

Online monitoring of energy content and impurities in hydrogen using a micro gas chromatograph

Eva Krolis^{1*}, and Füsün Karaburun-Yavuz¹

¹Qmicro B.V., Neptunusstraat 21, 7521 WC, Enschede, The Netherlands

Abstract. Hydrogen is increasingly considered as a clean alternative to natural gas, creating a need for reliable online measurements of its energy content and impurity concentrations. This study evaluates the performance of the DynamiQ-X micro gas chromatograph (GC) for monitoring factory-grade hydrogen. Helium and hydrogen were used as carrier gases in a two-unit configuration, measuring in parallel. Gas mixtures were prepared according to frequently cited impurity limits, and the system's repeatability, accuracy and detection limits were evaluated. The measured calorific value and Wobbe index met market requirements, while the component repeatabilities were high and primarily determined by the concentration. The limits of detection (LOD) and quantification (LOQ) were low for all components, with minimal differences between both carrier gases. Notably, an oxygen LOQ below 1 ppm was achieved when hydrogen was used as the carrier gas. The results demonstrate that the equipment is suitable for online monitoring of factory-grade hydrogen and can achieve consistent and reliable analyses.

1 Introduction

As the energy sector pushes toward net zero, hydrogen is gaining momentum as a clean alternative to natural gas. While blending up to 20% hydrogen into natural gas networks serves as a transitional step, the long-term goal is a dedicated hydrogen infrastructure, serving industrial, commercial and even domestic consumers [1]. This shift introduces new challenges, one of which is in accurately measuring the energy content and impurities. Industry-grade hydrogen with minimum purification degrees of 98% or 99.5% can be used in factories and distribution through a pipeline system [1-3]. To ensure safe and efficient use, online monitoring of the calorific value and Wobbe index is essential, alongside precise measurement of the hydrogen content and impurities [4].

The DynamiQ micro Gas Chromatograph (GC) is equipped with several MEMS micro-machined chip components, which are connected by a patented chip to chip connection technology. This architecture enables a compact instrument footprint in an explosion proof design. The GC operates in a backflush-to-detector configuration, which increases the lifetime of the columns and reduces the total analysis time to typically less than a minute [5].

This study evaluates the performance of the DynamiQ micro GC using impurity thresholds from standards and market requirements. Helium and hydrogen carrier gas are compared, where helium allows for hydrogen quantification and hydrogen carrier gas improves the oxygen detection limit. Accuracy and repeatability of both carrier gases are compared and assessed across a range of gas mixtures and evaluated

against the international recommendation OIML R140 [6]. Additionally, limits of detection (LOD) and quantification (LOQ) are determined following the methods specified in ISO 21087:2019 [7].

2 Materials and methods

Standards and market requirements for industry-grade hydrogen are still under development. The impurity types and levels as well as the minimum purification degree of either 98% or 99.5% remain under active discussion. ISO 14687:2025 [4] specifies the minimum quality characteristics of hydrogen fuel for residential, commercial, industrial, vehicular and stationary applications. While the focus has mostly been on Grade D, regarding fuel cell applications, grade A specifies industrial-grade limits intended for internal combustion engines. The technical specification CEN/TS 17977:2023 [1] defines hydrogen quality to be distributed by rededicated natural gas infrastructure, aiming to balance the requirements for the producer, grid operators and end-users. Additionally, the European Association for Streamlining of Energy Exchange has developed a Common Business Practice [2] for hydrogen in the natural gas grid, leading to a proposed specification. In 2023, DNV and KIWA conducted a study [3] for the Dutch Ministry of Economic Affairs and Climate Policy, recommending a minimum hydrogen purity of 99.5%, in contrast to other studies.

While these standards and recommendations largely agree on the limits of impurities, some differences remain. The most frequently cited values are

* Corresponding author: eva.krolis@qmicro.com

summarized in Table 1. For oxygen, the limit is 0.1 mol% in grids with no exit points to underground gas storages or sensitive customers, otherwise a maximum of 10 ppm is allowed. All parameters up to and including carbon dioxide can be analyzed using the DynamiQ micro GC.

Table 1. Summary of standards and recommendations for industry-grade hydrogen.

Parameter	Limit
Hydrogen	≥98% (or ≥99.5%)
Wobbe index	42 – 46 MJ/m ³
Inerts (N ₂ , Ar, He)	≤2%
Hydrocarbons	≤2%
Oxygen	≤0.1 % or ≤10 ppm
Carbon monoxide	≤20 ppm
Carbon dioxide	≤20 ppm
Water	≤250 or ≤60 ppm
Water dewpoint	≤-8 °C at 70 bar
Hydrocarbon dewpoint	≤-2 °C at 1-70 bar
Total sulphurs	≤7 ppm
Ammonia	≤13 ppm
Halogenated compounds	≤0.05 ppm

Both helium and hydrogen were used as carrier gases for the DynamiQ micro GC. Helium grade 5.0 was used, while hydrogen was generated on-site using a hydrogen generator, providing comparable purity. The generated hydrogen also served as the balance gas for preparing mixtures with the desired impurities, as depicted in Figure 1. For each impurity, at least five evenly spaced concentrations were prepared to assess linearity. Additionally, measurements near 1 ppm were performed to determine the limit of detection (LOD) and limit of quantification (LOQ). Finally, a composition representative of industry-grade hydrogen was measured to evaluate the calculation of calorific value and Wobbe index.

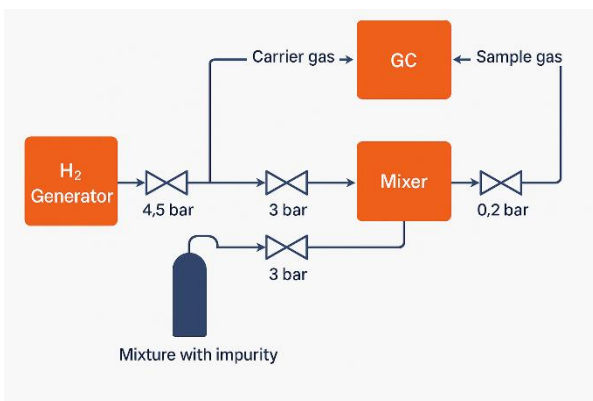


Fig. 1. Measurement setup.

The DynamiQ-X can contain up to four GC units that each perform in parallel a different GC analysis under

individually optimized method conditions. They consist of an injector, columns and thermal conductivity detectors (TCDs), as depicted in Figure 2. For these analyses, only two GC units were needed where the same setup could be used for both helium and hydrogen carrier gas. The instrument consists of a stream selector with 4 sample streams. One sample stream can be measured at the same time but the two GC units analyze this gas simultaneously with parameters optimized for different components.

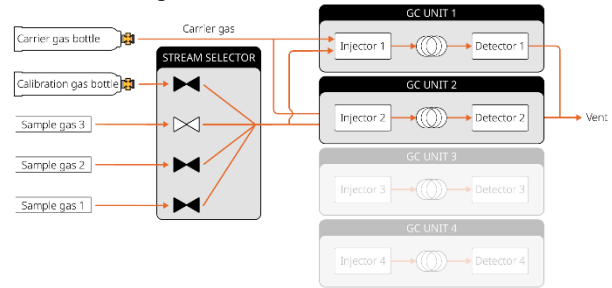


Fig. 2. Schematic of the stream selector and GC units.

The DynamiQ-X is designed for continuous monitoring and works therefore stand-alone. The generated data can be communicated via Modbus and the instrument is WELMEC 7.2 compliant [8, 9]. The ATEX/IECEX certified analyzer is housed in an explosion-safe marine-grade aluminium IP65 enclosure. The instrument has a volume of 10 L and a low carrier gas consumption of one gas bottle for over one year [5].

The two GC units consist of an injector and two detectors integrated on a chip, a pre-column and an analytical column. This configuration enables the use of backflush technology, which decreases the analysis time and prevents late-eluting or unwanted compounds from entering the analytical column. During sample injection, the system operates in foreflush mode. At a defined point in the analysis, the flow through the pre-column is reversed and directed to the backflush detector (TCD BF), where a combined peak of all late-eluting components is recorded. Simultaneously, components that have already reached the analytical column continue to elute at the foreflush detector (TCD FF). A schematic is given in Figure 3.

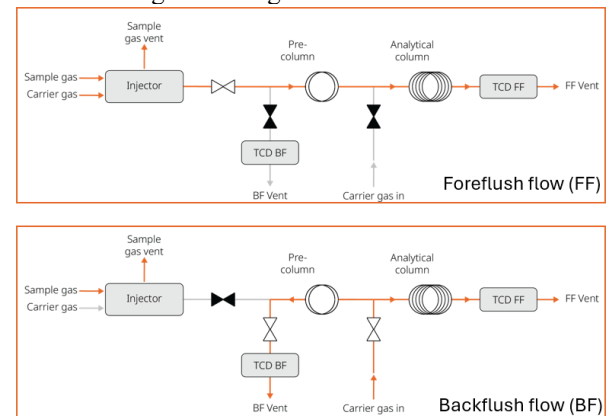


Fig. 3. Schematic of foreflush (FF) and backflush (BF) flow.

The thermal conductivity detectors (TCDs) operate by detecting changes in heat transfer from a heated filament as different components pass through. The magnitude of the signal is determined by the difference

in thermal conductivity between the carrier gas and the analyte. Helium and hydrogen are commonly used carrier gases because of their high thermal conductivities. Hydrogen has a lower viscosity than helium, resulting in shorter retention times. Consequently, analyses with hydrogen carrier gas are faster, with an analysis time of 35 seconds compared with 45 seconds with helium carrier gas.

3 Results and discussion

3.1 Chromatograms

The chromatograms using hydrogen as the carrier gas are shown in Figure 4, with a total analysis time of 35 seconds. The first GC unit is configured to measure oxygen, nitrogen, methane and carbon monoxide. As indicated in Table 1, the concentrations of oxygen and carbon monoxide are expected to be significantly lower than those of nitrogen and methane. Nevertheless, all components exhibit sufficiently well-defined peak shapes for reliable integration.

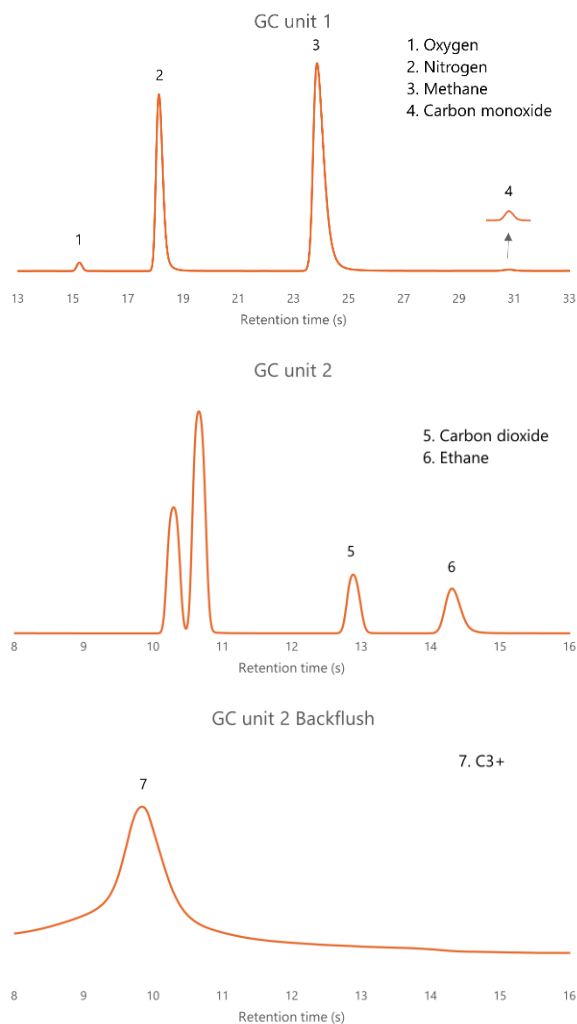


Fig. 4. Example chromatograms using hydrogen carrier gas

Since the sample gas is directed to both GC units simultaneously, the same component types appear in the chromatogram of GC unit 2. However, they are neither separated nor quantified there. On the foreflush detector

of GC unit 2, carbon dioxide and ethane are measured, while hydrocarbons from propane and higher (C3+) are detected on the backflush detector. During post-processing, ethane and the C3+ hydrocarbons are combined and reported as C2+, as higher hydrocarbons are only expected to occur in low amounts. Due to limitations in available sample gases, a mixture containing high amounts of higher hydrocarbons up to n-hexane had to be used. Despite this, the peak shape is still good, only slightly broader, indicating that the method works well even with heavier hydrocarbons that are not expected in real-life samples.

The chromatograms using helium as the carrier gas are shown in Figure 5, with a total analysis time of 45 seconds. The same components are measured on both GC units as when hydrogen is used as the carrier gas. In addition, the hydrogen concentration can be quantitatively determined on GC unit 1 when helium carrier gas is used. Because hydrogen has a higher thermal conductivity than helium, this results in a negative peak in the chromatogram. Despite the large hydrogen peak eluting before oxygen, the separation between hydrogen and oxygen is good.

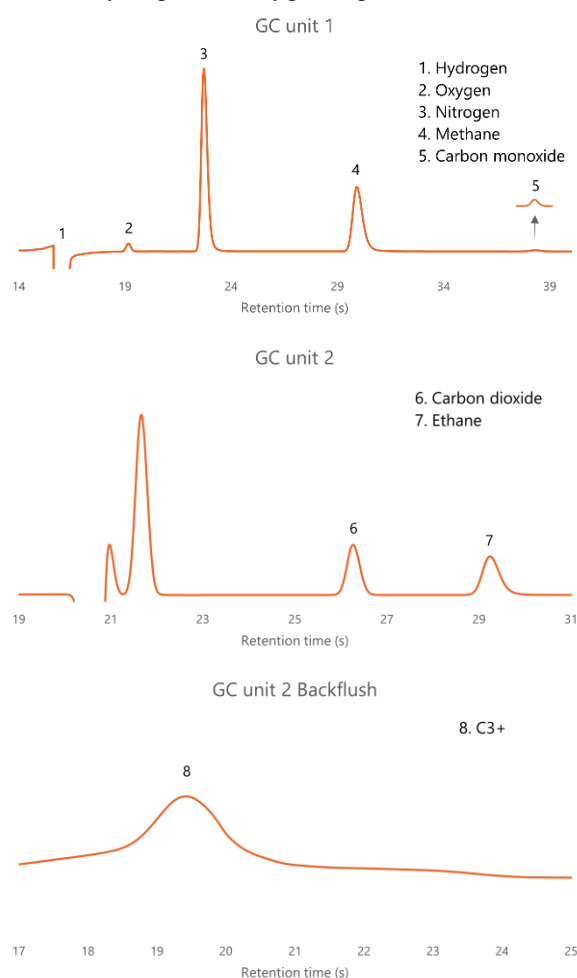


Fig. 5. Example chromatograms using helium carrier gas

3.2 Repeatability

The repeatability was evaluated as the relative standard deviation (RSD) of the concentrations between 10 consecutive measurements, where the results are

presented in Table 2. The RSDs were determined at the maximum allowed concentration limits from the assessed standards and recommendations. For impurities present at percentage levels, the RSDs are well below 0.5%. For carbon dioxide, carbon monoxide and oxygen, with a limit of 10 or 20 ppm, the RSDs are higher due to the lower signal. The repeatability of carbon dioxide and of oxygen measured with hydrogen carrier gas remain below 1%. When oxygen is measured with helium carrier gas, the repeatability is slightly higher (below 2%), as the large hydrogen peak affects the local baseline. Carbon monoxide shows the highest spread, with RSDs below 3% for both carrier gases. This is attributed to its longer retention and low concentration, which leads to a broader, flatter peak that is more challenging to integrate consistently.

Table 2. Relative standard deviation (RSD) of the concentrations

Component	Concentration	Relative standard deviation (RSD)	
		Helium carrier	Hydrogen carrier
Methane	2%	0.10%	0.05%
C2+	2%	0.08%	0.15%
Nitrogen	2%	0.03%	0.03%
Carbon dioxide	20 ppm	0.63%	0.58%
Carbon monoxide	20 ppm	2.30%	2.89%
Oxygen high range	0.1%	0.14%	0.08%
Oxygen low range	10 ppm	1.62%	0.57%

3.3 Calorific value and Wobbe index

The calorific value and Wobbe index were determined in accordance with ISO 6976:2016 [10], as described in literature [1, 3]. A combustion temperature of 15 °C, a metering temperature of 15 °C and a metering pressure of 101.325 kPa were used. The relative error of the average measurement and the repeatability, expressed as the RSD of 10 consecutive measurements, are given in Table 3 and Table 4. The relative error of the calorific value is well below 0.50%, which complies with the requirement of accuracy class A in international recommendation OIML R140 [6]. Although OIML R140 is intended for fuel gases such as natural gas, its performance criteria can be applied to factory-grade hydrogen as well in absence of a dedicated metrological recommendation.

Table 3. Average measurement, relative error and relative standard deviation (RSD) of 10 consecutive measurements of the calorific value

	Helium carrier	Hydrogen carrier
Average (MJ/m ³)	12.430	12.442
Relative error	0.064%	0.023%
RSD	-0.009%	0.091%

Table 4. Average measurement, relative error and relative standard deviation (RSD) of 10 consecutive measurements of the Wobbe index

	Helium carrier	Hydrogen carrier
Average (MJ/m ³)	42.6413	42.629
Relative error	0.028%	0.009%
RSD	0.010%	-0.020%

3.4 Limits of detection (LOD) and quantification (LOQ)

To determine the limits of detection (LOD) and quantification (LOQ), measurements were performed at impurity concentrations around 1 ppm, as this is close to the expected detection limit. The first method to determine the LOD is to identify the lowest analyte concentration that can be reliably distinguished from the background noise. In gas chromatography, a signal-to-noise ratio of 3 is generally accepted as the criterion for the instrument limit of detection:

$$LOD = \frac{3 \times Noise}{RF} \quad (1)$$

where *Noise* is the RMS noise and *RF* is the response factor of the impurity. The response factor is obtained from the calibration curve, by dividing the measured peak area by the analyte concentration. The instrument limits of detection are summarized in Table 5.

Table 5. Instrument limit of detection, based on the noise.

Component	LOD based on noise (ppm)	
	Helium carrier	Hydrogen carrier
Methane	0.08	0.08
C2+	0.07	0.35
Carbon dioxide	0.04	0.08
Carbon monoxide	0.19	0.21
Oxygen	0.06	0.02

Following the definitions in ISO 21087 [7], this represents the instrument detection limit. The method detection limit, which takes the whole measurement procedure into account, is calculated as:

$$x_{LOD} = 3 \times s'_0 \quad (2)$$

where *s'₀* is the standard deviation of 10 consecutive measurements. The method limits of detection are shown in Table 6. For all components except carbon monoxide, the LOD is below 1 ppm. Carbon monoxide elutes late on the first GC unit, resulting in a flatter peak shape that is more difficult to integrate and slightly increases the standard deviation.

Table 6. Method limit of detection, based on the standard deviation.

Component	LOD based on <i>s'₀</i> (ppm)	
	Helium carrier	Hydrogen carrier
Methane	0.36	0.43
C2+	0.52	0.78
Carbon dioxide	0.18	0.20
Carbon monoxide	1.04	1.21
Oxygen	0.33	0.08

The limit of quantification is the lowest concentration of an impurity that can be quantified with acceptable precision and accuracy. It is calculated as:

$$x_{LOQ} = k_Q \times s'_0 \quad (3)$$

where k_Q depends on the maximum allowed concentration in the specification. In this study, $k_Q = 10$ for all impurities.

The limits of quantification are given in Table 7. All quantification limits are below 5 ppm. Generally, components that elute earlier exhibit lower LOQs, primarily due to a better peak shape. Differences between helium and hydrogen as carrier gas are small for most components. The only notable exception is oxygen, where hydrogen carrier gas achieves an LOQ below 1 ppm. This improved performance is caused by good separation of oxygen from other components and its short retention time, resulting in a sharp peak.

Table 7. Limit of quantification, based on the standard deviation.

Component	LOQ based on s'_0 (ppm)	
	Helium carrier	Hydrogen carrier
Methane	1.21	1.43
C2+	1.72	2.61
Carbon dioxide	0.58	0.65
Carbon monoxide	3.48	4.04
Oxygen	1.10	0.25

4 Conclusions

This study evaluated the performance of the DynamiQ-X for measurements of energy content and impurities in factory-grade hydrogen. The system operated reliably with both helium and hydrogen as carrier gases, without requiring hardware modifications. The most frequently cited limits for impurities were summarized from literature and used to prepare sample gases. The measured calorific value and Wobbe index met market requirements, and the repeatabilities of the impurity measurements were high, governed primarily by the impurity concentration. The limits of detection and quantification were low, with only minor differences between the two carrier gases. Notably, an oxygen LOQ below 1 ppm was achieved when hydrogen was used as the carrier gas.

Overall, the results indicate that the equipment is suitable for online monitoring of energy content and impurities in factory-grade hydrogen. As hydrogen quality monitoring becomes increasingly important for both regulatory compliance and process control, the DynamiQ-X provides a robust basis for achieving consistent and traceable measurements.

References

1. European Committee for Standardization (CEN), CEN/TS 17977:2023 Gas infrastructure – Quality of gas – Hydrogen used in rededicated gas systems (2023)

2. EASEE-gas Quality Harmonisation Working Group, Common Business Practice on Hydrogen (2022)
3. E.A. Polman, M.L. Doelman, S. van Greuningen, J.W. Turkstra, M. van Essen, H. Vlap, A follow-up study into the hydrogen quality requirements, KIWA Technologies and DNV (2023)
4. International Organization for Standardization (ISO), ISO 14687:2025 Hydrogen fuel quality – Product specification (2025)
5. Qmicro by Sensirion, DynamiQ-X process GC – Gas chromatographs for on-line gas analysis (2024)
6. International Organization of Legal Metrology, International Recommendation OIML R140 – Measuring systems for gaseous fuel (2007)
7. International Organization for Standardization (ISO), ISO 21087:2019 Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles (2019)
8. European Cooperation in Legal Metrology (WELMEC) e.V., WELMEC Guide 7.2 – Software Guide (EU Measuring Instruments Directive 2014/32/EU) – Version 2022 (2022)
9. Qmicro by Sensirion, Application note – Natural gas and natural gas blended hydrogen (2025)
10. International Organization for Standardization (ISO), ISO 6976:2016 Natural gas – Calculation of calorific values, density, relative density and Wobbe indices from composition (2016)