ANALYSIS OF TRACE-LEVEL IMPURITIES IN HYDROGEN

To achieve sustainable development goals related to climate change and to improve air quality, the reduction of carbon emissions due to transport and mobility are fundamental [1]. Transport is currently responsible for over a quarter of greenhouse gas emissions in developed countries and is worldwide the primary source of urban air pollution [2]. The deployment of hydrogen as a sustainable fuel has the potential to substantially reduce emissions of greenhouse gases and harmful air pollutants. In 2050, hydrogen may account for 32% of the fuel demand in Europe [3]. The fuel cell system in a hydrogen vehicle requires very high-quality hydrogen because trace levels of impurities can adversely affect fuel cell performance and durability [1]. For example, formaldehyde and formic acid at concentrations higher than 200 nmol/mol can cause significant fuel cell performance degradation [4]. To ensure the hydrogen quality, a specification has been developed (ISO 14687), setting upper concentrations of a series of impurities (Table 1). To demonstrate the conformity with this standard it is required to validate by measurement that the levels of the impurities are below the required thresholds.

Existing analytical methods suitable for measuring ISO 14687 impurities in fuel cell graded hydrogen mainly involve techniques based on gas chromatography. However, a combination of several analytical techniques and methodologies are necessary to perform the full scope of analysis required. In Table 1 are summarized the analytical methods that we have chosen for the characterization of hydrogen purity. In this article, we will focus on the GC-FID and HPLC systems.

2 Materials and methods

In this section, we will develop the analytical systems and gas generators used for the characterization of trace-level impurities in hydrogen.

2.1 Gas supply

Air generators (airmopure, Chromatotec®, France) and Hydrogen generators 99.9999% with dew point below -15°C (Hydroxychrom, Chromatotec®, France) were used for the flames of FIDs, valve actuations of the GC-FIDs. The VOCs content of gas generated by both generators was verified experimentally using auto-TDGC-FID and Non-Methanic Hydrocarbon Concentration (NMTHC) for both analyzers was below 0.1 $\mu g.m^{-3}$. Using these generators, only power supply and water are needed to run the analytical systems.

2.2 auto-GC-FID system for the measurement of Total hydrocarbons

For the monitoring of total hydrocarbon compounds (THC), an automatic gas chromatograph (auto-GC-FID) equipped with a flame ionization detector (FID) has been used (ChromaTHC, Chromatotec®, France). For each analysis, sample was drawn into the system with a flow rate of 25 $ml.min^{-1}$. The sample was injected in a three-dimensional columns system (one polar capillary column and tow packed columns) located inside the heated oven of the GC using hydrogen as carrier gas. The system allows the separation and quantification of methane and non-methane hydrocarbons in two minutes. Total hydrocarbon content is calculated with the sum of methane and non-methane (NMTHC).

2.3 auto-GC-FID system with methanizer for CO and CO_2 measurement

For the monitoring of carbon monoxide and carbon dioxide, an auto-GC-FID (ChromaCO, Chromatotec®, France) equipped with FID has been used. For each analysis, sample was drawn into the system with a flow rate of 25 $ml.min^{-1}$. The sample was injected in a packed column system located inside the heated oven of the GC using hydrogen as carrier gas. Before detection, the sample goes through a catalytic system which reduces CO and CO_2 to CH_4. The system allows the separation and quantification of CO and CO_2 with a cycle time of 10 minutes.

2.4 auto-HPLC system for formaldehyde and formic acid

The reference ISO 16000-3 method for aldehydes detection is based on active sampling using 2,4-Dinitrophenylhydrazine (DNPH) tube followed by hydrazones quantification by HPLC-UV (HPLC system, Chromatotec®) [5]. This method allows the quantification of all aldehydes present in ambient air but can be applied for hydrogen impurities characterization [6]. Once sampling is achieved, DNPH tubes are eluted with 2–3 mL of acetonitrile (99.8%). An amount of 20 µL of the resulting hydrazones solution is then injected and quantified by HPLC/UV using an external calibration. Hydrazones are separated through a nonpolar C18 column using acetonitrile / water (75:25) and detected at 360 nm. For formic acid analysis, similar method can be applied following the protocol described by Uchiyama et al. [7]. To ensure complete reaction with DNPH, half of the eluted solvent must be heated up to 80°C for 5h.

Table 1: Fuel quality requirements specified by ISO/DIS 14687-2 for Types I & II Grade D and summary of analysis methods

Components	Maximum impurities concentration (µmol/mol)	Electrolytic water sensor	GC-DID	C-FID	GC-ED	HPLC-VU	FT-UV	GC-ELCD
Water	5	■						
Total hydrocarbons	2			■				
Oxygen	5		■					
Helium	300		■					
Nitrogen	100		■					
Argon	100		■					
Carbon dioxide	2			■				
Carbon monoxide	0.2			■				
Total sulfur compounds	0.004				■			
Formaldehyde	0.01			■		■		
Formic acid	0.2					■		
Ammonia	0.1						■	
Total halogenated	0.05							■

2.5 Other systems for hydrogen impurities measurement

For the other impurities, several analytical systems are required. Electrolytic water sensor will be used for the monitoring of water at ppm level in H_2 gas (DETH2S, Chromatotec®, France). For measurement in H_2, specific metal coating is required to ensure accurate measurements.

Gas chromatograph analyzer equipped with pulse ion discharge detector (DID) will be used for monitoring of permanent gases (Chroma DID, Chromatotec®, France). Helium carrier gas and specific column for Ar/O_2 separation are used for the quantification of N_2, O_2 and Ar with a single analytical system [8].

The total sulfur compounds will be analyzed by auto-GC equipped with specific electrochemical detector (H2S TS MEDOR, Chromatotec®, France).

Total halogenated compounds can be characterized by auto-GC-ELDC (Chroma ELCD, Chromatotec®, France).

Finally, ammonia will be characterized using Fourier Transform Spectrometry for UV-Visible with specific preconcentration system (DET NH3, Chromatotec®, France). The techniques presented in this section will not be developed in the results section (please contact the author for more information).

Table 2: Stability of NMTHC measurement with injection of benzene standard.

Sampling date	Concentration (ppb(v))	Retention time (s)
10/12/2020 08:40	1128.32	38.67
10/12/2020 12:41	1090.11	38.75
10/12/2020 16:42	1067.32	38.65
10/12/2020 20:43	1071.31	38.67
11/12/2020 00:44	1070.31	38.55
11/12/2020 04:45	1081.29	38.60
11/12/2020 08:46	1084.30	38.63
11/12/2020 12:11	1053.88	38.63
Mean	**1080.86**	**38.64**
Standard deviation	**22.24**	**0.06**
RSD in %	**2.06%**	**0.15%**
Nber of measurements	**8**	**8**
Period in hours		

3 Results and Discussion

Here are described the three analytical methods for the characterization of hydrogen impurities.

3.1 Total hydrocarbon measurement

The system allows the separation of H_2, O_2, N_2 and CO_2 from methane and NMTHC. Chromatogram obtained on the system can be seen in the Figure 1 (acquisition starts after the elution of permanent gases). Therefore, the system can quantify trace-level impurities in hydrogen after being calibrated with classical cylinder which uses N_2 as balance gas.

The relative standard deviation on benzene for 8 measurements performed over 24h is 2.06% (Table 2) and the low detection limit (LDL) is 50 ppb for methane and 20 ppb for NMTHC (eq benzene).

3.2 CO and CO_2 measurements

2-Dimensional gas separation is required for the analysis of CO and CO_2. First the sample is injected into a Porapak Q column to separate CO_2 from the permanent gases. Then the permanent gases will be injected into a 5A molecular sieve column to separate and analyze CO. For both molecules, a catalytic system (Methanizer, Chromatotec®, France) will reduce CO and CO_2 to CH4 under hydrogen at 400°C before quantification with the FID. The cycle time is 10 minutes and the LDL is less than 10 ppb (200 ppb is the maximum required in the ISO 14687).

3.3 Formaldehyde and formic acid measurements

Following the reference ISO 16000-3 method, formaldehyde can be quantified from few ppt to ppm level depending on the sampling volume. For measurement at ppb level, 60 L of the sample is required (1h sampling). Typical chromatogram is shown in the Figure 2. Formaldehyde (elution at 242 s) is perfectly separated from acetaldehyde (elution at 272 s).

This technique is very sensitive and powerful for the characterization of aldehydes, ketones and formic acid but it is not fully automatic as it requires trained people for the elution of DNPH cartridges [7]. A new automatic sampling DNPH system is currently developed in collaboration with ICPEES (CNRS, France) and should be available soon [9], [10]. Also, for formaldehyde and acetaldehyde, auto-GC-FID system can be used with LDL below 1 ppb and cycle time of 15 minutes without interferent [9].

4 Conclusion

In this article, we present a cost-effective and fully automatic turnkey solution for the measurement of trace level impurities in hydrogen where all results are listed in a dedicated software. A combination of several analytical techniques and methodologies are necessary to perform the full scope but it can be done automatically using industrial automatic gas chromatograph systems.

5 Bibliography

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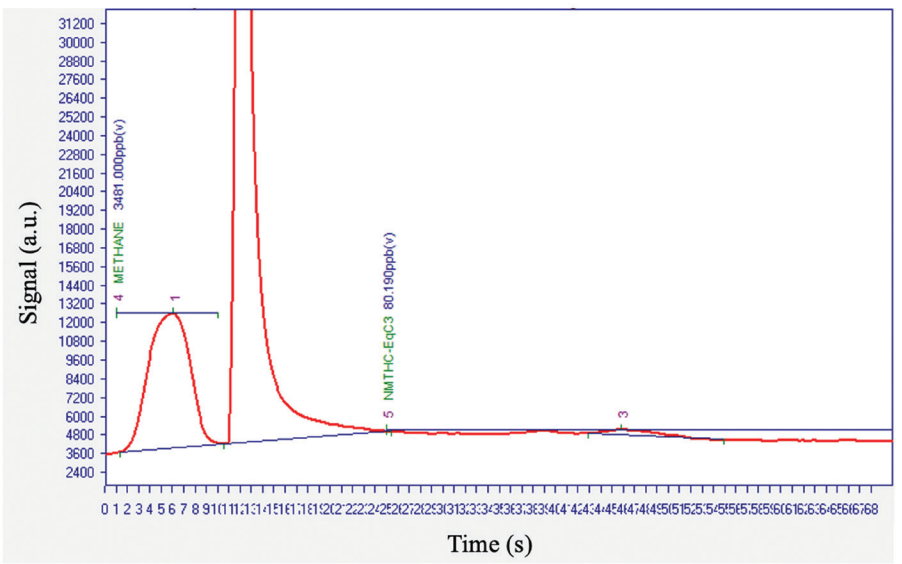

Figure 1: Chromatogram obtained on auto-GC-FID for Methane and NMTHC measurment

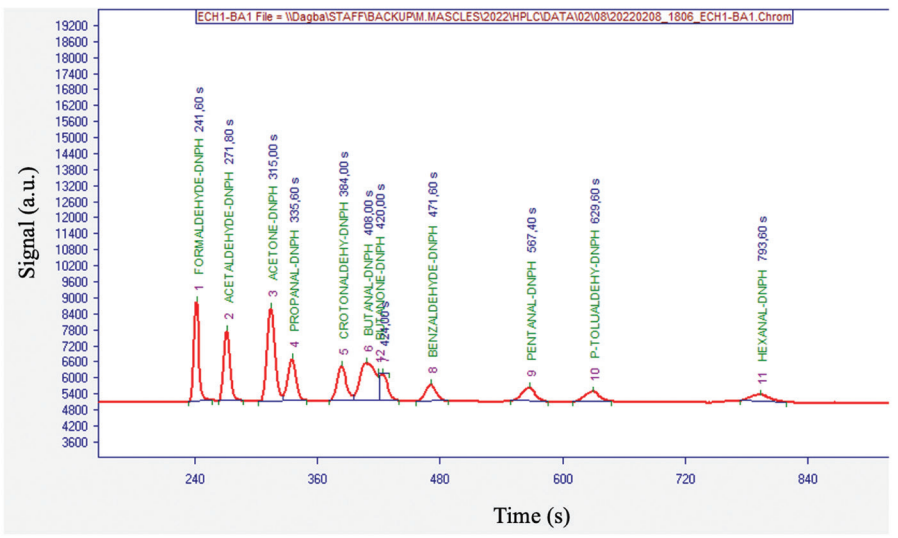

Figure 2: Chromatogram obtained for the injection of 13 aldehydes / ketones mixture

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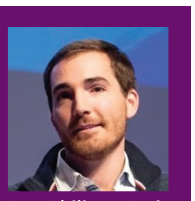
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