

# Reducing helium dependency in gas chromatography for natural gas blends with hydrogen

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**Abstract.** The transition toward blending hydrogen in natural gas networks requires a new generation of gas chromatographs, capable of accurately measuring hydrogen. At the same time, the ongoing helium shortage highlights the need to reduce helium consumption in gas chromatography. This research evaluates the analytical performance of the DynamiQ-X NG2220 micro gas chromatograph using three carrier gas combinations: helium-argon, hydrogen-argon and argon alone. Ten natural gas blends containing up to 20% hydrogen were measured to assess calorific value accuracy, limits of detection, and overall performance in accordance with OIML R140 and ISO 10723. All carrier gas combinations produced calorific values within the limits of OIML R140 accuracy class A. Operation with argon as the only carrier gas showed lower detector response and therefore higher limits of detection but remained suitable for fiscal metering ranges. Carrier gas consumption was low for all methods, and replacing helium with a hydrogen or argon can save approximately 19.2 litres of helium per day during continuous operation. Overall, the DynamiQ-X NG2220 demonstrated reliable performance with all tested carrier gases without needing any hardware changes, supporting the use of hydrogen or argon as viable alternatives to helium for online monitoring of natural gas blends with hydrogen.

## 1 Introduction

Injecting sustainably produced hydrogen into the natural gas grid can significantly reduce greenhouse gas emissions. Many European governments have implemented policies to support hydrogen blending of up to 20% in their existing natural gas networks [1, 2]. This shift presents challenges for composition control in fiscal metering, as currently installed gas chromatographs equipped with thermal conductivity detectors (TCDs) cannot measure hydrogen without an additional column and detector, as well as an additional carrier gas [1]. Since helium generally cannot be used for measuring hydrogen due to similar thermal conductivities, argon or nitrogen are required.

At the same time, the ongoing helium shortage further emphasizes the need to reduce helium consumption in gas chromatography [3]. As helium becomes increasingly scarce and expensive, instruments that operate reliably with alternative carrier gases, or that minimize carrier gas usage, will gain importance. Hydrogen, with its high thermal conductivity, can serve as a fitting substitute for helium, but its use introduces safety concerns. Hydrogen is highly flammable when mixed with air, has low ignition energy and permeates materials easily, making leaks likely to ignite. For this reason, hydrogen carrier gas is often generated onsite using a generator, though this is not always feasible or permitted under local legislation and safety guidelines.

Additionally, for the measurement of hydrogen in natural gas blends, argon or nitrogen remain essential.

Switching exclusively to argon can address this, but its significantly lower thermal conductivity results in reduced signal response which may impact measurement accuracy or limits of detection.

The DynamiQ micro Gas Chromatograph (GC) used in this study incorporates several MEMS micro-machined chip components, connected through a patented chip to chip technology. This architecture enables a compact instrument footprint in an explosion proof design [4]. The DynamiQ-X NG2220 version was developed for online measurements of natural gas blends with hydrogen, providing a full analysis within 45 seconds. It is certified to meet OIML R140 accuracy class A requirements [5, 6], using helium and argon as carrier gases.

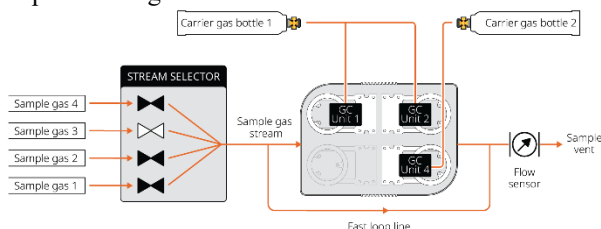
In this study, the DynamiQ-X NG2220 was evaluated using three carrier gas combinations, helium and argon, hydrogen and argon and solely argon, across a range of natural gas compositions containing hydrogen. No hardware changes were required when switching between carrier gases. The accuracy of the derived calorific values was assessed by comparison to the international recommendation OIML R140 [5]. Additionally, performance evaluations following ISO 10723 [7] were conducted to assess measurement errors and associated uncertainties. Limits of detections for all individual components were determined, and the carrier gas consumption was recorded. Together, these evaluations provide a basis for assessing the suitability of different carrier gas combinations for fiscal metering of natural gas blends with hydrogen.

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## 2 Materials and methods

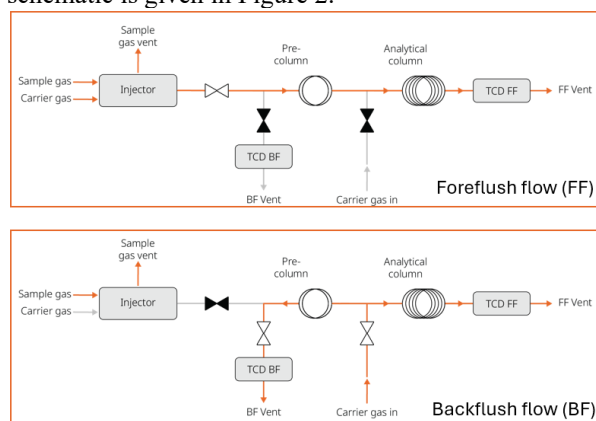
### 2.1 Equipment

The DynamiQ-X NG2220 contains three GC units that each perform in parallel a different GC analysis under individually optimized conditions using thermal conductivity detectors (TCD). The instrument consists of a stream selector with 4 sample streams. One sample stream can be measured at the same time but the three GC units analyze this gas simultaneously with parameters optimized for different components, as depicted in figure 1.



**Fig. 1.** Schematic of the stream selector and GC units.

The three 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 2.



**Fig. 2.** Schematic of foreflush (FF) and backflush (BF) flow.

The first GC unit features a U-type column designed for separating and measuring methane, carbon dioxide and ethane. For the analysis of the heavier hydrocarbons, the second GC unit is used, equipped with a P-type column. This column effectively separates propane, butanes and pentanes. All hexanes and higher hydrocarbons are directed to the backflush detector, resulting in a combined peak. The DynamiQ-X NG2220 includes a third GC unit to measure permanent gases

using an M-type column. This column is used to measure hydrogen, oxygen and nitrogen [6].

The third GC unit can be used with a different carrier gas than GC units 1 and 2, as depicted in Figure 1. For this study, the carrier gas for GC units 1 and 2 was varied between helium, hydrogen and argon, while the carrier gas for GC unit 3 was argon for all measurements.

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 [6, 8]. 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 [4].

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. In contrast, argon has a lower thermal conductivity, leading to a lower signal response.

### 2.2 Sample gases

A set of ten Certified Reference Materials (CRMs), containing 13 components, was used in this study. The ranges were chosen to be representative of, or broader than, those encountered in fiscal metering of natural gas with added hydrogen up to 20%. Table 1 summarizes the concentration ranges, with the mixtures distributed approximately evenly across these ranges. The sample gases were prepared by high precision gravimetry in accordance with ISO 6142-1 [9] and calibrated with traceable comparison methods compliant with ISO 6143 [10] by the ISO 17025-accredited laboratory EffecTech [11].

**Table 1.** Component ranges.

Component	Range sample gases
Methane	65-93%
Carbon dioxide	0.1-12%
Ethane	0.1-15%
Propane	0.1-6%
2-methylpropane	0.01-1.2%
n-Butane	0.01-1.2%
2,2-dimethylpropane	0.01-0.06%
2-methylbutane	0.01-0.5%
n-Pentane	0.01-0.5%
n-Hexane (C6+)	0.01-0.25%
Hydrogen	0.01-20%
Oxygen	0.01-3%
Nitrogen	0.1-20%

## 2.3 Methodology

The DynamiQ-X NG2220 was factory-tuned and calibrated for operation with helium and argon carrier gases, for which the standard analysis time is 45 seconds. For the hydrogen-argon carrier gas combination, the carrier pressure and the backflush time of GC units 1 and 2 were reduced to account for the lower viscosity of hydrogen. In contrast, argon has a higher viscosity and a lower thermal conductivity than both helium and hydrogen. Consequently, when argon was used as the only carrier gas, the carrier pressure and backflush time were increased to shorten the retention times and sharpen the peaks. Additionally, the injection time was increased to compensate for the reduced detector response associated with argon. After calibration, each CRM was measured 10 times for every carrier gas combination.

All measurement methods were stored in the instrument's internal memory, and no hardware changes were required when switching between carrier gases. The only waiting time involved was allowing the detectors to stabilize, enabling the instrument to resume operation within 30 minutes after changing carrier gases.

## 3 Results and discussion

### 3.1 Calorific value

The calorific value (CV) was determined following ISO 6976 [12] using a combustion temperature of 15 °C, a metering temperature of 15 °C and a metering pressure of 101.325 kPa. The resulting relative errors for each carrier gas combination are given in Table 2. These errors were evaluated against the limits specified in OIML R140, which defines performance requirements for measuring systems of gaseous fuel [5]. For accuracy class A, the maximum permissible relative error is 0.50% and all CVs fall within this limit.

**Table 2.** Relative error on the calorific value.

Sample gas	Actual CV (MJ/m <sup>3</sup> )	Error (%)		
		Helium Argon	Hydrogen Argon	Argon Argon
Gas 1	25.92	0.09	-0.41	0.16
Gas 2	31.79	0.10	-0.02	-0.02
Gas 3	34.01	0.16	0.11	-0.07
Gas 4	39.29	-0.01	-0.02	0.02
Gas 5	39.31	-0.04	-0.05	0.06
Gas 6	45.47	-0.01	-0.12	-0.07
Gas 7	26.12	0.28	-0.46	0.30
Gas 8	35.88	-0.07	-0.10	-0.01
Gas 9	40.21	-0.44	-0.35	-0.44
Gas 10	45.23	-0.03	-0.14	0.06

The largest deviations occur at the extremes of the CV range, which coincide with mixtures containing the highest concentrations of some components. Nevertheless, all errors remain well within the accuracy class, and there are no substantial differences found between the different carrier gas configurations.

### 3.2 Performance evaluation – ISO 10723

ISO 10723 [7] describes a procedure for a performance evaluation of a natural gas analyzer to determine the errors and associated uncertainties on parameters such as the calorific value. In accordance with this method, the instrument response was first characterized using the ten CRMs. A Monte-Carlo simulation was then performed to construct a data set of 10.000 hypothetical, naturally occurring compositions of natural gas. For each simulated composition, the error was obtained by taking the difference between the calorific value determined from the true and measured composition.

Following the nomenclature in ISO 10723, the absolute value of the mean error in calorific value ( $|\overline{\delta CV}|$ ) and the sum of this error with its expanded uncertainty ( $|\overline{\delta CV}| + U_c(\overline{\delta CV})$ ) were determined for all three carrier gas combinations. The former can be compared to a pre-defined maximum permissible bias (MPB), while the latter can be evaluated against a maximum permissible error (MPE), depending on the application requirements.

Table 3 depicts the calculated errors and associated uncertainties. The error in calorific value for the helium-argon and hydrogen-argon carrier gas combinations are comparable. When argon is used as the sole carrier gas, the errors increase, primarily due to the lower detector response for low concentration components, particularly the C6+ fraction. However, the expanded uncertainties of all three carrier gas combinations are of similar magnitude. As a result, the sum of the error with its expanded uncertainty, which is used to assess compliance with a maximum permissible error, shows a much smaller difference between the three carrier gas configurations.

**Table 3.** Errors and uncertainties from ISO 10723 performance evaluation.

	Helium Argon	Hydrogen Argon	Argon Argon
$ \overline{\delta CV} $ (MJ/m <sup>3</sup> )	0.0019	0.0022	0.0287
$ \overline{\delta CV}  + U_c(\overline{\delta CV})$ (MJ/m <sup>3</sup> )	0.0371	0.0637	0.0853

### 3.3 Limits of detection

Due to differences in thermal conductivity between helium, hydrogen and argon, the detector response, and therefore the peak size, varies with the carrier gas. The

limit of detection (LOD) per component is calculated as three times the standard deviation of the noise, converted to concentration:

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

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.

When argon is used as the sole carrier gas, the noise level is slightly higher. Additionally, hydrocarbons show lower response factors compared to helium or hydrogen because the difference in thermal conductivity is smaller. Together, these effects negatively impact the LOD for measurements, resulting in higher values. Hydrogen behaves similarly to helium in both noise level and response factor, which explains why the LODs for hydrogen-argon and helium-argon measurements are comparable. Table 4 summarizes the limits of detection for all components per carrier gas combination used.

**Table 4.** Limits of detection (LOD) per component.

Component	Limit of detection (ppm)		
	Helium Argon	Hydrogen Argon	Argon Argon
Methane	0.3	0.2	1.1
Carbon dioxide	0.2	0.2	5.1
Ethane	0.4	0.3	2.7
Propane	0.2	0.1	0.5
2-methylpropane	0.2	0.1	0.6
n-Butane	0.2	0.1	0.7
2,2-dimethylpropane	0.3	0.2	1.2
2-methylbutane	0.3	0.2	1.3
n-Pentane	0.3	0.2	1.7
C6+	0.3	0.2	16.2
Hydrogen	0.2	0.2	0.2
Oxygen	1.6	1.6	1.5
Nitrogen	3.2	3.0	3.1

### 3.4 Carrier gas usage

The carrier gas consumption remains roughly the same across the different carrier gas combinations. Thanks to the short cycle time of only 45 seconds, the total consumption is about 15 ml per measurement. Switching from helium-argon to either hydrogen-argon or argon-argon carrier gas eliminates the use of helium, saving approximately 10 ml of helium per measurement. In fiscal metering, continuously measuring is common, corresponding to 1920 injections per day. Under these conditions, replacing helium-argon with an alternative carrier gas combination would save approximately 19.2 litres of helium per day.

## 4 Conclusion

This study assessed the DynamiQ-X NG2220 micro GC for fiscal metering of natural gas blends with hydrogen using helium-argon, hydrogen-argon and argon-only carrier gas combinations. All three setups produced calorific values within the limits of OIML R140 accuracy class A. ISO 10723 performance evaluations showed that helium-argon and hydrogen-argon carrier gases deliver nearly identical errors and uncertainties. When argon is used as the sole carrier gas, the errors increase, primarily due to the lower detector response for low concentration components. However, the combined error and expanded uncertainty remain comparable and suitable for practical use.

The analysis of the limits of detection showed that helium and hydrogen provide the strongest detector response, whereas argon yields higher LODs. Despite this, all LODs were sufficient for the concentration ranges relevant to fiscal metering. The carrier gas consumption was low for all methods and switching from helium-argon to either hydrogen-argon or argon-argon can save roughly 19.2 litres of helium per day under continuous operation.

Overall, the instrument functions reliably with all tested carrier gases without any hardware changes needed. Hydrogen provides a strong alternative to helium where safety regulations permit. Using argon as the only carrier gas is feasible with some loss in sensitivity but significant saving of helium consumption and with the benefit that only one carrier gas bottle is required.

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