

Gas Chromatography – Conditional Based Monitoring and Live Uncertainty Calculation

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1 INTRODUCTION

On-line gas chromatography is now commonplace in the North Sea and is frequently used within Fiscal and Custody Transfer measurement systems. The uncertainty of the analysis from the gas chromatograph (GC) is of the utmost importance with the resultant analysis frequently at the core of economic transactions [1].

In recent years there has been a lot of interest in condition based monitoring (CBM) and in-situ verification of measurement devices. However, perhaps surprisingly, it would be reasonable to state that although the correct functioning of the GC is critical in today's measurement systems, comparatively little attention has been paid to verification and monitoring strategies [2, 3, 4, 5].

The modern gas chromatograph is an extremely repeatable device however there remains several fundamental issues. For example, if the valve timing in the GC is wrong or drifts over time a systematic error can ensue. A recent study performed by the author identified a situation where such an error was present, and if it remained undetected, would have resulted in an on-going error in the calorific value of up to 1.4%. This error would equate to a value of more than £300,000 per month based on a production of 100 mmscfd.

Under the assumption of suitable sampling and conditioning the uncertainty of the GC measurement is generally driven by the repeatability of the GC and the quality of the (certified) working reference mixture (WRM). Various methods presently exist which may be used to obtain the GC repeatability. ISO 10723 [6] describes a method of performance evaluation using multiple calibration gas compositions to obtain the linearity of the GC as well as its repeatability. However, this method is only valid as long as the GC maintains the performance characteristics measured on the day of the test. ASTM D1945 [7] provides a standard test method for the analysis of gas with a GC using stated levels for the expected repeatability and reproducibility. ISO 6974 [8], following similar principles detailed in ISO 10723, describes data processing for the tailored analysis of natural gas with the aim of defining the uncertainty in the mole fractions of the components measured. However there remains little practical guidance and, to the Authors belief, no implementation of CBM systems for GCs.

This paper presents a novel philosophy for monitoring the health of the GC whilst also providing an on-line estimate of the reproducibility of each mole fraction and overall uncertainty in the Calorific Value (CV) and density. The method has been demonstrated using data from a GC presently in use on a platform in the North Sea.

2 GC MAINTENANCE

2.1 Current Practice

Within the UK North Sea the following steps are generally taken to ensure that the performance of the GC is maintained at a satisfactory level:

1. Periodic health check by a GC specialist.
2. ISO 10723 multilevel calibration to determine the GC linearity and measurement bias.
3. Regular calibration using a certified working reference mixture.
4. Periodic repeatability check using the tolerances provided by ASTM 1945D.

It is common for all these activities to be performed by different parties. The result is a number of different reports that need to be combined and reviewed as a whole to obtain the full picture of the GC performance.

The following sections provide very brief overview of the available methods and standards presently in common use.

2.1.1 ISO 10723

ISO 10723 is a standard relating to the performance evaluation for online analytical systems. It has gained particular prevalence following the publication of the EUETS measurement and reporting guidelines [9] where annually repeated validation by EN ISO 17025:2005 [10] accredited laboratory was specified.

A number of test gases are used to establish:

- The ability of the GC to measure the components specified.
- The repeatability of the measurement of each component over their specified ranges.
- The relationship between response and concentration of each component over their specified ranges.

2.1.2 ASTM D 1945

This defines standard test method for analysis of natural gas by gas chromatography. Of particular interest to this paper are the sections that detail repeatability and reproducibility.

Repeatability is defined within the standard as the difference between two successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials. Table 1 details the defined maximum tolerances considered acceptable for repeatability as stated in the standard.

Mol % Lookup	Tolerance %
0 to 0.1 Mol%	0.01 %
0.1 to 1 Mol%	0.04 %
1 to 5 Mol%	0.07 %
5 to 10 Mol%	0.08 %
Over 10 Mol%	0.10 %

Table 1. ASTM D 1945 repeatability limits

A similar table exists for the reproducibility.

2.1.3 Other available methods

- ISO 6974 provides guidelines for the analysis of natural gas with the aim of determining the mole fractions of the principal components. The standard is split in to five sections, with Part 2 describing the determination of the measuring system characteristics and the statistical approach to data handling and error calculation with the aim of defining the uncertainties in the component mole fractions.
- ISO 6976 [11] is a standard detailing a calculation method for the determination of calorific values, density, relative density and wobbe index from composition. Within ISO 6976 precision is expressed as a calculated physical property value that results solely from random errors in analytical procedure in terms of repeatability and reproducibility. The standard defines equations for both repeatability and reproducibility.

3 THE PROPOSED METHOD

The common practice of performing distinct tests by different vendors at different times has led to the realisation that there are distinct advantages associated with collating all the information from the GC maintenance activities in to one place, combining all the data and results and presenting it in a clear, concise and easily interpreted manner. This information, when used in conjunction with a number of additional novel techniques, results in a condition based monitoring system with an expert system capability providing early detection of potential GC failures coupled with the ability to assist with the determination of the required course of actions to rectify any identified problems.

The proposed method consists of the following:

1. Acquisition of GC analysis parameters.
2. Analysis of events timing.
3. Analysis of individual calibration data prior to use as a foot-print.
4. Analysis of each calibration and comparison with the foot-print data.
5. Analysis of historical data.
6. Acquisition of working reference mixture uncertainty.
7. Analysis of repeatability.
8. Extended reproducibility assessment providing the basis for a live uncertainty calculation.
9. Estimation of the bias based on the ISO 10723 performance evaluation method.

The result of this is an expert system which can provide a live estimate of the uncertainty incorporating the uncertainty of the working reference mixture used for routine calibration, the repeatability and the long term reproducibility. An estimate of the uncertainty of other calculated parameters such as density and calorific value may also be determined.

Knowledge of the live operating uncertainty not only provides assurance that the measurement is meeting the required specification, but may also be used to determine when maintenance of the GC needs to be performed.

Steps one to five are covered by section 3.1. The remaining items are discussed with a working example using live data from an operational GC.

3.1 Foot-printing and analysis of historical data

A previous publication in 2009 described a method to analyse three-column gas chromatographs using the correlation between the component's molecular weights and their response factors [2].

This method lead to a condition based monitoring philosophy, GCAS[®], which utilises the techniques described within the paper to ensure that the status of a GC is healthy prior to foot-printing. Figure 1 shows a typical calibration data page.

30th International North Sea Flow Measurement Workshop
23 – 26 October 2012

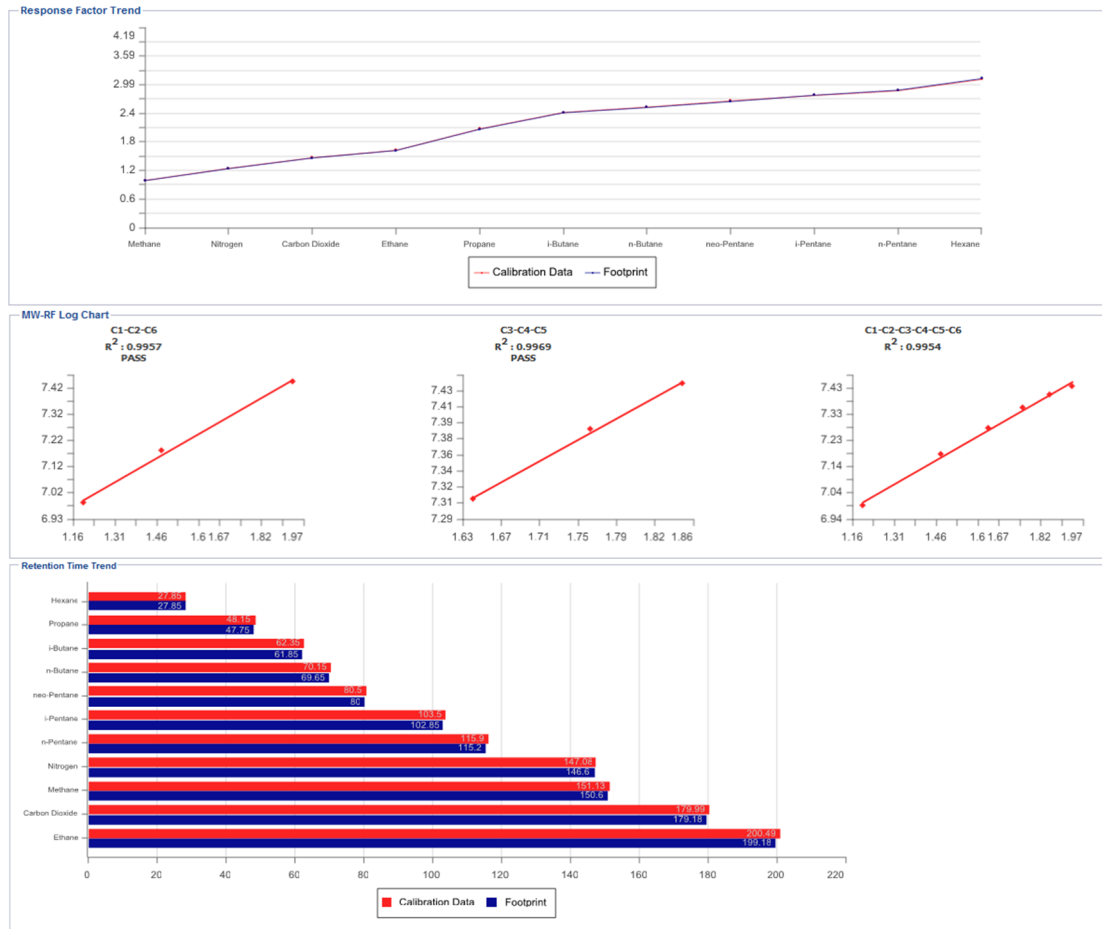


Figure 1. GCAS[®] Calibration data page

The term “foot-print” in this context is used to mean a healthy GC status which is captured and used as a reference against which future calibrations are compared.

Examples of the historical data analysis based on the foot-print data are:

- Response factor deviation control chart.
- Retention time deviation control chart.
- Analysis of the quality of the correlation of the log-log plot of molecular weight and response factor.

An example chart is shown in Figure 2, which shows the deviation of the response factor for methane from the foot-print.

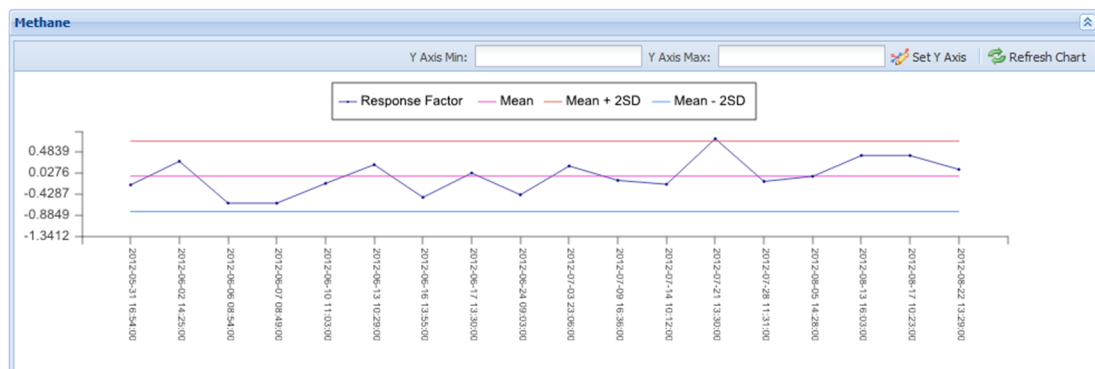


Figure 2. Deviation of response factor chart - Methane

3.2 Uncertainty of Working Reference Mixture

The working reference mixture uncertainty is normally provided in the UKAS certification accompanying the mixture cylinder. In this example the working reference mixture, with its associated uncertainty, is given in Table 2.

Component	WRM (%mol/mol)	Absolute Uncertainty (k=2)	Expanded Relative Uncertainty (%)	Standard Relative Uncertainty
Methane	75.605	0.05	0.0661	0.03305
Nitrogen	0.5	0.01	2.0000	1
carbon dioxide	1.784	0.011	0.6166	0.3083
Ethane	12.301	0.08	0.6504	0.3252
Propane	6.938	0.022	0.3171	0.15855
i-butane	0.8926	0.005	0.5602	0.2801
n-butane	1.6218	0.0094	0.5796	0.2898
neo-pentane	0.1026	0.0022	2.1442	1.0721
iso-pentane	0.2259	0.0021	0.9296	0.4648
n-pentane	0.1973	0.0024	1.2164	0.6082
n-hexane	0.0991	0.0017	1.7154	0.8577

Table 2. Working Reference Mixture relative uncertainty

3.3 Uncertainty from the GC repeatability

The repeatability of each component may be established as per ISO 10723 as a function of concentration (Figure 3). The standard deviation of the response for each component is expressed as:

$$s_i = a + b \times x_i^* + c \times x_i^{*2} + d \times x_i^{*3}$$

s_i is standard deviation

a, b, c, d are the coefficients of linear regression of s_i on x_i^*

x_i^* is un-normalised concentration of component i

Equation 1. relationship between standard deviation and concentration

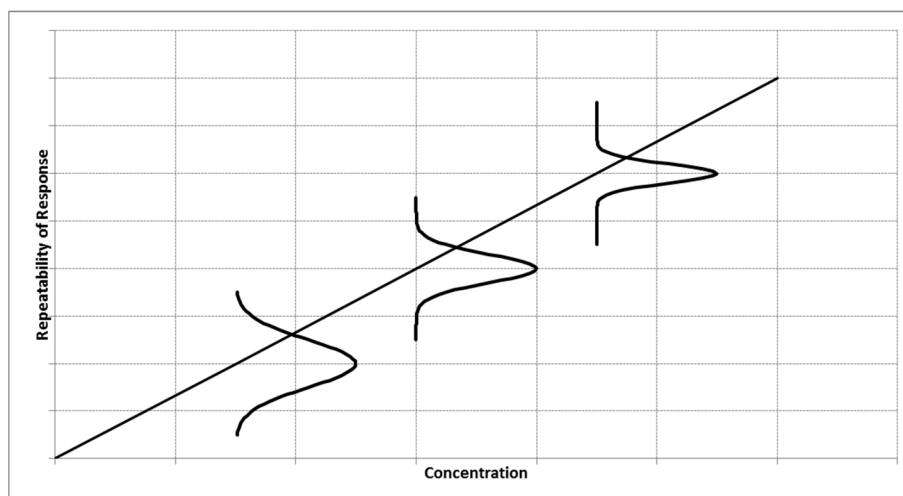


Figure 3. Repeatability of response as function of component concentration

The repeatability of each measured component is a function of the repeatability of the response on the working reference mixture and the repeatability of the response at the concentration being measured. The calculation of the standard deviation of the sample mixture is described in both ISO 6974-2 and ISO 10723. The following equation is defined in ISO 10723:

$$\left[\frac{s(x_i^*)}{x_i^*} \right]^2 = \left[\frac{s(y_{is})}{y_{is}} \right]^2 + \left[\frac{s(y_{istd})}{y_{istd}} \right]^2$$

y_{is} and y_{istd} are the instrument responses to component i in the sample and standard

$s(y_{is})$ and $s(y_{istd})$ are the respective standard deviations

x_i^* is the un-normalised concentration of component i

$s(x_i^*)$ is the standard deviation of the un-normalised components x_i^*

Equation 2. Standard deviation of component x_i^*

Having calculated the standard deviation of each un-normalised component, the standard deviation of the normalised mole fractions as defined by ISO 6974-2 is given:

$$s(x_i) = x_i \times \sqrt{\frac{1 - 2x_i^*}{x_i^{*2}} \times s(x_i^*)^2 + \sum_{w=1}^q s(x_w^*)^2}$$

x_i is the normalised mole fraction of component i

x_i^* is the un-normalised mole fraction of component i

Equation 3. Standard deviation of the normalised component x_i

3.3.1 Working example

Table 3 shows coefficients relating the mole fraction to standard deviation from a gas chromatograph presently in use on a North Sea platform.

Component	Coefficients of linear regression		
	a	b	c
Methane	329875.9302	0	0
Nitrogen	-534.812	6659.9222	0
CO2	24070.3	0	0
Ethane	13096.0458	5547.2357	0
Propane	-9075.6688	15604.4898	0
i-Butane	6941.0164	0	0
n-Butane	-2236.4662	21367.3294	0
neo-Pentane	437.4404	69901.5654	0
i-Pentane	4301.6545	41299.3758	0
n-Pentane	13469.4126	0	0
Hexane	23779.2293	0	0

Table 3. Coefficients of linear regression

Table 4 shows the standard deviation of the response of each component in the working reference mixture and the sample gas.

Component	WRM (%mol/mol)	Std Dev of WRM	Sample Gas (%mol/mol)	Std Dev of sample gas
Methane	75.605	329876	83.03	329876
Nitrogen	0.5	2795	0.39	2063
CO2	1.784	24070	1.83	24070
Ethane	12.301	81333	8.56	60580
Propane	6.938	99188	4.17	55995
i-Butane	0.8926	6941	0.55	6941
n-Butane	1.6218	32417	1.09	21054
neo-Pentane	0.1026	7609	0.03	2534
i-Pentane	0.2259	13631	0.09	8019
n-Pentane	0.1973	13469	0.18	13469
Hexane	0.0991	23779	0.08	23779

Table 4. Standard deviation of working reference mixture and sample gas

The standard deviation of each component can then be calculated using Equation 2:

Component	Std Dev of WRM	Std Dev of Sample Gas	Std Dev of un-normalised component
Methane	0.000487	0.000447	0.000499
Nitrogen	0.000431	0.000406	0.000003
CO2	0.000883	0.000861	0.000022
Ethane	0.000392	0.000418	0.000070
Propane	0.000664	0.000616	0.000063
i-Butane	0.000308	0.000500	0.000005
n-Butane	0.000762	0.000734	0.000017
neo-Pentane	0.003350	0.012461	0.000013
i-Pentane	0.002104	0.003136	0.000009
n-Pentane	0.002290	0.002511	0.000007
Hexane	0.007322	0.009102	0.000012

Table 5. Standard deviation of un-normalised components

Based on the standard deviation of the un-normalised component, the standard deviation of normalised component can then be determined from Equation 3.

Component	Std Dev of normalised component	Relative uncertainty
Methane	0.000143	0.019006
Nitrogen	0.000004	0.077837
CO2	0.000023	0.131377
Ethane	0.000087	0.071210
Propane	0.000068	0.098314
i-Butane	0.000007	0.077343
n-Butane	0.000019	0.115847
neo-Pentane	0.000013	1.290049
i-Pentane	0.000009	0.380257
n-Pentane	0.000007	0.343006
Hexane	0.000012	1.168120

Table 6. Relative uncertainty of each component based on the GC repeatability

3.4 Uncertainty from GC reproducibility

GUM [12] defines reproducibility as closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement, including time.

The reproducibility of a GC can be determined by analysing the calibration data from periodic calibrations. The responses are converted to un-normalised mole percentages based on the foot-print response factors and then normalised. The standard deviations of the normalised components are then calculated to obtain the GC reproducibility.

The following presents such an analysis of the reproducibility based on the same data provided in Table 2.

To get the reproducibility of the GC, the following steps are performed:

1. Take the foot-print data
 - a. Take the foot-print response factor for each component ($RF_{i,FP}$)
 - b. Take the gas composition from the WRM certificate ($x_{i,WRM}$)
2. Take periodic calibration data (i.e. daily, weekly, etc)
 - a. Record the response factor from calibration data ($RF_{i,cal}$)
 - b. Calculate the Peak Area of the calibration ($R_{i,cal}$) from the response factor ($RF_{i,cal}$) and the composition of working reference mixture ($x_{i,WRM}$).

$$R_{i,cal} = RF_{i,cal} \times x_{i,WRM}$$

3. Calculate the un-normalised components (x_i^*) from the peak area of the calibration ($R_{i,cal}$) and foot-print response factor

$$x_i^* = \frac{R_{i,cal}}{RF_{i,FP}}$$

4. Calculate the normalised composition (x_i)

$$x_i = \frac{x_i^*}{\sum_{i=1}^q x_i^*} \times 100$$

5. Calculate the standard deviation of each component. N is the number of calibrations that have been performed following the foot-print calibration

$$s(x_i) = \sqrt{\frac{\sum_{n=1}^N (x_{i,n} - \bar{x}_i)^2}{N - 1}}$$

6. Calculate the relative uncertainty of each component from the standard deviation.

$$U(x_i) = \frac{s(x_i)}{x_{i,WRM}}$$

The following is an example of the calculation of the normalised composition from the calibration response factor.

Component	WRM (%mol/mol)	Foot-print Response Factor	Calibration Response Factor	Calibration Peak Area	Un-normalised composition	Normalised Composition
methane	75.605	10139000	10045000	757427621	74.7044	75.4329
nitrogen	0.5	12710000	12584000	6275226.32	0.4937	0.4990
carbon dioxide	1.784	15179000	14990000	26670868.77	1.7571	1.7774
ethane	12.301	16616000	16432000	201591178.8	12.1324	12.2548
propane	6.938	21522000	21275000	147212451.1	6.8401	6.9150
i-butane	0.8926	24821000	24523000	21830875.87	0.8795	0.8853
n-butane	1.6218	26052000	25750000	41650019.5	1.5987	1.6131
neo-pentane	0.1026	27393000	26785000	2740814.802	0.1001	0.1016
iso-pentane	0.2259	28652000	28414000	6401611.094	0.2234	0.2246
n-pentane	0.1973	29829000	29362000	5777678.864	0.1937	0.1962
n-hexane	0.0991	32514000	32446000	3206826.752	0.0986	0.1001

Table 7. Calculation of normalised composition

The same procedure is then performed for each calibration and the standard deviation calculated. The standard deviation and relative uncertainty of each component is shown in Table 8.

Component	Standard Deviation	Relative Uncertainty
methane	0.0117	0.0155
nitrogen	0.0009	0.1857
carbon dioxide	0.0013	0.0747
ethane	0.0106	0.0861
propane	0.0080	0.1157
i-butane	0.0025	0.2757
n-butane	0.0024	0.1502
neo-pentane	0.0004	0.3456
iso-pentane	0.0006	0.2499
n-pentane	0.0006	0.3280
n-hexane	0.0002	0.2182

Table 8. Standard deviation and relative uncertainty of normalised components

3.5 Combined Uncertainty

Once the uncertainty from each uncertainty source is calculated, the combined uncertainty can be determined.

Component	WRM Relative Uncertainty	Repeatability Relative Uncertainty	Reproducibility Relative Uncertainty	Combined Relative Uncertainty
methane	0.03305	0.0190	0.0155	0.0412
nitrogen	1	0.0778	0.1857	1.0534
carbon dioxide	0.3083	0.1314	0.0747	0.3593
ethane	0.3252	0.0712	0.0861	0.3647
propane	0.15855	0.0983	0.1157	0.2738
i-butane	0.2801	0.0773	0.2757	0.5590
n-butane	0.2898	0.1158	0.1502	0.4063
neo-pentane	1.0721	1.2900	0.3456	1.7810
iso-pentane	0.4648	0.3803	0.2499	0.7403
n-pentane	0.6082	0.3430	0.3280	0.9001
n-hexane	0.8577	1.1681	0.2182	1.4977

Table 9. Combined relative uncertainty

Based on the relative uncertainty and relative sensitivity of each component, as well as the uncertainty from the ISO 6976 calculation [11], the combined expanded uncertainty from the calibration gas, repeatability, reproducibility, and calculation can be determined. The expanded uncertainty in this example for CV and standard density is shown in Table 10 and Table 11 respectively.

Component	mole Fraction	Norm Mol %	Expanded relative uncertainty	Coverage factor	Standard relative uncertainty	Relative Sensitivity	$U(x_i) * c(x_i)$
Methane	0.7561	0.7540	0.0823	2	0.0412	-0.1513	-0.0062
Nitrogen	0.0050	0.0050	2.1067	2	1.0534	-0.0050	-0.0053
CO2	0.0178	0.0178	0.7185	2	0.3593	-0.0178	-0.0064
Ethane	0.1230	0.1227	0.7295	2	0.3647	0.0501	0.0183
Propane	0.0694	0.0692	0.5477	2	0.2738	0.0696	0.0191
i-Butane	0.0089	0.0089	1.1180	2	0.5590	0.0142	0.0079
n-Butane	0.0162	0.0162	0.8125	2	0.4063	0.0259	0.0105
neo-Pentane	0.0010	0.0010	3.5620	2	1.7810	0.0022	0.0040
i-Pentane	0.0023	0.0023	1.4805	2	0.7403	0.0049	0.0037
n-Pentane	0.0020	0.0020	1.8003	2	0.9001	0.0043	0.0039
Hexane	0.0010	0.0010	2.9953	2	1.4977	0.0028	0.0041
ISO 6976	N/A	N/A	0.1000	2	0.0500	1.0000	0.0500
Combined Standard Uncertainty							0.0595
Coverage Factor (k)							2
Combined Expanded Uncertainty (%)							0.1190
CV absolute uncertainty (MJ/m3)							0.05620

Table 10. CV combined expanded uncertainty

Component	mole Fraction	Norm Mol %	Expanded relative uncertainty	Coverage factor	Standard relative uncertainty	Relative Sensitivity	$U(x_i) * c(x_i)$
Methane	0.7561	0.7540	0.0823	2	0.0412	0.5563	0.0229
Nitrogen	0.0050	0.0050	2.1067	2	1.0534	0.0064	0.0068
CO2	0.0178	0.0178	0.7185	2	0.3593	0.0361	0.0130
Ethane	0.1230	0.1227	0.7295	2	0.3647	0.1706	0.0622
Propane	0.0694	0.0692	0.5477	2	0.2738	0.1414	0.0387
i-Butane	0.0089	0.0089	1.1180	2	0.5590	0.0240	0.0134
n-Butane	0.0162	0.0162	0.8125	2	0.4063	0.0436	0.0177
neo-Pentane	0.0010	0.0010	3.5620	2	1.7810	0.0034	0.0061
i-Pentane	0.0023	0.0023	1.4805	2	0.7403	0.0075	0.0056
n-Pentane	0.0020	0.0020	1.8003	2	0.9001	0.0066	0.0059
Hexane	0.0010	0.0010	2.9953	2	1.4977	0.0040	0.0059
ISO 6976	N/A	N/A	0.1000	2	0.0500	1.0000	0.0500
Combined Standard Uncertainty							0.0961
Coverage Factor (k)							2
Combined Expanded Uncertainty (%)							0.1923
Density absolute uncertainty (Kg/m3)							0.09081

Table 11. Standard density - combined expanded uncertainty

3.6 Systematic Error

It is common for GCs to not implement the response functions obtained from the ISO 10723 calibration. Using a single response factor that is assumed to pass through the origin will introduce a systematic error when the sample gas is of a different composition to the working reference mixture. The magnitude of the bias on each component can be estimated from the response functions.

GUM states that it is unnecessary to classify components as “random” or “systematic” (or in any other manner) when evaluating uncertainty because all components of uncertainty are treated in the same way. It further states that occasionally where a correction for a systematic effect has not been applied to the reported result of a measurement, no attempt should be made to take the effect into account by enlarging the “uncertainty” assigned to the result. Only in very special circumstances should corrections for known significant systematic effects not be applied to the result of a measurement. Figure 4 shows the bias introduced for Methane in the present example when using the response factor from a single point calibration. This highlights the importance of using a suitable working reference mixture.

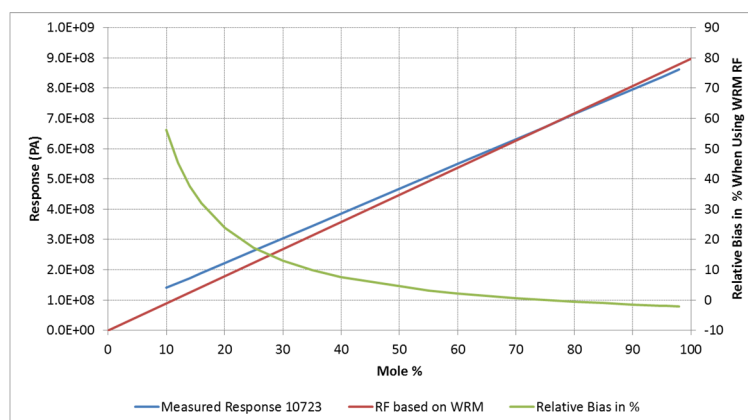


Figure 4. Bias introduced when using response factor from single point calibration

The above uncertainty calculation has not taken into account the bias introduced by operating away from the working reference mixture calibration point. It is recommended that for scenarios where significant bias is predicted the response functions from the ISO 10723 multi-level calibration are implemented to remove the known bias. If this is not performed, then consideration should be taken when expressing the uncertainty of the calorific value.

3.7 Expert System

The methods described above facilitate the determination of the live uncertainty of calculated quantities such as CV and standard density, as provided in the example. Coupled with the use of suitable control charts, this allows prescribed limits to be entered, above which intervention is required. For example a control chart of CV uncertainty can easily be set up which can clearly demonstrate that the system is operating within its target uncertainty. This can also quickly alert the operator to problems and to help decide when maintenance is due.

It is expected that the use of the correlation parameters from the log-log chart combined with control charts will be able to provide significant assistance in determining the cause and hence solutions to any problems. At this level, the method is approaching that of an expert system, which may loosely be defined as a computer system that emulates the decision-making ability of a human expert.

4 CONCLUSION

This paper has described methods that may be used for monitoring the performance of gas chromatographs. Data commonly available from the WRM certificate, ISO 10723 multilevel calibrations, and long term reproducibility can be utilised to provide live uncertainty calculations giving assurance that GC performance is within prescribed limits throughout the year.

The principle is equally applicable to calculations such as line density based on compressibility from AGA 8 [13] and any other compositional based calculations. The application of the method is expected to help to maintain the GC within its specified requirements throughout the year.

5 NOTATION

GC	Gas Chromatograph		curves of the measuring system.
CBM	Conditional Based Monitoring		
CV	Calorific Value		
EUETS	European Union Emission Trading Scheme	WRM	Working Reference Mixture. Mixture which is used as a working standard for regular calibration of the measuring system
k	Coverage factor		
a, b, c, d	Coefficients of linear regression of s_i on x_i^*	GUM	Guide to the expression of uncertainty in measurement
s_i	standard deviation	$RF_{i,FP}$	Foot-print response factor for component i
x_i^*	Un-normalised concentration of component i	$RF_{i,cal}$	Calibration data response factor for component i
x_i	Normalised concentration of component i	$x_{i,WRM}$	Mole fraction of component i in WRM
$s(x_i^*)$	Standard deviation of the un-normalised components x_i^*	$R_{i,cal}$	Peak Area from calibration of component i
y_{is}	Instrument responses to component i in the sample	N	Number of calibrations that have been performed following the foot-print calibration
y_{istd}	Instrument responses to component i in the standard	$c(x_i)$	Relative sensitivity coefficient of component i mole fraction
$s(y_{is})$	Standard deviations of component i in the sample	$U(x_i)$	Relative uncertainty of component i mole fraction
$s(y_{istd})$	Standard deviations of component i in the standard	mmscfd	Million standard cubic feet per day
$s(x_i)$	Standard deviation of the normalised mole fractions		
q	Number of components analysed		
CRM	Certified Reference Mixture. Mixture which is used for the determination of the response		

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