	6	0	11	0	2	0	21
Ethane	5	0	6	0	2	1	14
Ethanol	1	0	5	0	1	0	7
Isopropyl alcohol	3	0	2	0	1	0	6
Propane	2	0	4	0	1	1	8
Heptane	0	0	1	0	0	0	1
Cyclohexane	0	0	1	0	0	0	1
n-butane	0	0	1	0	0	1	2
Isobutane	0	0	4	0	0	0	4
Octene	0	0	4	0	0	0	4
Decene	0	0	4	0	0	0	4

* Total hydrocarbons (Methane basis) above 2 µmol/mol but only due to the presence of methane so not a violation of the specifications

Total halogenated

Very few halogenated compounds have been found in hydrogen samples. Only dichloromethane, tetrachloroethylene and tetrachlorohexafluorobutane have been mentioned so far.

Total sulfur

The most commonly identified sulfur compounds in hydrogen samples are H_2S, COS and CS_2. Tert-butyl mercaptan and tetrahydrothiophene have been found in one sample.

6 - Selection of compounds per family

A webmeeting was organised the 6th of December in order to select some compounds per family based on the literature survey of hydrogen purity reports. It was discussed to select compounds to cover a wide range of boiling points. Present partners were RISE, NPL, VSL, IFE, SINTEF, AP2E.

6.1 - Hydrocarbons

The following compounds were selected:

Methane, Ethane, propane, butanes, acetone, methanol, ethanol, octane, decane. It is foreseen that no adsorbent will be able to adsorb all these compounds. More likely, the use of two adsorbents in series should be studied; a weak one to adsorb for example octane, decane (for example Tenax) and a stronger one, for example Carbosieve 569. The light compounds will pass through the weak adsorbent and shall be trapped onto the strong one.

6.2 - Halogenated compounds

The following compounds were selected: dichloromethane, tetrachloroethylene, tetrachlorohexafluorobutane, dichlorobenzene and eventually if proven possible during activity A4.3.3, chloroform. A wide range of boiling points are then covered.

6.3 - Sulfur compounds

The following compounds were selected: carbonyl sulphide (COS, if proven possible during activity A4.3.3), carbon disulphide (CS2, if proven possible during activity A4.3.3), tert-butyl mercaptan, tetrahydrothiophene, methylmercaptan.

7 – Other tasks

7.1 – Activities in WP2

In WP2, a TD-GC-MS method shall be developed by RISE, NPL and CEM. It is preferred to use the same compounds. New primary reference gas mixtures will be prepared and validated in A2.3.2. Some of these if possible can be used for the short-term stability studies. For example, the PRGMs containing tetrachlorohexafluorobutane or the PRGMs containing one halogenated compound that preferably can be chosen for the list of halogenated compounds selected here.

7.2 – A4.3.2

When performing the literature survey on sorbents for the selected compounds, the following parameters have to be included in a performance chart:

- Breakthrough volume (defined as the volume of gas that will purge an analyte through one 1 gram of adsorbent resin in a desorption tube at a specific temperature)
- Limit of detection (for a proposed volume of gas sampled)

7.3 – A4.3.4 to A4.6

The calibration used when performing the short-term stability studies needs to be defined before the tests. Several options have been discussed as the use of permeation tubes, spiked tubes with solutions, dynamic gas mixers. The concentration for the target compounds need also to be defined before.