GLOBAL FLOW MEASUREMENT WORKSHOP
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The Monitoring and Reporting Regulation (MRR) – Achieving Compliance through ISO 6974 and Condition Based Monitoring

Anwar Sutan, i-Vigilant Technologies
Alix Mann, Shell
Paul Daniel, i-Vigilant Technologies

1 Introduction

Article 30 of the Monitoring and Reporting Regulation (MRR) [1] requires operators to determine calculation factors either as default values or through analysis, depending on the applicable tier. For natural gas, this can be achieved by analysing sampled gas or using online gas chromatographs (GCs). When emissions are determined through gas sampling, the "1/3 rule" applies.

Tier 4 imposes the strictest uncertainty requirement of 1.5%, meaning the contribution from sampling uncertainty must not exceed 0.5% (1/3 of 1.5%). This calculation is based on the variability of sampling data but does not account for the uncertainty of the sampling system itself. In contrast, online GCs - even without undergoing an ISO 10723 performance evaluation test [2] - can achieve an uncertainty for the calorific value (CV) and emission factors of less than 0.2%, offering significantly greater accuracy.

However, due to an interpretation of Article 32 [1] the use of online gas chromatographs can lead to high compliance costs. There are even cases where operators choose not to use available online GCs for emissions determination, but instead rely on gas sampling, ultimately opting for a significantly less accurate method in order to reduce costs.

Gas chromatographs play a key role in measuring the composition that is used for the determination of emissions. The accuracy of the measurement of the gas composition is dependent on many factors such as:

1. The ability of the sample system to transport a representative sample.
2. The repeatability of the gas chromatograph.
3. The uncertainty of the calibration gas.
4. The competency of the technicians handling the calibration and operation of the GC.

The Monitoring and Reporting Regulation (MRR) [1] requires that operators using online gas chromatographs for the determination of emissions must obtain approval from the competent authority and ensure that the instruments undergo an initial validation and annually repeated validations. In most cases, the annually repeated validation is interpreted as conducting a performance evaluation test in accordance with the ISO10723 [2] standard, but based on the latest MRR and guidance documents this is no longer explicit.

This paper examines the MRR and its supporting documents, detailing a method by which the principles outlined in ISO 6974 [1] (Natural gas - Determination of composition with defined uncertainty by gas chromatography), coupled with condition based monitoring, can be used as an approach for achieving compliance with the MRR.

Furthermore, this paper highlights how utilising this method for validation not only ensures compliance with the MRR but also delivers significant advantages over both manual sampling and using solely the ISO10723 standard.

2 Definitions

The following definitions are provided by The International Vocabulary of Metrology (VIM) [4].

Calibration: An operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication.

Verification: Provision of objective evidence that a given item fulfils specified requirements

Validation: verification, where the specified requirements are adequate for an intended use.

Primary measurement standard: standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention.

Working measurement standard: standard that is used routinely to calibrate or verify measuring instruments or measuring systems.

Metrological traceability chain: sequence of measurement standards and calibrations that is used to relate a measurement result to a reference NOTE 1 A metrological traceability chain is defined through a calibration hierarchy. NOTE 2 A metrological traceability chain is used to establish metrological traceability of a measurement result.

Metrological traceability: property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty

Within this paper the term 'calibration' is used in a slightly different manner. The VIM definition of calibration does not imply an adjustment, in fact it explicitly states that calibration should not be confused with adjustment of a measuring system. However, due to the historic use of the term by GC manufacturers, the term calibration is used within this paper when the response factors (calibration coefficients) are accepted and used for measurement of future analysis cycles.

The term validation is used as per the VIM, in that the system has been verified and fulfils the specified requirement and that these requirements are adequate for the intended use. However, in the context of this paper it is implicitly assumed that the instrument is validated without undergoing any adjustment.

It is important to note that all the methods discussed within this paper ensure that fundamental metrological traceability is in place and that there is a traceability chain through a well-defined calibration hierarchy.

3 Relevant Regulation and Documentations

This section provides details of the relevant regulations and supporting documents and extracts the parts that are relevant to the validation requirements for online gas chromatographs.

3.1 Regulation (EU) No 601/2012 (Monitoring and Reporting Regulation - MRR) [3]

1. Article 32 Calculation factors based on analyses

   - Article 32-1. *The operator shall ensure that any analyses, sampling, calibrations and validations for the determination of calculation factors are carried out by applying methods based on* ***corresponding EN standards****.*

   - Article 32-2. *Where online gas chromatographs or extractive or non-extractive gas analysers are used for emission determination, the operator shall obtain approval from the competent authority for the use of such equipment. The equipment shall be used only with regard to composition data of gaseous fuels and materials****. As minimum quality assurance*** *measures, the operator shall ensure that an initial validation and* ***annually repeated validations*** *of the instrument are performed.*

2. Article 34 Use of laboratories

   - The operator shall ensure that laboratories used to carry out analysis for the determination of calculation factors are accredited in accordance with EN ISO 17025 for the relevant analytical methods.

3.2 MRR Guidance document No. 5 (7/10/2021) about Article 32 [5]

1. Section 6. Online Gas Analysers

   Article 32(2) requires the operator to obtain approval from the competent authority for the use of equipment where online gas chromatographs or extractive or non-extractive gas analysers are used for emission determination. To obtain approval the relevant information might best be addressed by using a procedure describing the equipment, the method used for sampling and analysis and the relevant standards. The use of these systems is limited to the determination of composition data of gaseous fuels and materials. As minimum quality assurance measures, the MRR requires that the operator shall ensure that an initial validation and ***annually repeated validations*** *of the instrument are performed.*

   It is recommended that the operator meets the requirements of EN ISO 9001 and that calibration services and the suppliers of calibration gases are accredited in accordance with EN ISO/IEC 17025. Also, where applicable, the initial and annually repeated validation of the instrument should be carried out by a laboratory accredited in accordance with EN ISO/IEC 17025.

   The following standard may be considered:

   - ***EN ISO 10723****: "Natural gas - Performance evaluation for on-line analytical systems".*

   - ***ISO 6974****: "Natural gas – Determination of composition with defined uncertainty by gas chromatography – Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C1 to C8 hydrocarbons using three capillary columns"*

3.3 MRR Guidance document No. 5 (7/10/2021) ANNEX III FAQ [5]

Article 32(2) gives the operator some freedom to demonstrate compliance. However, the minimum quality assurance measures for the use of online gas chromatographs are an initial validation and annually repeated validations. The approach described in section 13.5.3 of Annex I of MRG 2007 [7] is still considered appropriate for carrying out initial and ongoing validations. However, Section 9.3 of the guidance document [5] states:

Where operators seek approval by the CA using any other approach than the one provided in MRG 2007, the CA may evaluate the proposal in the light of the hierarchy in Article 32(1):

- *Apply methods based on corresponding EN standards,*

- *Where applicable standards are not available, the methods shall be based on suitable ISO standards or national standards.*

3.4 Conclusion from the relevant regulation and documents

From the relevant documents above, the following main points may be summarised:

1. As minimum quality assurance measures, Online gas chromatographs are subject to initial validation and annually repeated validation.

2. Validations are to be carried out by applying methods based on corresponding EN standards.

3. **EN ISO 6974** [3] and EN ISO 10723 [2] can be considered

Points of clarification with respect to the latest Guidance document (No. 5 (5/10/2021)) [5]:

1. *It is recommended that the operator meets the requirements of EN ISO 9001 and that calibration services and the suppliers of calibration gases are accredited in accordance with EN ISO/IEC 17025. Also, where applicable, the initial and annually repeated validation of the instrument should be carried out by a laboratory accredited in accordance with EN ISO/IEC 17025.*

   The recommendation that calibration gases are supplied by an ISO/IEC 17025 [7] accredited laboratory is to ensure traceability and that the specified uncertainty of the composition is achieved with a good level of confidence. Where instruments are returned to laboratories for calibration, the recommendation to, "*where applicable*", select ISO17025 accredited laboratories also makes good sense.

   The GC calibration can be performed at the location of the gas chromatograph using gases supplied from an ISO 17025 laboratory which ensures that the chain of traceability remains intact. The recommendation that the calibration activity be undertaken by an ISO 17025 accredited laboratory only really makes sense and hence is only generally applicable if the device is returned to a laboratory. Instruments are not normally calibrated on-site by an ISO 17025 laboratory. The references, such as pressure gauges, dead weight testers, temperature probes, working reference gas mixtures (often called calibration gases) are calibrated by an accredited laboratory but used on site by competent site personnel. This is essentially the chain of calibration traceability, from primary standards, secondary standards through to working standards. The calibration gas on site is a Working Reference Mixture, in that is supplied with a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

   Like all other instruments calibrated in the field, it is important that the calibration of a Gas Chromatograph is performed by competent persons using suitably traceable working reference standards. Provided this is achieved the requirement of the MRR has been clearly met along with the recommendations of the latest guidance.

4 The use of ISO 6974 to Demonstrate Compliance with MRR

ISO 6974 [3] is a key standard for the determination of composition and associated uncertainty by gas chromatography, particularly for the analysis of natural gas and similar mixtures. It provides detailed guidelines to ensure the accuracy, precision, and repeatability of the GC system, which are critical for performance validation.

ISO 6974-1 [8] outlines the methodology for determining the mole composition of natural gas using gas chromatographic methods described in ISO 6974-3 and subsequent parts. It also provides essential guidance for setting up the analysis, including defining the structure of the method, establishing working ranges, and setting analytical procedures.

ISO 6974-2 [9] focuses on calculating the uncertainty of the component mole fractions of natural gas determined through gas chromatography.

By integrating the procedures outlined in ISO 6974-1 and ISO 6974-2, a robust method for GC validation is established, enabling the determination of the composition and uncertainty of the GC measurement.

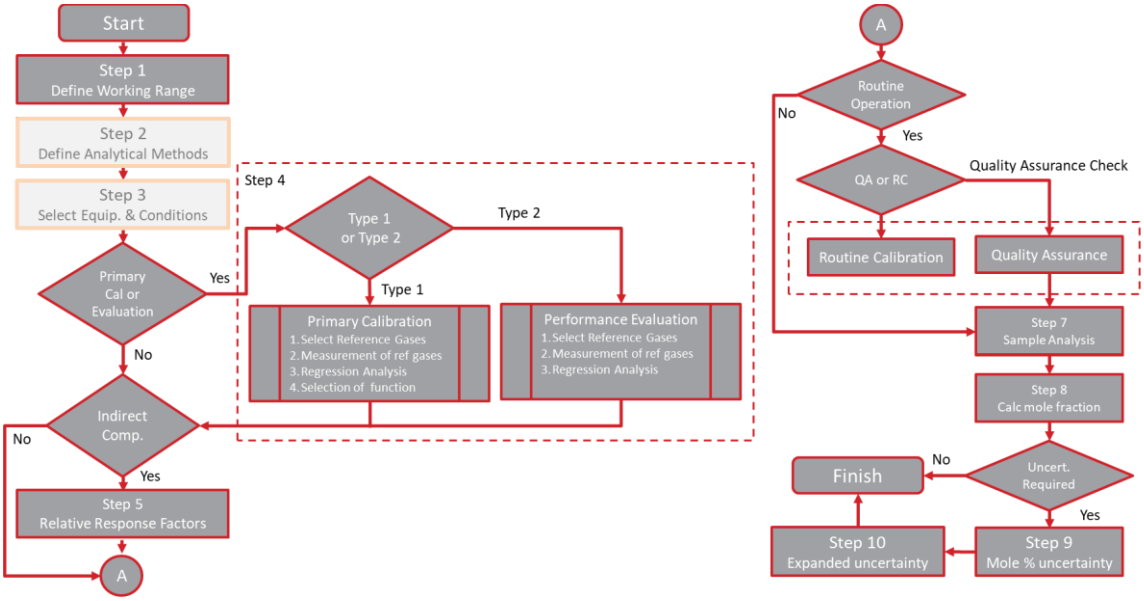

Figure 1. ISO 6974-1 and ISO 6974-2 flow chart

Figure 1 above shows the flow chart from ISO 6974. Steps 2 and 3 are key for design phase to ensure the correct analytical method is selected. Once the device has been selected and installed in the field this process has already been completed and a suitable online gas chromatograph is in use.

This document will now outline the key steps defined in ISO 6974-1 and ISO 6974-2, demonstrating how this method ensures full compliance with these standards. All data presented in this section is sourced from measurements taken from the GC at Bacton Gas Plant (BGP).

4.1 Define the Working Range

When a GC is used, the gas composition is continuously determined and therefore the maximum and minimum concentration measured for each component over the previous year can normally be used to identify the working range of the gas chromatograph (GC). Based on historical data from 1/9/2024, to 1/11/2024, the following ranges for gas composition were observed:

Description	GC Working Range	
	Min	Max
Methane	87.1328	93.2464
Nitrogen	0.9156	3.4488
CO_2	0.6487	1.7910
Ethane	3.2019	6.2647
Propane	0.7164	1.8259
i-Butane	0.1376	0.2754
n-Butane	0.1374	0.2767
Neopentane	0.0000	0.0241
i-Pentane	0.0409	0.0913
n-Pentane	0.0375	0.0704
Hexane	0.0622	0.1246

Table 1. BGP GC Working Range

4.2 Primary Calibration / Performance Evaluation (ISO 10723)

The following statement is taken directly from ISO 6974: *"If a primary calibration or performance evaluation is not required, and if the analyser will be used for routine operation, proceed to a quality assurance (QA) check or routine calibration".*

ISO 6974 then defines the frequency required to perform primary calibration or performance evaluation in the following situations:

1. Immediately following initial installation of the system by the supplier

   For a brand-new GC, it is clear that a performance evaluation or primary calibration is required to determine the performance of the GC and so an ISO10723 evaluation is suitable. Following the initial ISO 10723 performance evaluation or primary calibration, as well as any subsequent evaluations or calibrations, a comparison can be made between the mole composition results from single-point calibration and multilevel calibration. This allows for an assessment of the impact of the GC's non-linearity on gas composition measurements.

2. Immediately following return to operation after replacement of a major part of the system, e.g. injection valve, column or detector

   If we consider as an example, the Emerson model 500 GC, a major part would be the detector. The replacement of a valve and column, as long as it can be proven that this does not change the peak area detected, does not change the calibration in a manner that would require an ISO 10723 performance evaluation. This can be checked by comparing the calibration result against the initial footprint prior to changing the valve or column. The initial footprint here is a record of the GC performance taken when the GC is known to be in a healthy condition.

3. Immediately following return to operation after failure to pass a QA check of the system

   The proposed monitoring strategy involves calibration of the GC on a daily basis using an ISO17025 certified reference mixture. If this method is used to monitor the GC, the QA check is not relevant as the GC is being calibrated on daily basis. To enhance the monitoring of the performance of the GC, the proposed monitoring strategy calculates the uncertainty of each component from the daily calibration results and in turn establishes the uncertainty of the CV and/or the emission factor. This method ensures that the GC performs within its required tolerance at all times.

4. At intervals that have been demonstrated to be appropriate for the application, e.g. no longer than 12 months

   The ISO 6974 standard requires primary calibration or performance evaluation to be conducted at intervals that have been demonstrated to be appropriate, e.g. no longer than 12 months. However, this period is only an example provided by the standard and is not a recommendation nor strict requirement.

The determination of when a primary calibration is required can be readily determined from the Routine Calibrations using condition-based monitoring, maintaining control charts for each component and establishing the uncertainty of each component and the key parameters of CV and emission factor

When deciding whether to implement the Multi-Level Calibration (MLC) constant (primary calibration) or rely solely on Type 2 analysis (performance evaluation), the choice should be based on technical considerations. Primary calibration (applying the MLC constant from performance evaluation to the GC) is necessary if there is non-linearity evident in the instrument over its working range, which will introduce a bias that is significant.

Determining the bias in each component and its impact on key measurements is not trivial. ISO 10723 addresses this by employing Monte Carlo simulations to estimate the distribution of errors in the normalised mole fractions. The mean of this distribution represents the overall bias for each measurand across the specified measurement range.

In the example illustrated in Figure 2 below, the reference gas range for methane used in the ISO 10723 performance evaluation spans from 63.63% to 98.49%. A Monte Carlo simulation conducted over this range yields a mean error of -0.01 MJ/m³, with an associated uncertainty of ±0.087 MJ/m³. The absolute mean error plus its uncertainty results in a total of 0.097 MJ/m³.

Given that the Maximum Permissible Error (MPE) typically used is 0.1 MJ/m³, the instrument's performance in this case is considered acceptable.

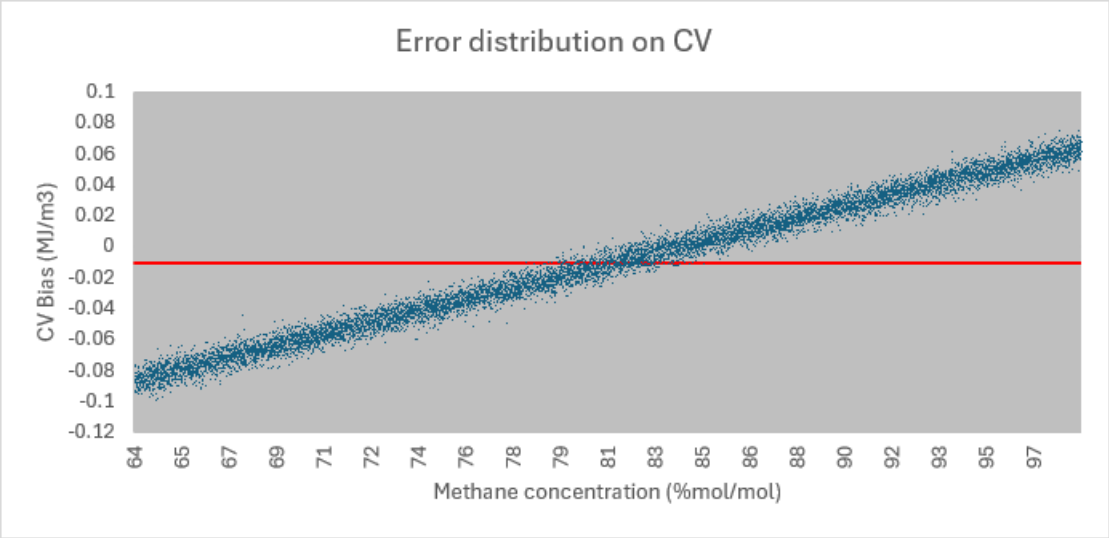

Figure 2. Error distribution example

However, although the overall mean error appears small, its impact can be more significant in practice. If the gas chromatograph (GC) typically operates in a narrower range—such as between 95% and 97% methane—the error becomes more concentrated and consistently exceeds 0.04 MJ/m³, corresponding to a 0.1% error on a 40 MJ/sm³ calorific value.

Rather than relying on Monte Carlo-simulated compositions to estimate the mean error as prescribed in ISO 10723, it is proposed here to determine the bias introduced into the GC measurement using the actual gas compositions encountered during operation. Table 2 below shows comparison between gas composition from single-point and multi-level calibrated GC taken from BGP GC.

Component	Single-pt	MLC	Difference
Methane	91.3284	91.3429	0.0145
Nitrogen	1.1397	1.1398	0.0001
CO_2	1.5174	1.5158	-0.0017
Ethane	4.1565	4.1475	-0.0090
Propane	1.1390	1.1377	-0.0013
i-Butane	0.2664	0.2638	-0.0026
n-Butane	0.2257	0.2261	0.0004
Neopentane	0.0000	0.0000	0.0000
i-Pentane	0.0729	0.0728	-0.0001
n-Pentane	0.0521	0.0520	0.0000
Hexane	0.1018	0.1017	-0.0001
CV (MJ/sm3)	39.3127	39.3079	-0.0048
CV (% discrepancy)			-0.012%

Table 2. Single-pt vs MLC composition

Figure 3 below illustrates an example where the calorific value (CV) from both a single-point and a multi-level calibrated GC are tracked, revealing a bias of just 0.013% (equivalent to 0.005 MJ/m³) attributable to GC non-linearity. This is well within the ISO 10723 tolerance of 0.1 MJ/m³. If the gas composition were to shift in a way that increases this bias, the method would detect it, enabling the development of a new calibration gas mixture based on an analysis of historical composition data.

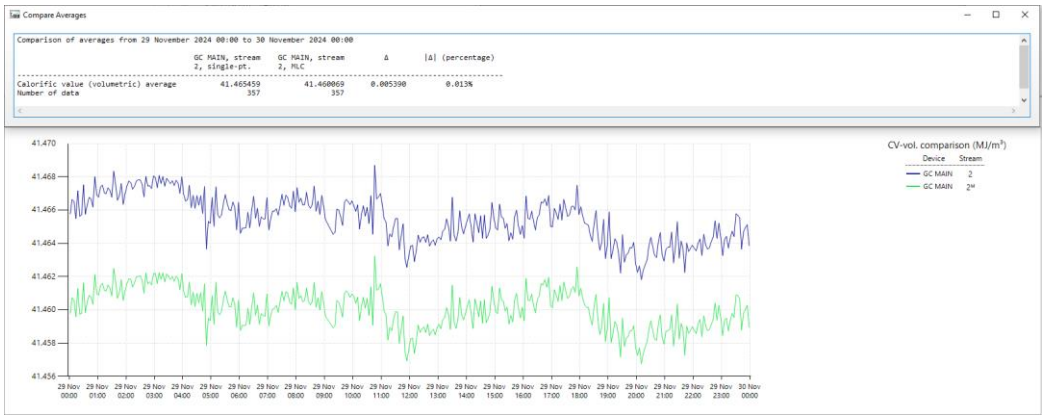

Figure 3. Bias due to GC non-linearity (MLC vs single point calibrated CV)

The following BGP GC measurement data compares the calorific value (CV) calculated using the MLC constant with the CV derived from measurements using single-point calibration. The chart below (Figure 4) clearly illustrates that the bias across the GC's working range is negligible in this case.

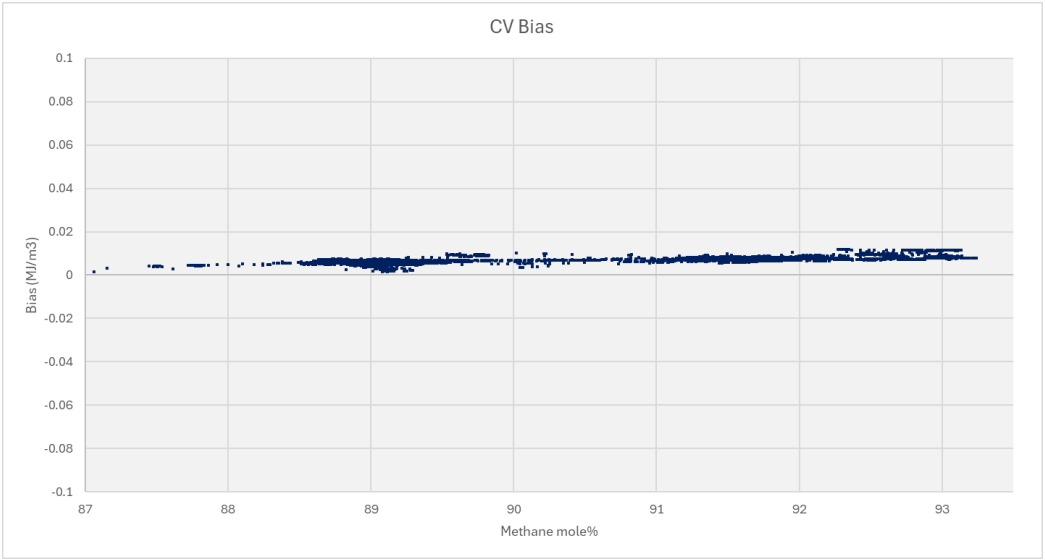

Figure 4. GC Bias across working range

The chart shown in Figure 4 above illustrates the bias in GC measurements when the MLC constant is not applied compared to the "true" function. The average bias is 0.007 MJ/m³ (0.017%), well within the allowable limit of 0.1 MJ/m³ provided in ISO10723 calibration report. This confirms that the bias resulting from GC non-linearity is negligible, making primary calibration unnecessary for this GC.

Further tests were conducted using the MLC constants from the last four ISO 10723 performance evaluation tests. The results were very similar as shown in Figure 5 below.

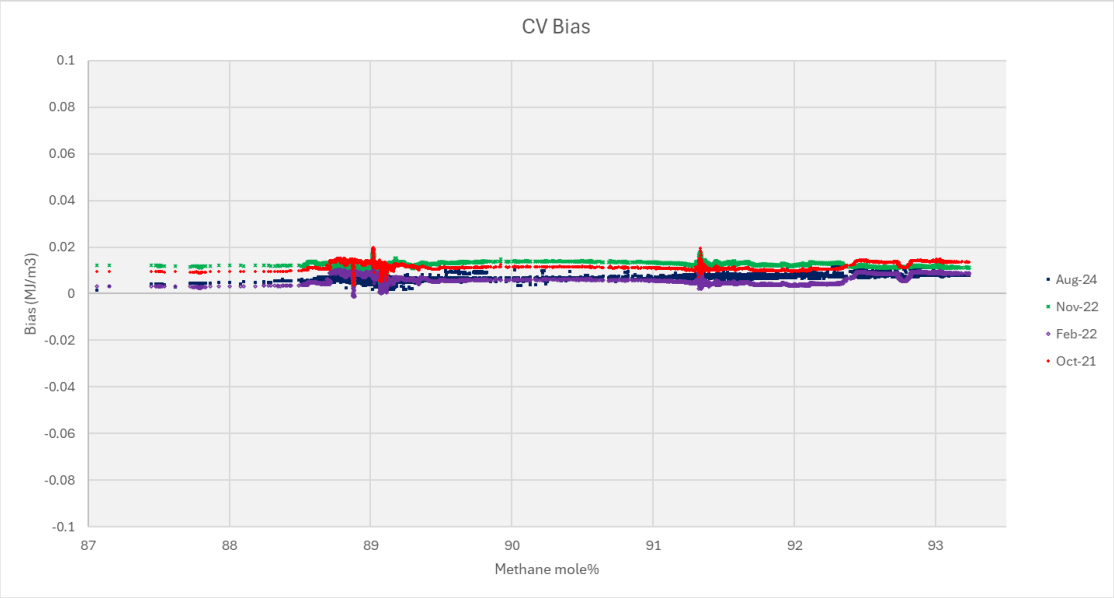

Figure 5. GC Bias across working range using MLC constants from last four ISO10723 performance evaluations

In this case there is no tangible benefit in performing the ISO 10723 performance evaluation test on a yearly basis because the instrument is linear, reproducible and no major components have been replaced. The proposed method of daily calibration, component control charts, component uncertainty calculations and CV uncertainty calculations will detect any drift of the GC. This continuous monitoring of the GC calibration performance provides daily validation which can identify the need to perform ISO 10723 on an as-required basis.

Given these factors, the ISO 10723 test interval can be extended to a point where the monitoring of the Routine Calibration as detailed above highlights a shift in the instrument, or a major GC component has been replaced. Otherwise, it is recommended that a maximum five-yearly ISO 10723 performance evaluation frequency be adopted.

The Annual validation required by MRR is accomplished by the generation of a yearly performance analysis report based on the GC calibration performance (using ISO 17025 certified calibration gas).

4.3 Relative Response Factors

In BGP, the pentanes and C6+ components are measured indirectly. The relative response factor of BGP GC are as follows:

Component	Rel Resp Factor	Reference component
Neo-Pentane	0.85	Propane
i-Pentane	0.8	Propane
n-Pentane	0.8	Propane
C6+	0.65	Propane

Table 3. BGP GC relative response factor

4.4 Routine Calibration / Quality Assurance

ISO 6974 recommends undertaking a quality assurance check or routine calibration periodically. Whilst the length of time is not specified, this can be daily, every two days, or weekly. This serves as an additional form of validation. Typically the GC will perform a simple check with limits used based on the deviation from the previous calibration. However, the method discussed here undertakes a series of more rigorous checks.

The method involves two simple steps. Step 1 is to ensure that the Response Factor (RF) is generally in ascending order when arranged from light components to heavy components. The following is the RF trend from BGP GC from 24/2/2025 shown in Figure 6 below clearly shows ascending trend:

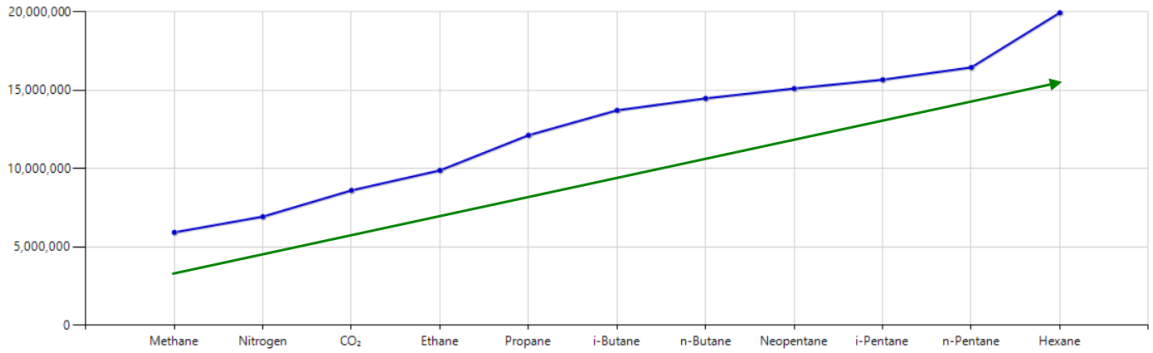

Figure 7. Response factor trend showing ascending

Step 2 involves comparing the current calibration results with those from a previous calibration when the GC was confirmed to be operating optimally (footprint). For example, the following shows the BGP GC calibration result from 1/4/2025 (red) compared to the calibration footprint from 24/2/2024 (blue).

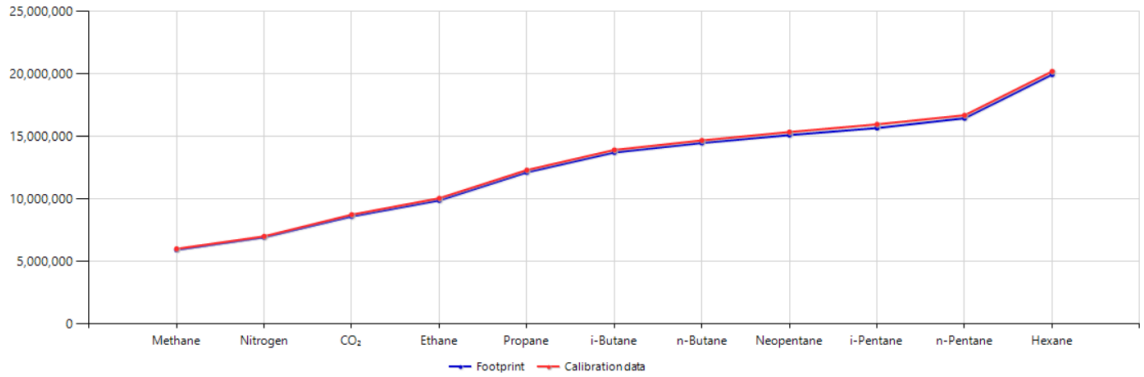

Figure 8. Daily calibration data vs footprint

The trend above clearly shows that there has been no significant shift in the calibration results, indicating that the GC calibration parameters are stable.

Additionally, the trend helps safeguard against the use of faulty calibration gases, this is a common issue especially in colder areas. Condensation of the calibration gas may happen within the bottle, and this can cause the gas mixture composition to change and therefore not representative of the calibration gas certificate. When condensation happens, the response factor of the heavier components will drop. This type of problem would not be detected by a performance evaluation test as this happens on the day-to-day operation of the GC.

In the example below (not from BGP GC), GC was calibrated using a stratified calibration gas due to cold weather. The RF of the neopentane, i-pentane, n-pentane and hexane are clearly lower than expected as the RF trend is not ascending anymore. Accepting this calibration result will cause a bias of £3.9 million per year (on the production of 100 mmscfd) had the proposed monitoring system not been in place and the issue went undetected. The calibration performed using stratified calibration gas when compared to initial footprint is shown below:

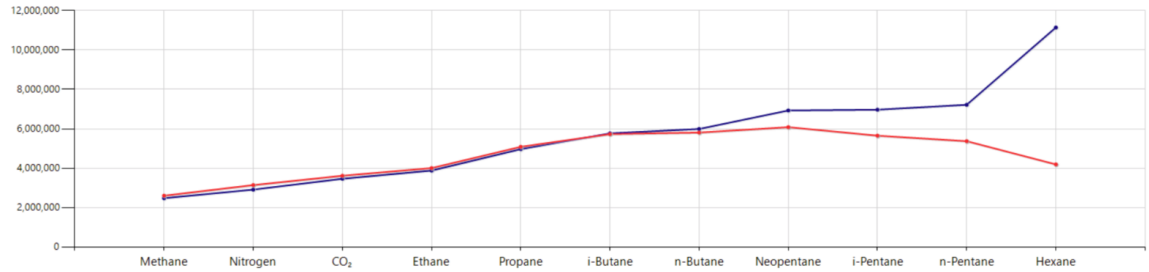

Figure 9. Bad calibration data vs footprint

On Figure 9 above, the blue line represents the expected calibration result (footprint), while the red line shows the calibration result after the new calibration gas was installed. In this case, the issue arose because the new calibration gas had been stored in a cold environment, causing stratification within the bottle. The proposed method of monitoring the system immediately flagged this issue, allowing for an informed decision not to use the new calibration gas. Despite the gas being supplied from an ISO 17025 accredited

laboratory, it was determined to be unfit for use due to its compromised quality brought about by incorrect handling.

The above method is effective for spot checks, but for long-term monitoring, the proposed method uses control charts. The chart below illustrates how the variation in response factors (RF) from the calibration footprint is tracked. Since the GC is a system where each component is correlated, there should be synchronous variation in the RF shifts. For example, the trend below demonstrates excellent GC performance, with synchronous RF variation across all components.

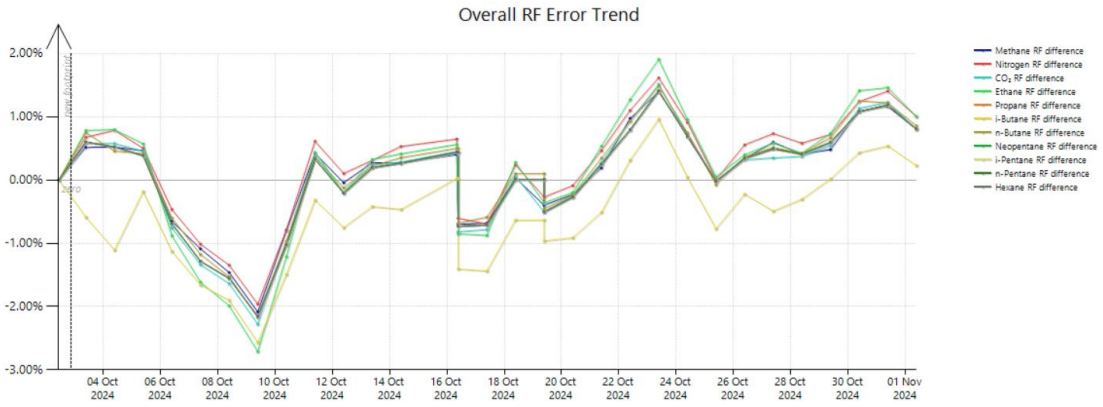

Figure 10. RF control chart

The above chart provides a qualitative overview of the GC's performance. However, relating the relative fluctuation in a component to the impact this has on the determination of the required parameter (CV / Emission Factor) is not straight forward. For example, a large relative deviation in a component that is very small would tend to have a smaller impact. The data can be analysed quantitatively and used to present the uncertainty associated with the desired GC parameter.

4.5 Sample Analysis and Calculation of Component Mole Fractions

As the sample has been taken from a source where the gas may change with time (natural-gas pipeline), it is not possible to carry out repeat analyses of the gas sample. The standard says that the analyser shall be operated under statistical control and the standard deviation predetermined in order to be able to calculate the uncertainties of the component mole fractions. Using this method, this is done on a component level by analysing daily calibration results, utilising the footprint to determine the variance of each normalised component over time which can then be presented as an uncertainty of each of the component mole fraction.

4.6 Mole% Uncertainty

The calculation of uncertainty of the mole% is described in ISO 6974-2:2012. The uncertainty is calculated by running a known gas composition such as described in ISO 10723:2012. This method instead calculates the uncertainty based on the reproducibility of the daily calibration results. RF values, such as those shown in the Figure 10 trend, are converted into a long-term uncertainty value for the GC. This can be used to monitor its ongoing performance. Below is the uncertainty trend for each mole component of the BGP GC.

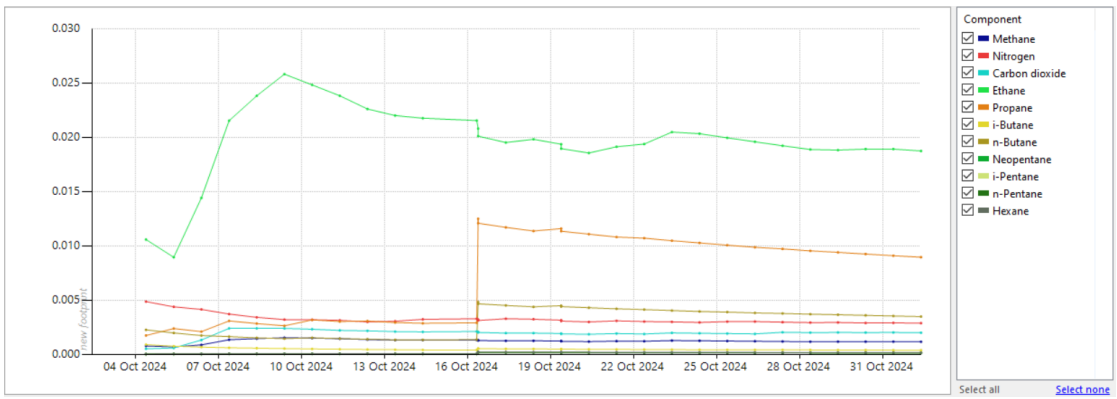

Figure 11. BGP GC Mole composition uncertainties

4.7 Expanded Uncertainty of Calorific Value (CV)

The expanded uncertainty of the calorific value (CV) is then derived from the individual mole% composition uncertainty. Figure 12 below shows the CV expanded uncertainty trend derived from the individual mole% uncertainty.

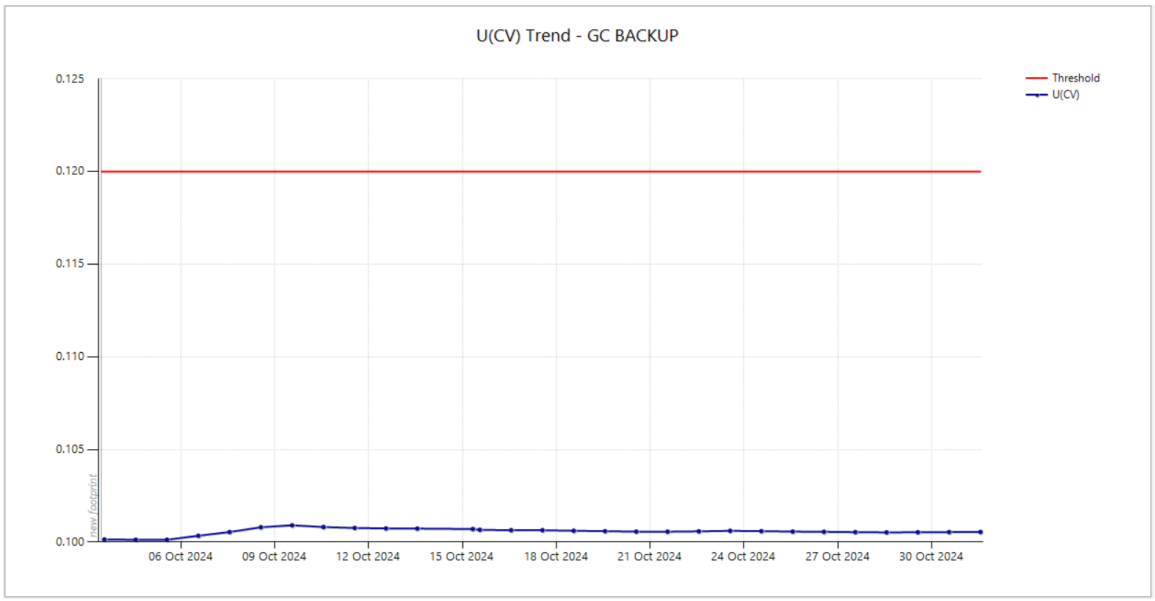

Figure 12. BGP GC CV uncertainty

This is a very powerful tool for GC validation, as it monitors the performance of the GC based on its true uncertainty, derived from the actual variation in the device determined during calibration with an ISO 17025 certified calibration gas. Alarm settings can be configured according to the GC's inherent capabilities. Figure 13 illustrates how this system can provide an early indication of GC failure. In this case the method detected an issue two months before the actual failure occurred, which led to maintenance (in this case, a diaphragm replacement).

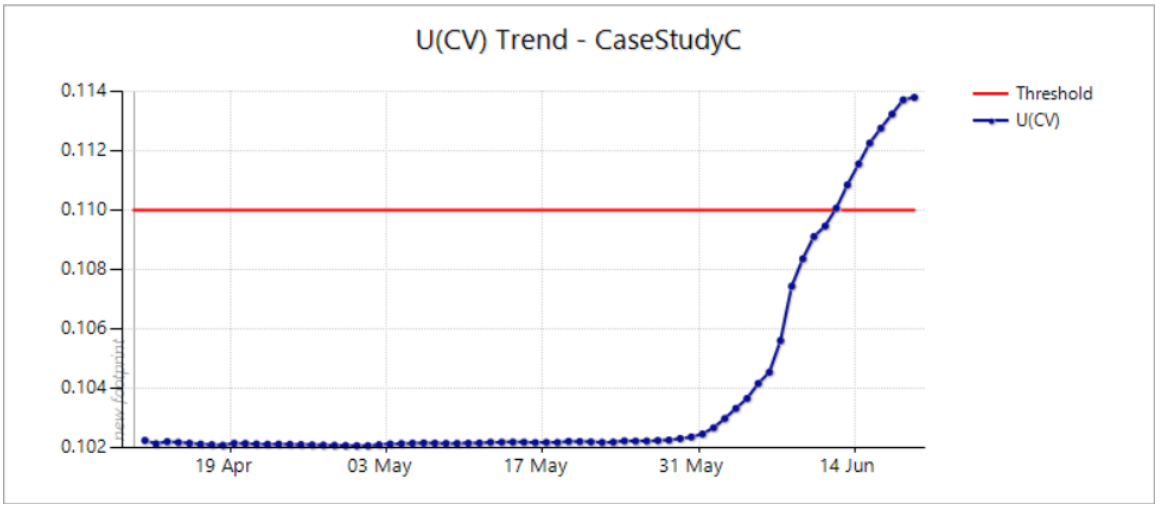

Figure 13. Example of how uncertainty is used to detect issue with GC

This process is automatically handled by this method using software. When the uncertainty reaches the alarm limit, the user is notified, prompting corrective action to be taken to address the issue. This notification serves as a trigger for performing maintenance on the GC. It is important to note that, in most cases, when this method alerts the user that something is wrong with the GC, the device is still operating within the permissible uncertainty limit for ETS reporting. This early warning system allows for intervention before the GC fails completely.

The above steps demonstrate how this method automatically collects data from the GC and fulfils all requirements outlined in ISO 6974-1 and ISO 6974-2 as shown in flow chart in Figure 1. Table 4 below shows the summary of which section in this paper corresponds to which step in the ISO 6974 flow chart.

Step in ISO6974	Section in this paper
Step 1 (ISO 6974-1) – Define working range	Section 4.1 – Define the Working Range
Step 2 (ISO 6974-1) – Define analytical methods	Analytical method has already been established – outwith the scope of this paper
Step 3 (ISO 6974-1) – Select equipment and conditions	Equipment and condition has already been established – GC measuring natural gas
Step 4 (ISO 6974-1) – Response characteristics (primary calibration or performance evaluation)	Section 4.2 – Primary Calibration / Performance Evaluation (ISO 10723)
Step 5 (ISO 6974-1) – Relative response factors	Section 4.3 - Relative Response Factors
Step 6 – (ISO 6974-1) Routine calibration / quality assurance check	Section 4.4 – Routine Calibration / Quality Assurance
Step 7 (ISO 6974-1) - Sample analysis	Section 4.5 - Sample Analysis and Calculation of Component Mole Fractions
Step 8 (ISO 6974-1) – Calculation of component mole fractions	Section 4.5 - Sample Analysis and Calculation of Component Mole Fractions
Step 9 (ISO 6974-2) – Calculation of uncertainty of mole fractions	Section 4.6 - Mole% Uncertainty
Step 10 - Calculation of the expanded uncertainty of mole fractions	Section 4.6 - Mole% Uncertainty and section 4.7 - Expanded Uncertainty of Calorific Value (CV)

Table 4. Summary of compliance with ISO 6974-1 and ISO 6974-2

With this method, the GC's health is continuously validated in compliance with ISO 6974 [3], and therefore in compliance with the MRR requirements [1] [5]. Not only is the annual validation performed as required, but enhanced checks are performed on a daily basis, using an ISO 17025 certified calibration gas, ensuring strict adherence to the metrological traceability chain and ongoing compliance and optimal GC performance.

A yearly analysis of GC performance is recommended to be conducted to supplement the daily validation in order to demonstrate the performance across the year, and to demonstrate that no shift has occurred and whether an ISO 10723 performance evaluation should be undertaken. This annual analysis is proposed as the method for annual validation, providing a more robust, efficient and cost-effective approach to ensure continued compliance and optimal GC performance.

5 Other Supporting Features

Other than the full compliance with the ISO 6974, this method also provides additional features for GC validations as follows:

1. Duty – Standby GC comparison

   Where two GCs have been installed in a duty/standby arrangement, this method can compare GC data and see how close the agreement between the two GCs is. This traditional limit for action is a discrepancy of 0.05% of CV result. This is much better than the requirement of 0.1 MJ/sm3 (approximately 0.25% of 40 MJ/sm3 CV).

   The following is example taken from BGP GC comparing duty and standby GC.

Figure 14. Duty / Standby GC CV comparison on BGP

The discrepancy of the average data between the duty and standby GC as shown in Figure 14 is 0.03% (0.0014 MJ/sm3). The comparison between the two GCs can also be used as a cross check. If there is a significant discrepancy (>0.05%), then one of the GCs has an issue and this can prompt alarm for troubleshooting.

Comparing the two GCs may also provide cost-saving opportunities by allowing performance evaluation testing to be conducted on one GC, while the other is cross-validated by comparing its data against the tested GC.

2. Spot sample data comparison

This method also performs a comparison of spot samples on component level as well as on the calculated parameters (including the emission factor). The manual sample results are entered into the software, with the time and date of the sample and a comparison undertaken.

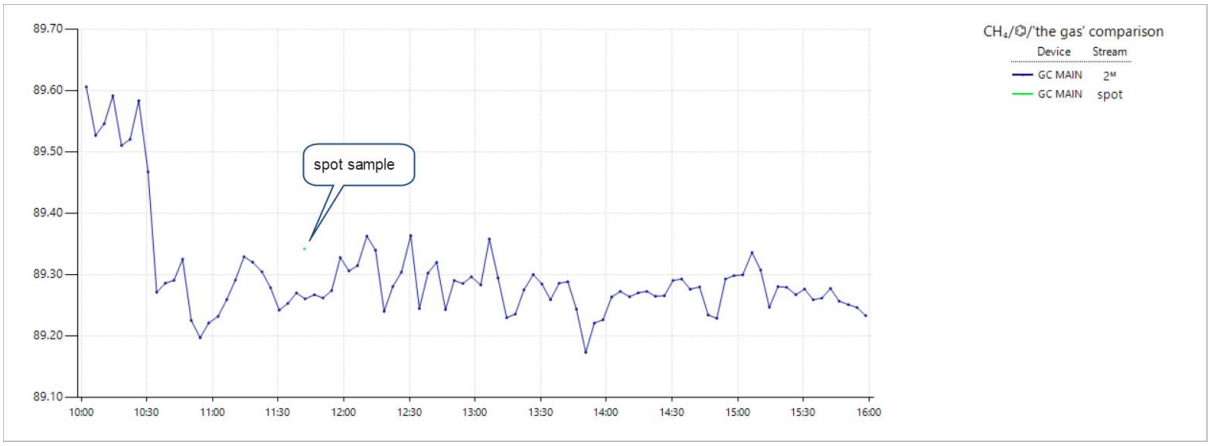

Figure 15. Trend of Methane from BGP GC vs spot sample result

The result of the spot sample can then be compared side by side against the GC reading taken at the same time. The tolerance for each component is normally based on the reproducibility limits specified by ASTM D1945 standard. Comparison of data from 15/8/2023 is shown in Figure 16 below.

Input/Output	GC MAIN, stream [Spot Sample], from 15/08/2023 11:38 to 15/08/2023 11:49	GC MAIN, stream 2, MLC, from 15/08/2023 11:38 to 15/08/2023 11:49	Δ	Δ (percentage)	[Editable] |Δ| limit (0 = disable)	[Editable] |Δ|% limit (0 = disable)
Methane	89.341472	89.310050	-0.031422	-0.035%	0.1500	0.1680%
Nitrogen	1.168944	1.143178	-0.025767	-2.254%	0.1000	8.7475%
Carbon dioxide	1.275967	1.271241	-0.004726	-0.372%	0.1000	7.8663%
Ethane	5.994453	6.037676	0.043223	0.716%	0.1200	1.9875%
Propane	1.630841	1.644854	0.014012	0.852%	0.1000	6.0796%
i-Butane	0.204943	0.206177	0.001234	0.598%	0.0700	33.9515%
n-Butane	0.248652	0.246150	-0.002502	-1.016%	0.0700	28.4379%
Neopentane	0.002501	0.000000	-0.002501	-∞	0.0200	0.0000%
i-Pentane	0.050911	0.053269	0.002359	4.428%	0.0200	37.5451%
n-Pentane	0.037508	0.040539	0.003031	7.477%	0.0200	49.3353%
Hexane	0.043809	0.046867	0.003058	6.525%	0.0200	42.6739%
Heptane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Octane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Nonane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Decane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Z (compressibility)	0.997000	0.996995	-0.000006	-0.001%	0.0000	0.0000%
CV (volumetric) • MJ/m³	42.330666	42.371273	0.040607	0.096%	0.0000	0.0000%
Molar mass composition	18.110171	18.118990	0.008819	0.049%	0.0000	0.0000%
Wobbe index	53.467324	53.505426	0.038102	0.071%	0.0000	0.0000%
Relative density	0.626806	0.627115	0.000309	0.049%	0.0000	0.0000%
Standard density	0.810412	0.810812	0.000400	0.049%	0.0000	0.0000%
CV (mass-based) • MJ/kg	47.098511	47.121493	0.022982	0.049%	0.0000	0.0000%
Mass of CO_2 • g/mol	48.423958	48.476795	0.052837	0.109%	0.2424	0.5000%
Emission factor • t·CO_2/t·	2.673854	2.675469	0.001615	0.060%	0.0134	0.5000%
Emission factor • t·CO_2/TJ	56.771526	56.778102	0.006576	0.012%	0.2839	0.5000%
Emission factor • m³/kmol	22.346866	22.346732	-0.000134	-0.001%	0.1117	0.5000%
Emission factor • kg·CO_2/m³	2.166924	2.169301	0.002377	0.110%	0.0108	0.5000%
Emission factor • t·CO_2/m³	0.002167	0.002169	0.000002	0.110%	0.0000	0.5000%

Figure 16. Spot sample vs GC reading using ASTM D1945 reproducibility limit

The limit is user configurable. For example BGP have used different limits as follows:

- Concentration less than 1%: ±0.02 mol%
- Concentration more than 1%: ±0.2 mol%

Figure 17 below shows the updated tolerance as per BGP requirements showing no alarm.

Input/Output	GC MAIN, stream [Spot Sample], from 15/08/2023 11:38 to 15/08/2023 11:49	GC MAIN, stream 2, MLC, from 15/08/2023 11:38 to 15/08/2023 11:49	Δ	Δ (percentage)	[Editable] |Δ| limit (0 = disable)	[Editable] |Δ|% limit (0 = disable)
Methane	89.341472	89.310050	-0.031422	-0.035%	0.2000	0.1680%
Nitrogen	1.168944	1.143178	-0.025767	-2.254%	0.2000	8.7475%
Carbon dioxide	1.275967	1.271241	-0.004726	-0.372%	0.2000	7.8663%
Ethane	5.994453	6.037676	0.043223	0.716%	0.2000	1.9875%
Propane	1.630841	1.644854	0.014012	0.852%	0.2000	6.0796%
i-Butane	0.204943	0.206177	0.001234	0.598%	0.0200	33.9515%
n-Butane	0.248652	0.246150	-0.002502	-1.016%	0.0200	28.4379%
Neopentane	0.002501	0.000000	-0.002501	-∞	0.0200	0.0000%
i-Pentane	0.050911	0.053269	0.002359	4.428%	0.0200	37.5451%
n-Pentane	0.037508	0.040539	0.003031	7.477%	0.0200	49.3353%
Hexane	0.043809	0.046867	0.003058	6.525%	0.0200	42.6739%
Heptane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Octane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Nonane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Decane	0.000000	0.000000	0.000000	0.000%	0.0200	0.0000%
Z (compressibility)	0.997000	0.996995	-0.000006	-0.001%	0.0000	0.0000%
CV (volumetric) • MJ/m³	42.330666	42.371273	0.040607	0.096%	0.0000	0.0000%
Molar mass composition	18.110171	18.118990	0.008819	0.049%	0.0000	0.0000%
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Relative density	0.626806	0.627115	0.000309	0.049%	0.0000	0.0000%
Standard density	0.810412	0.810812	0.000400	0.049%	0.0000	0.0000%
CV (mass-based) • MJ/kg	47.098511	47.121493	0.022982	0.049%	0.0000	0.0000%
Mass of CO_2 • g/mol	48.423958	48.476795	0.052837	0.109%	0.2424	0.5000%
Emission factor • t-CO_2/t	2.673854	2.675469	0.001615	0.060%	0.0134	0.5000%
Emission factor • t-CO_2/TJ	56.771526	56.778102	0.006576	0.012%	0.2839	0.5000%
Emission factor • m³/kmol	22.346866	22.346732	-0.000134	-0.001%	0.1117	0.5000%
Emission factor • kg-CO_2/m³	2.166924	2.169301	0.002377	0.110%	0.0108	0.5000%
Emission factor • t-CO_2/m³	0.002167	0.002169	0.000002	0.110%	0.0000	0.5000%

Figure 17. Spot sample vs GC reading using BGP contractual tolerance

The spot sample vs GC inter-comparison is also specified in the MRR. When combined with full compliance of ISO 6974, this additional test further strengthens the validation process, establishing a comprehensive and robust framework for assessing GC performance.

6 Conclusion

This paper has introduced a method for monitoring the performance of Gas Chromatographs and demonstrated that all MRR and associated guideline requirements as described in section 3 can be met by following EN ISO 6974. The method described helps ensure easy demonstrable compliance with ISO 6974 and, by extension, the MRR requirements. By automating data collection and analysis from the GC, this method not only fulfils the key provisions of ISO 6974-1 and ISO 6974-2, but also includes continuous performance validation, response factor variation monitoring, uncertainty assessment and a clear auditable history of instrument performance.

This method of using daily validation provides real-time, continuous assessments of GC health. Furthermore, a yearly analysis of the data, conducted alongside the daily validation, can provide an effective annual validation. In line with EN ISO 6974 it is recommended that an ISO 10723 performance evaluation test is conducted initially to demonstrate the instrument linearity, following the replacement of a major part, if the routine daily or annual validation indicates such a requirement, or if 5 years has lapsed.

Additionally, the methods advanced validation features, such as duty/standby GC comparisons and GC data cross-validation against spot samples, further enhance the robustness of the GC validation framework, ensuring greater accuracy and reliability in performance monitoring.

This approach not only meets regulatory standards but also improves efficiency and reduces costs. This method ensures that the GC performance remains in compliance, enables early issue detection, and optimizes overall system reliability.

7 References

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[9] BS-EN-ISO 6974-2;, “Natural gas — Determination of composition and associated uncertainty by gas chromatography Part 2: Uncertainty calculations,” *ISO,* 2012.

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