GAS CHROMATOGRAPHY AND SAMPLE LET DOWN SYSTEM – CONDITIONAL BASED MONITORING AND LIVE UNCERTAINTY CALCULATION

Hemant Narayan
Measuremation Inc, USA
hrayan@measuremation.com

Jennifer Rabone*
Swinton Technology Limited, UK
jennifer.rabone@swintontechnology.com

1. INTRODUCTION

On-line gas chromatography 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.

The modern gas chromatograph is an extremely repeatable device. However, to ensure that the system remains both accurate and repeatable, requires that suitable monitoring and maintenance are in place.

Even though a GC may be repeatable, it does not preclude the possibility of emergence of systematic errors. A systematic error may ensue due to several different reasons. These may include such things as non-representative sample provided to the GC, poor calibration gas handling resulting in a non-homogenous reference mixture, unsuitable selection of the reference gas mixture resulting in biases due to linearity or the assumed response functions, peak drifts, valve leakage etc. A recent study performed by the author identified a situation where a systematic error was observed, which if remained undetected, would have resulted in an on-going error in the calorific value of up to 1.4%. This error equated to a value of more than £300,000 per month.

Once reasonable steps have been taken to ensure that the system is free from systematic error then the uncertainty of the GC measurement is generally driven by the repeatability of the GC and the quality of the (certified) reference gas mixture. There are various methods which may be used to obtain the GC repeatability. ISO 10723 describes a method of performance evaluation using multiple calibration gas compositions to obtain the linearity of the GC as well as its repeatability. ASTM D1945 provides a standard test method for the analysis of gas with a GC with stated levels for the expected repeatability and reproducibility. However, these methods are only valid as long as the GC maintains the performance characteristics measured on the day of the test.

To ensure the GC remains repeatable over a prolonged period of operation on-going monitoring is required.

This paper presents a novel philosophy for determining both the initial health of the sample pressure let down system and GC itself for providing continued monitoring and consequent assessment of the GC performance. The result is an ability to produce an on-line estimate of the repeatability of each component allowing the overall uncertainty in the Calorific Value (or any other parameter calculated from composition) to be established as required. The philosophy will be demonstrated using real data from several case studies to illustrate how an 'expert system' may be used to provide the uncertainty of the GC as well as indicate the time when the GC needs to be serviced, thereby providing assurance that the GC is operating within specified limits and meeting contractual obligations.

2. SAMPLE PRESSURE LET DOWN SYSTEM

Sample pressure let down system is an integral part of gas quality measurement. In gas composition analysis using gas chromatography, the measurements are carried out at reduced pressure; therefore pressure reduction system is necessary. It is important that the pressure reduction system provides representative sample to the GC. Condensation is the main source of sample non-representivity and therefore the most prevalent reason for gas analysis error.

This section will present the typical design of pressure let down systems, including issues with the pressure let down system, condensate going forward, as well as proposed verification check and a method to perform lag time calculation.

3. Sample Pressure Let Down System Design

The main function of the sample let down system is to provide representative sample for analytical equipment. However, in many occasions sampling and conditioning system fail to provide representative samples to the GC and such failure results in measurement error which sometimes goes undetected.

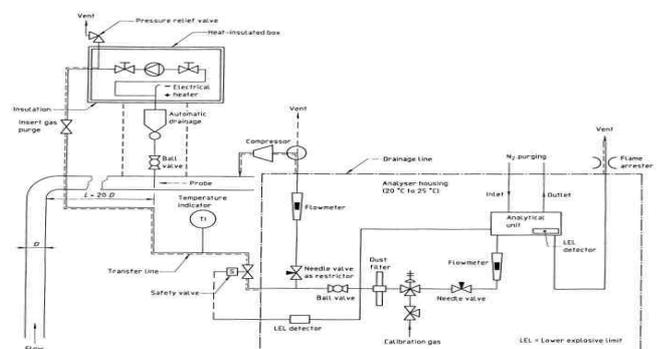ISO 10715:2001 [1] provides an example of simple direct sampling system as shown in Fig. 1.

Fig. 1 - Continuous sampling using pressure reducer [1]

ISO 10715:2001 [1] describes that automatic drainage is generally not acceptable as it could bias the sample. The

automatic drainage nowadays is normally achieved by a coalescer filter that will block all the intrusive liquid not allowing it to go into the GC. It is important to block this intrusive liquid to prevent damage of the equipment. Coalescer filter is first line of defence intended to eliminate glycol and condensate from entering the let-down system.

Pressure reduction is performed to provide sample with the required pressure range for the analytical equipment. Due to Joule-Thompson effect, the temperature will fall by about 0.5 ^{o}C/0.1 MPa during pressure reduction, and therefore there is a potential for further condensation of heavy ends [1]. To ensure that the Joule Thompson effect does not result in condensation, the transfer line shall always be heated to a temperature at least 10°C above the condensation temperature.

In many sampling system prior to gas entering the GC a membrane filter is installed, normally as part of the fast loop system. The function of the filter is to safeguard the GC from liquid penetration such as condensate formed by Joule-Thompson effect. The membrane filter is the last barrier to block liquid from entering the GC.

3.1. Issues with Sample Pressure Let Down System

There are several issues associated with direct sampling. Detailed technical design consideration is provided in ISO 10715:2001 [1]. This paper will focus on the issue of condensation.

In pressure let down system, high pressure drop may cause cooling and condensation which will affect the representative nature of the sample. When condensation occurs, sample is no longer representative and remedial action should be taken. However, most of the time the field technicians are not equipped by tools that may facilitate them to detect condensation. In many cases checks only performed to see if there is any sign of icing in the pressure let down system. In some cases, for instance if there is only one pressure regulator to drop the high pressure of the pipe to the required pressure of the analyser, clear indication of icing can be seen in the regulator.

Temperature indicators are not normally available in the sample line, and in many places available indicator only shows the temperature of the heated enclosure and not the temperature of actual transfer line. If temperature indicators are available, the operators have a daily record of them, however often there is no defined limit indicating the minimum required temperature, neither there are any particular instructions or procedures for actions in those cases if the temperature has dropped below the limit.

The lack of awareness of condensation in the sample let down system in combination with the design that will block any condensate from going into the GC can result in non-representative sample provided to GC. This can lead to a significant measurement error. A case study performed in one UK installation shows that a GC measurement resulted in lower CV due to losing heavy ends. This particular installation was losing more than £200,000 per month due to undetected heavy end drop out.

When heavy end drop out is suspected, for instance by performing verification check as described in section 2.3, a couple of these checks to trace the source of the issue can be performed as suggested by ISO 10715:2001 [1] among which are the following:

[1] Temperature check of each pressure stage should be conducted to ensure that the transfer line temperature is at least 10 ^{o}C higher than the gas hydrocarbon dew point temperature at every stage between pipeline and GC.

- Gas hydrocarbon dew point temperature can be taken from hydrocarbon dew point analyser (if available), or it can be taken from spot sample lab result.

[2] Drain the drip pot to see if there is any liquid entrained.

- Drip pots are intended to remove troublesome intrusive liquids.
- Drip pots may accumulate liquid slugs and then continuously vaporise into the sample stream. There is danger that their use may change the composition of the sampled gas.
- The concentrations of components which equilibrate between gas and liquid phase are likely to be altered by removal of the liquid.

[3] The other issue associated with the sample is the sample probe type and sample location. Wrong sample probe location or type may result in a non-representative sample taken from the pipeline. Please refer to ISO 10715:2001 [1] for detail consideration concerning the sample probe and pressure let down system design.

2.3 Verification Check of Sample Pressure Let Down System

Spot sampling can be used as a tool to provide information on how representative the sample provided by the sample let down system. Typical spot sample / sample let down system is shown in Fig. 2.
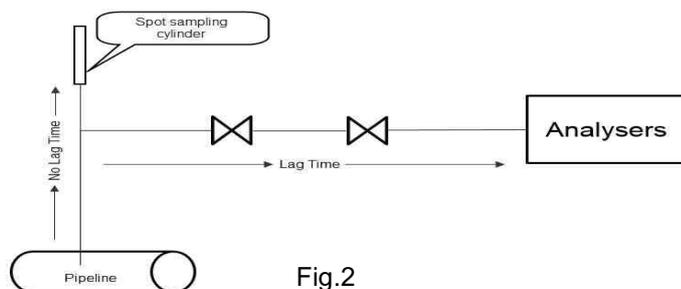

Fig.2

The following method can be used to verify the sample let down system as illustrated in Fig 2:

1. Take spot sample at hh:mm
2. Note analyser reading at hh:mm + lag time ± 1 cycle
3. Average analyser reading and compare the result against spot sampling result

On the assumption of correct manual sampling procedure, this method will compare the measurement of the same gas with two different measurement methods and therefore provides verification check of the sample pressure let down system (section 3 will provide Conditional Based Monitoring method to perform health check on the analyser).

Further analysis can be performed by taking the analyser reading continuously. Spot sampling result can be mapped according to the sampling time. The average gas composition with its standard deviation can then be recorded. This information is very useful to design such calibration gas which will be the most appropriate for the GC. Latest study also shows that with high stability gas, monthly spot sampling can provide similar result as flow proportional sampling with negligible increase in uncertainty.

Performing spot sampling on a monthly basis can also be considered as a monthly pressure let down system verification check. It is also recommended to perform daily checks of sample let down pressure and temperature of each stage. A low temperature limit can be provided in the check if the hydrocarbon dew point temperature is known. By combining the daily check and the verification check, operator can gain confidence that the sample pressure let down system provides a representative sample to the analytical equipment.

2.4 Lag time calculation

Lag time calculation is performed to establish the time required for the gas to travel from pipeline to GC including the cycle time of the GC. ISO 10715:2001 [1] provides this calculation; however it does not consider gas composition and its compressibility. This paper offers a more practical way of calculating the residence time.

In this paper the lag time calculation is performed by converting the volume into normal volume. Further calculation with the normal volume flow rate which is typically used by the Rotameter on gas chromatograph (i.e. Nml/min) will result in the lag time. By definition Normal volume is the volume of a gas at 0° C and 760 millimetres pressure as ascertained either by direct observation or by calculations in accordance with the law of Boyle and Charles [9].

Modified form of ideal gas equation is given by the following:

$$\frac{P1V1}{T1Z1} = \frac{P2V2}{T2Z2} \quad\ldots\ldots\ldots\ldots\ldots(1)$$

- P1 = Normal condition pressure (1.01325 Bara)
- o V1 = Gas volume at normal condition
- T1 = Normal Condition Temperature

- Z1 = Gas Compressibility at normal . condition (0 ^{0}C)
- P2 = Line Pressure
- V2 = Gas volume at line pressure and temperature
- T2 = Line Temperature
- Z2 = Gas Compressibility

Therefore, the normal volume can be derived using the following equation:

$$VI = \frac{P2V2T1Z1}{P1T2Z2} \quad\ldots\ldots\ldots\ldots\ldots(2)$$

(2) Once the normal volume is known, dividing it by the normal volume flow rate will result in the lag time of the gas. Example of the lag time calculation can be seen in Appendix 1.

Consideration should be made to design pressure sample let down system with short lag time while maintaining temperature above the condensation temperature.

3. GAS CHROMATOGRAPH CBM

This section will describe the design and operation of the gas chromatograph, issues with the gas chromatograph and conditional based monitoring (CBM) method to maintain the health of gas chromatograph.

3.1 Gas Chromatograph Design and Operation

This section provides an overview of a multi-column separation technique which is required to get the composition of a natural gas with inert components and hydrocarbon components ranging from C1 to C7+ in a practical time frame and without temperature ramping.

The three-column GC design is consistent with ISO 6974-5:2000 [3]. It uses three columns, a restrictor and two detectors housed in a controlled temperature chamber. The detectors are usually thermal conductivity detectors (thermistors), where the resistance is a function of the temperature. The reference and measurement detectors form a balanced Wheatstone-Bridge. Helium is the preferred carrier gas because it has a relatively high thermal conductivity. With only carrier gas flowing across the two detectors, the Wheatstone bridge is in balance. As the sample gases pass across the measuring detector the change in gas thermal conductivity results in a change in the rate of heat exchange between the thermistor and the surrounding gas which results in a change in the thermistor temperature. The change of temperature causes a change of resistance in the measurement detector, thus unbalancing the Wheatstone-Bridge. The magnitude of the voltage created by the unbalanced bridge and the time taken for the gas to pass across the detector forms a response curve proportional to the amount of the component in the carrier gas stream. The area under the response curve is proportional to the mol. percentage of component being measured. The actual

value of the component is determined by comparison of the measured response to the response obtained from a gas of known composition, usually referred to as the calibration gas.

On a single column GC where pressure, temperature, and flow rate is maintained at a constant rate, there is a very high correlation between the molecular weight of the saturated gas components and their response factors. With a three-column GC, restrictor tubing has to be applied to regulate the carrier gas flow to maintain and achieve a close-to-constant flow rate during valve actuation operations. Even with the pressure and temperature maintained constant, and with a restrictor tubing in place, slight flow rate differences still occur, thereby changing the response of the thermal conductivity detector. These fluctuations in flow rate reduce the correlation between the molecular weight of each component and its corresponding response factor.

For a three column GC, Fig. 3 shows the GC flow tubing path configuration for C1, N2, CO2, C2 and C7+. Similarly, Fig. 4 shows the flow tubing path of C3, iC4, nC4, neoC5, nC5, C6's. Any difference in the effective restriction presented by the restrictor tubing and column 3 would result in a difference in the flow rate between the two path configurations.
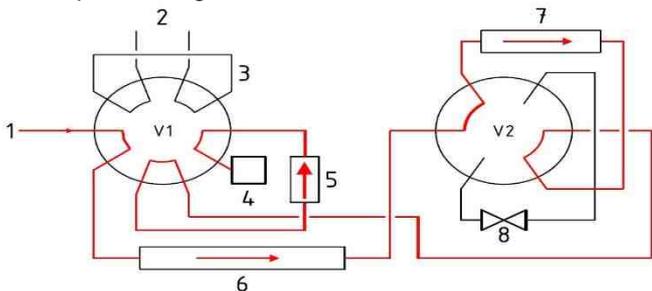
1. Carrier Gas Sample	5. Column 1
2. Introduction	6. Column 2
3. Sample Loop	7. Column 3
4. TCD Detector	8. Restrictor A

Fig. 3 - Three-column GC flow path of C1, C2, and C7+, adapted from ISO 6974-5:2000 [3]
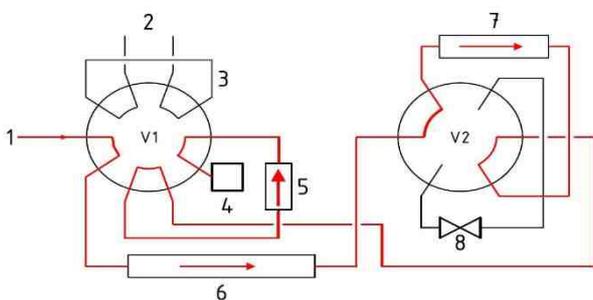
1. Carrier Gas Sample	5. Column 1
2. Introduction	6. Column 2
3. Sample Loop	7. Column 3
4. TCD Detector	8. Restrictor A

Fig. 4 - Three-column GC flow path of C3, nC4, nC5 and C6's, adapted from ISO 6974-5:2000 [3]

3.2 The Underlying Issues

Gas Chromatographs are, generally speaking, highly repeatable devices. In a number of situations, such a description can give a false sense of security, since repeatability may sometimes be incorrectly interpreted as accuracy. This is not the case. If configured incorrectly, the GC would give consistently and repeatedly the wrong result. This can happen for various reasons among which might be the incorrect handling of the calibration gas, poor quality of calibration gas, or valve timing issues.

The systematic drift of the response factors can be indicative of a number of problems. However, the detection of this through automatic GC calibration is not always possible. This is because the usual method of detection is to compare the shift between successive automatic calibrations. A gradual change in the response factor can easily result in a shift that remains within the tolerance limit set in the GC controller and hence continue without detection. Even with the incorrect calibration result, the GC can continue to give repeatable results. However, the results will not be accurate and the uncertainty of the measurement will invariably be increased.

The common industry practice in the UK is to have the GC audited / maintained by a specialist once a year. The GC is then expected to continue to perform within the uncertainty limit observed during the maintenance procedure. However, the GC performance and its uncertainty limit will only be valid if the GC continues to maintain the same performance characteristics as measured and recorded on the day of the calibration. If there is any shift in the characteristics of the GC, or the operating conditions, then the uncertainty statement made on the day of the annual maintenance will no longer be valid.

The uncertainty of the CV from a healthy GC is normally within the range of ±0.1 MJ/m3. The results from one of the case studies performed has identified a scenario where an error of up to 1.4% or 0.63 MJ/m^3 was present in the calculated CV due to incorrect calibration. This figure is 6 times greater than the nominal uncertainty level of the device and would have been very likely to remain undetected without the use of condition based monitoring tools.

3.3 Current Practice

As previously stated, 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.

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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.

3.3.1. ISO 10723

ISO 10723 [2] is a standard relating to the performance evaluation for online analytical systems. It has gained particular prevalence in Europe following the publication of the EUETS measurement and reporting guidelines [4] where annually repeated validation by an EN ISO 17025:2005 [7] 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.

3.3.2. ASTM D 1945

This defines a standard test method for the 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.

Table 1. ASTM D 1945 repeatability limits

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 %

A similar table exists for the reproducibility.
3.3.3. 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 [6] is a standard detailing a calculation method for the determination of calorific values, density, relative density and wobble 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.

Application of some fundamental methodologies and utilization of Gas Chromatography Analysis Software (GCAS®) can assist not only in identifying the previously mentioned problems, but also in formulating an implementation plan to rectify or eliminate them. Collection of the required calibration data and utilization of all of the tools from GCAS® will allow the industry to achieve the advantages & be able to:

- Maintain GC accuracy throughout the year
- Eliminate unnecessary error
- Predict future failure
- Help support and increase technician's competency level
- Reduce unnecessary specialist cost
- Provide guidelines as to the necessary course of action to rectify failures
- Create a fully auditable database of GC performance.

3.4. 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 including an expert system capability providing early detection of potential GC failures. This coupled with the ability to assist with the determination of the required course of actions to rectify any identified problems gives the responsible individual the essential support required when maintaining a chromatograph.

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 footprint.

4. Analysis of each calibration and comparison with the footprint data.
5. Analysis of historical data.
6. Acquisition of working reference mixture uncertainty.
7. Analysis of repeatability.
8. d 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 that 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 3.4.1. The remaining items are discussed with a working example using live data from an operational GC.

3.4.1. 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

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.

The term "footprint" 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. The Footprint page of GCAS® is shown in Fig. 5.
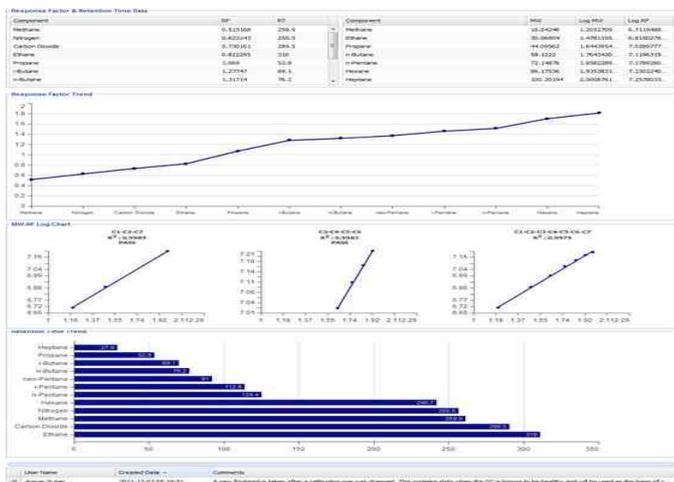

Fig. 5 - Footprint page from GCAS®

3.4.2. Response Factor (RF) and Retention Time (RT) Data

The Response Factor and Retention Time Data show the raw data of the response factor (RF) and retention time for each of the components, as well as the logarithm of the Molecular Weight (MW) and RF. This data is processed and presented through graphical trends for analysis. The Response factor and retention time data in the footprint page are shown in the first part of Fig. 5.

3.4.3 Response Factor Trend

The relationship between thermal conductivity and Molecular weight in hydrocarbon and inert gases is well known. The larger the molecular weight the lower the thermal conductivity.

The temperature of the thermistor changes whenever gas with a different thermal conductivity flows across it. The change in the temperature is dependent on the amount of the component (mole %) and the response of the thermistor to each component (Response Factor). The greater the difference in the thermal conductivity between the carrier gas and the component being measured, the greater the temperature change. Hence a gas with a much lower thermal conductivity than the carrier gas will result in larger response factor.

On a C7+ GC, the components measured ordered from high to low in thermal conductivity are: C1, N2, CO2, C2, C3, iC4, nC4, neoC5, iC5, nC5, C6's, C7+. The first step to verify the calibration result is to monitor the response factor data. If the response factors are plotted versus component in thermal conductivity order, then the response factor of C1 will be lowest, followed by N2, CO2, C2, etc. If the plot does not result in a monotonically increasing function, then this could point to some form of incorrect setting in GC, or an issue with the calibration gas. A typical graphical representation of the response factors is shown in Fig. 6.
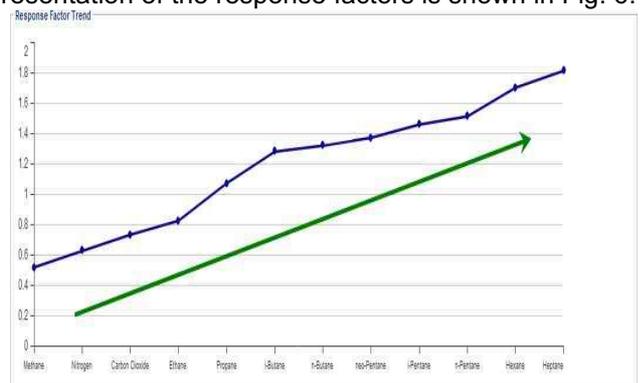

Fig. 6 - Response factor trend

3.4.4 MW – RF Log Chart

There are three critical valve timings within a 3-column chromatograph as shown in Fig - 7 (refer to 3.1 for key to the number descriptions):
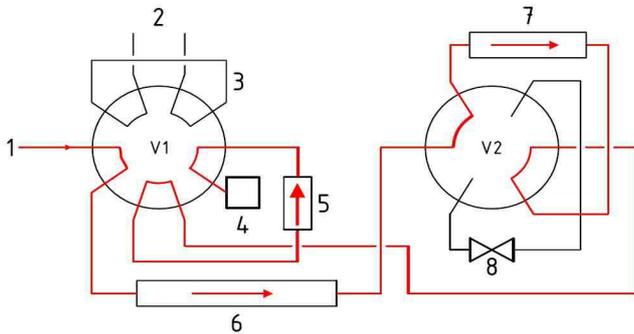
Fig - 7. Three-column GC flow path of C1, C2, and C7+, adapted from ISO 6974-5:2000 [3]

1. Back-flush the heaviest component. Back flush is initiated after C6 and lighter components are eluted from column 1 to 2, but before the heavy component leaves column 1.

2. Trap the light components in column 3. The valve actuation has to be one after all C2 is eluted into column 3, but before any C3 leaves column 2.

3. Allow lights to leave column 3. Valve actuation has to be done after all the middle components clear the measurement detector.

Valve-timing errors can result in the emergence of following situations:

- Some of the heavy components leave column 1 and flow through column 2
- Some of the middle components are back-flushed together with the heavy components
- Some C2 is left in column 2 after the valve 3 actuation to trap the lights
- Some C3 goes in to column 3 before valve 3 actuation to trap the lights
- Splitting of the first and last components on the column resulting in extraneous peaks on the chromatogram
- Extraneous peaks within the peak window of calibrated peaks may be recognized as the calibrated peaks

The impact of these valve timing issues will influence the correlation of the components. Any valve timing issues will reduce the correlation between components. The correlation between MW and RF is shown in Fig. 8.
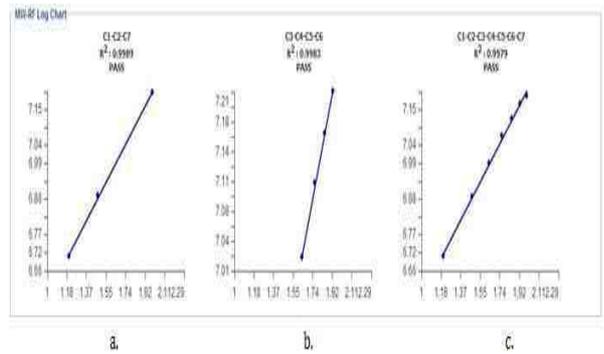

Fig. 8 - MW – RF Log Chart

Fig. 8a shows the correlation between C1, C2, and the heaviest component where the measurements are performed when carrier gas flow through column 3. Fig. 8b shows the correlation among the middle components where the measurements are performed while carrier gas flows through the restrictor. Fig. 8c shows the correlation among all components. The correlation obtained from the first two graphs is crucial as they show whether there is a valve timing issue in the GC. The cause and effect of the valve timing faults are as follows:

Some of heavy components leave column 1 and flow through column 2. This results in a smaller response factor for the heavy component. This can be seen from the graphical presentation (Fig. 9) in that the heavy component will be lower than it should be resulting in a lower than expected correlation between C1, C2 and the heavy component.
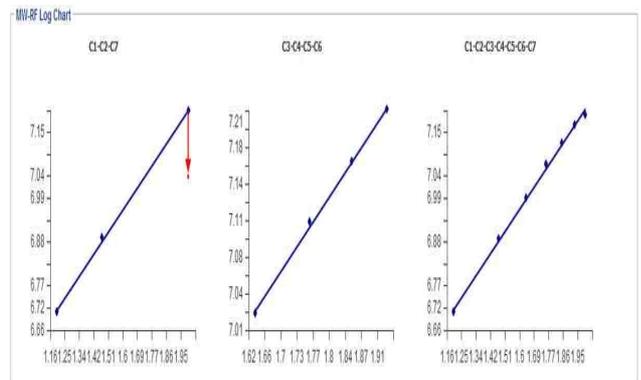

Fig. 9 - RF – MW correlation case 1

Some of the middle components are back-flushed together with the heavy component. This results in a smaller response factor for the heaviest middle component. From the graphical presentation (Fig. 10) we are able to see that the heaviest of the middle components is lower than expected and results in bad correlation for the middle components.
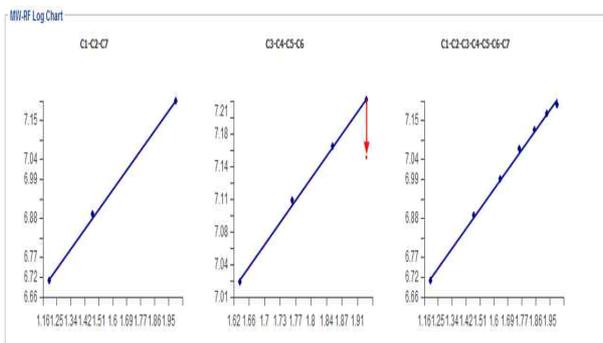
Fig. 10 - RF – MW correlation case 2

Some C2 is left in column 2 after the valve 3 actuation to trap the lights. This results in a smaller response factor for C2. From the graphical presentation (Fig.11) it can be seen that C2 will be lower than the line between C1 and the heaviest component. This results in a poor correlation between C1, C2 and the heavy component.
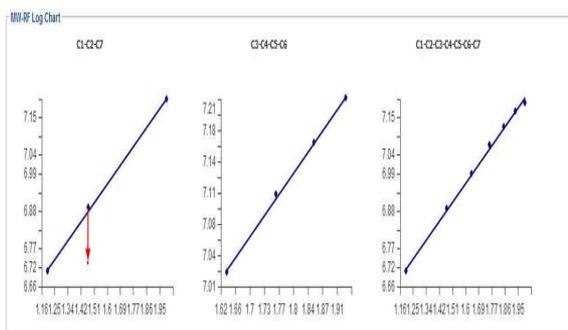

Fig. 11 - RF – MW correlation case 3

Some C3 goes in to column 3 before valve 3 actuation to trap the lights. This results in a smaller response factor of C3. From the graphical presentation (Fig. 12) it can be seen that C3 is lower than expected, which results in a poor correlation between C1, C2 and the heavy component.
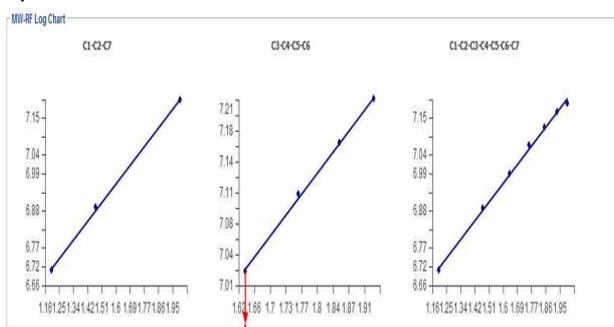

Fig. 12 - RF – MW correlation case 4

3.4.5. Retention Time

Retention time is defined as the elapsed time between the time of injection of a solute and the time of elution of the peak maximum of that solute [8]. It is an important parameter of a gas chromatograph because it can be used for identification purposes. Each gas component will have a unique retention time; therefore any gas component can be identified through its retention time. It

is also a very useful tool to analyse peak drift when the footprint retention time is compared against the routine automatic calibration retention time.

A shift in the retention time indicates the emergence of a potential problem. It may be valve leakage, a change in back pressure, a change in carrier gas pressure or a change in the oven temperature. A consistent drift in retention time can be used as a reliable indication of approaching failure. Therefore, preventive maintenance measures can be performed before actual failure occurs. The retention time trend of a footprint in GCAS$^{®}$ is depicted as the bottom histogram in Fig. 5.

3.4.6. Analysis of Historical Data

Examples of the historical data analysis based on the footprint 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 Fig. 13, which shows the deviation of the response factor for methane from the footprint.
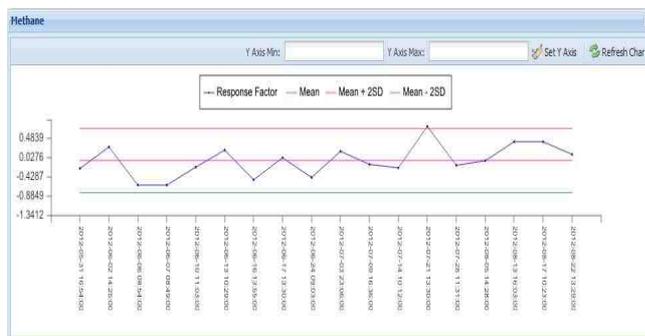
Fig. 13 - Deviation of response factor chart - Methane

3.5   Case Studies

Several case studies of the condition based monitoring system have been performed on different types of GC (C6+ and C7+). All the case studies have been performed remotely with the help of offshore metering technicians.

3.5.1 Calibration issue

The first case study was performed on a C6+ GC. The GC had been offline for some time and was to be brought back in to service. In order to bring the GC online, it was fitted with new calibration gas and a forced calibration was performed. By doing this, the GC accepted all calibration parameters (i.e. RF and RT). However, inspection of the Response Factor plot, Fig. 14, clearly indicated that the GC was not healthy.

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Fig. 14 - RF trend of first calibration

The first issue was that the trend was not ascending. When checked, the component data table (the data used to tell the GC the composition of the calibration gas) was not the same as the calibration gas certificate. After the component data table was adjusted, the Response Factor trend was better, however it was still indicating issues as shown in Fig. 15.

Fig. 15 - RF trend after component data table was adjusted

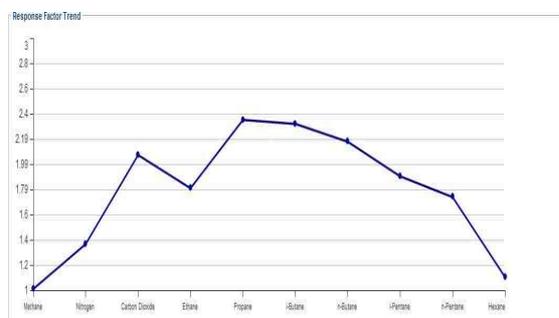From Fig. 15, the trend shows that the N2 and CO2 levels were too high, whilst the C6 level was too low. The N2 and CO2 levels can be high after changing the calibration gas as the sample line can fill with air. To rectify this issue, the calibration sample line was purged with calibration gas. After clearing the air, the RF trend was significantly better as shown in Fig. 16.
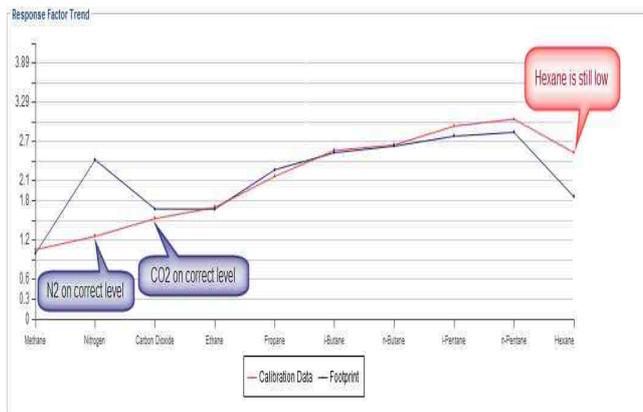

Fig. 16 - RF trend after calibration sample line was purged

The blue line shows the trend prior to purging, and the red line shows the trend after purging. N2 and CO2 were now at their expected levels, however there was still one remaining problem. The C6+ RF was still lower than expected. Inspection of the correlation between the MW and RF can be used to help determine the cause of the low C6+ response factor and is shown plotted in Fig. 17.
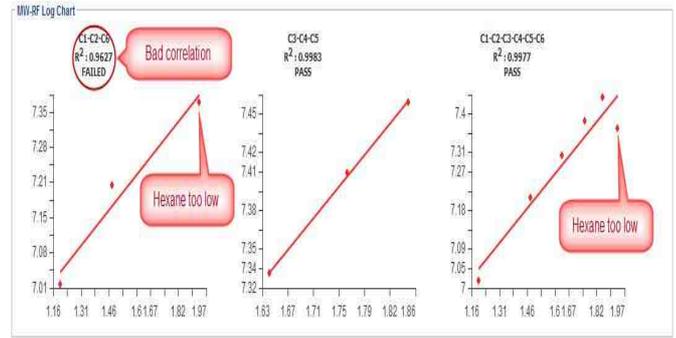
Fig. 17 - MW-RF Log Chart of calibration data

From the plots it was determined, based on the poor correlation between C1, C2, and C6+, that the problem was due to some of the heavy components (C6+) leaving column 1 to flow through column 2. As the result, not all of the C6+ was detected, resulting in a lowered C6+ response factor. Adjustment was performed to the valve timing to prevent C6+ from entering column 2. This resulted in the change of the response factor chart as depicted in Fig. 18.
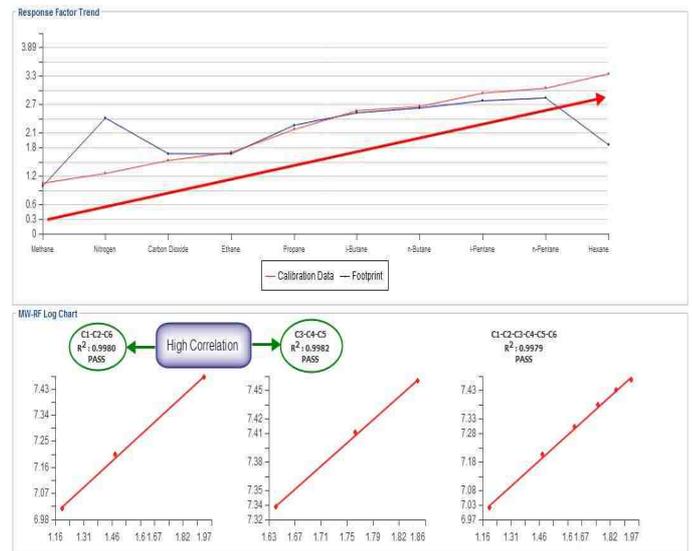
Fig. 18 - RF Trend and MW-RF Log Chart of a healthy GC

The charts now clearly indicate that the problem with the GC has been rectified and the trends are all as expected. The error introduced by this problem may not be overtly apparent at the individual component level, however analyses of the resultant calculated calorific values of the two calibrations, clearly shows the difference to be significant. The potential difference in the final output result is given in Table 2.

Table 2:
Unhealthy vs Healthy result comparison,
Value per KWh data is taken from Quarterly Energy Prices, December 2013 [5]

	Wrong RF	**Correct RF**	**Difference**
CV (MJ/Sm3)	45.07	44.44	1.41%

Volume (mmscf)	100	100	
Volume (m3)	2,831,684	2,831,684	
Energy (GJ)	127,624	125,840	1,784
Energy (KWh)	35,451,330	34,958,311	493,019
Value per KWh	£ 0.02459	£0.02092	
Value /day	£ 871,748	£859,625	£ 12,123
Value /month	£ 26,152,446	£25,788,746	£ 363,700

Table **2** shows that the difference in calorific value was 1.41% and that that this error would equate to more than £300,000 per month based on a gas rate of 100 mmscf/d. This case study clearly shows how important it is to calibrate the GC correctly. Failure to do so can prove to be very costly.

3.5.2 Calibration gas quality issue

The second case study was performed on a C7+ GC. Within this case study, the C7+ response factor was degrading over time whilst the response factors of the other gases remained stable.

As shown in the previous case study, when the heaviest component has a response factor lower than expected, it is usually a sign of a valve timing issue. However, the occurrence of a constant and continued degradation of the response factor points to some other cause. In this case, there was a suspicion that the calibration gas quality had degraded, possibly caused by low and reducing pressure in the calibration gas bottle

A low pressure in the calibration gas bottle can make the gas non-homogenous and make the heavy component condense out of the mixture. This will cause the Response factor of the heavy component to be lower than expected. The trending tool detected this scenario with a gradual reduction in response factor for C7+ as seen in Fig. 19.

Fig. 19 C7+ response factor descends over time due to low pressure in calibration bottle

When it was finally decided to carry out an intervention at the end of this study case, it was found out that there was only 2.6 barg of pressure left in the calibration gas bottle.

After changing the calibration gas bottle, all the response factors went back to normal and showed good correlation. When compared against the last data sets before and after the change of the calibration gas bottle, it turned out that there was +0.35% error in the CV.

The importance of the calibration gas for Chromatography cannot be over emphasised. This case study showed that a stable consistent quality of calibration gas is important to maintain the overall accuracy of the GC. This also indicates the requirement to have procedures in place to change the calibration gas bottle before the pressure gets too low and to ensure that other potential causes leading to non-homogeneity of the stated gas mixture are avoided.

3.6 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 **3**.

Table 3. Working Reference Mixture relative uncertainty

Component	WRM (%mol/mol)	Absolute Uncertain-ty (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

3.7 Uncertainty from the GC repeatability

The repeatability of each component may be established as per ISO 10723 as a function of concentration (Fig. 20). The standard deviation of the response for each component is expressed as:

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$$s_i = a + b*x_i^{*2} + c*x_i^{*2} + d*x_i^{*3} \quad .....(3)$$

Where, 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

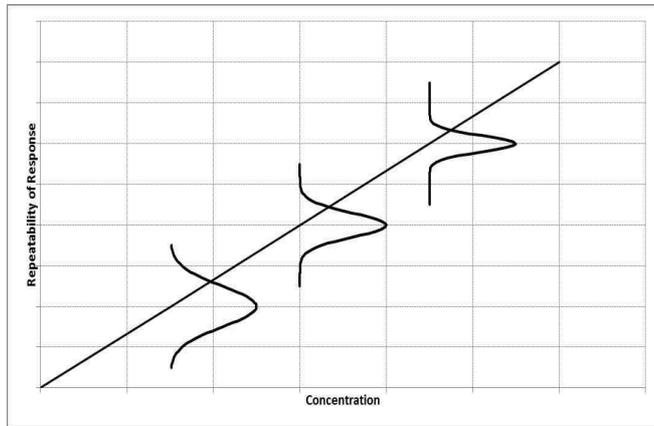Equation 3. relationship between standard deviation and concentration.

Fig. 20 - 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:

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

Equation 4

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

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

x_i^* is the un-normalised component of i

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

Equation 4. standard deviation of the 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:

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

Equation 5

x_i is the normalised mole fraction of component i.

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

Equation 5. Standard deviation of the normalised component x_i

3.7.1 Working example

Table 4 shows coefficients relating the mole fraction to standard deviation from a gas chromatograph presently in use on a North Sea platform.

Table 4. Coefficients of linear regression

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

Table 5. Standard deviation of working reference mixture and sample gas

Compo-nent	WRM (%mol/mol)	Std Dev ofWRM	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

The standard deviation of each component can then be calculated using Equation 4:

Table 6. Standard deviation of un-normalised components

Component	Std Dev of WRM	Std Dev of Sample Gas	Std Dev of Un-Normalized Component
Methane	0.000487	0.000447	0.000499
Nitrogen	0.000431	0.000406	0.000003
CO_2	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

Based on the standard deviation of the un-normalised component, the standard deviation of normalised component can then be determined from Equation 5.

Table 7. Relative uncertainty of each component based on the GC repeatability

Component	Std Dev of Normalized Component	Relative uncertainty
Methane	0.000143	0.019006
Nitrogen	0.000004	0.77837
CO_2	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

3.8 Uncertainty from GC reproducibility

GUM [10] defines reproducibility as closeness of the agreement between the results of measurements of the same measure and 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 footprint 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 **3**.

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 ($x_{i,wrm}$).

$$R_{i,cal} = RF_{i,cal} * x_{i,wrm} \ldots\ldots\ldots (6)$$

3. Calculate the un-normalised components (x_i^*) from the peak area of the calibration (RF) and foot-print response factor

$$x_i^* = \frac{R_{i,cal}}{RF_{i,FP}} \ldots\ldots\ldots\ldots(7)$$

4. Calculate the normalised composition (x_i^*)

$$x_i^* = \frac{x_{i*}}{\sum_{i=1}^{q} x_{i*}} \ldots\ldots\ldots\ldots(8)$$

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

$$s(x_i) = \sqrt{\frac{\sum_{n=1}^{N}(x_{i,n}-x_i)}{N-1}} \ldots\ldots(9)$$

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

$$s(x_i) = \frac{a(xi)}{xi,wrm} \quad \text{...............}(10)$$

neo-pentane	2740814.802	0.1001	0.1016
iso-pentane	6401611.094	0.2234	0.2246
n-pentane	5777678.864	0.1937	0.1962
n-hexane	3206826.752	0.0986	0.1001

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 **9**.

Table – 8 Calculation of normalised composition

Component	WRM (% mol/mol)	Foot-print response factor	Calibration response factor
methane	75.605	10139000	10045000
nitrogen	0.5	12710000	12584000
CO_2	1.784	15179000	14990000
ethane	12.301	16616000	16432000
propane	6.938	21522000	21275000
i-butane	0.8926	24821000	24523000
n-butane	1.6218	26052000	25750000
neo-pentane	0.1026	27393000	26785000
iso-pentane	0.2259	28652000	28414000
n-pentane	0.1973	29829000	29362000
n-hexane	0.0991	32514000	32446000

Table 9. Standard deviation and relative uncertainty of normalised components

Component	Standard Deviation	Relative Uncertainty
methane	0.0117	0.0155
nitrogen	0.0009	0.1857
CO_2	0.0013	0.0747
ethane	0.0106	0.0861
propane	0.0080	0.1157
i-butane	0.0025	0.2757

3.9 Combined Uncertainty

Once the uncertainty from each uncertainty source is calculated, the combined uncertainty can be determined. Combine relative uncertainty is shown in Table **10**.

Based on the relative uncertainty and relative sensitivity of each component, as well as the uncertainty from the ISO 6976 calculation [6], 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 **11** and Table **12** respectively.

3.10 Systematic Error

It is common for GCs not to 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 [10] 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

Component	Calibration Peak Area	Un-normalised Composition	Normalised Composition
methane	757427621	74.7044	75.4329
nitrogen	6275226.32	0.4937	0.4990
CO_2	26670868.77	1.7571	1.7774
ethane	201591178.8	12.1324	12.2548
propane	147212451.1	6.8401	6.9150
i-butane	21830875.87	0.8795	0.8853
n-butane	41650019.5	1.5987	1.6131

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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. Fig. 21 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.
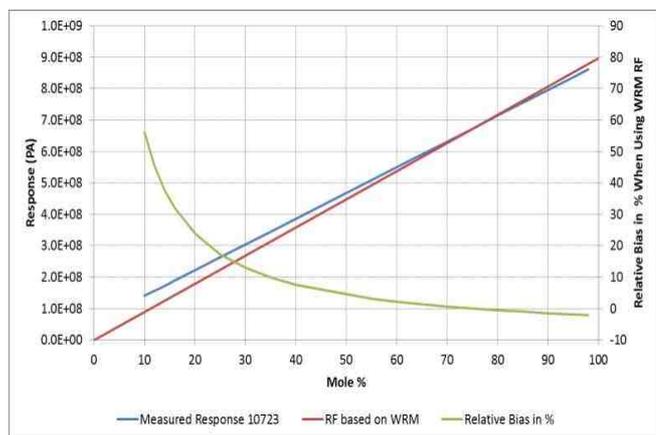

Fig. 21 - Bias introduced when using response factor from single point calibration

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 [2] 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.

3.11 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 on an expert system, which may loosely be defined as a computer system that emulates the decision-making ability of a human expert.

4.0 Conclusion

This paper has described methods that may be used for monitoring the performance of sample pressure let down system and gas chromatographs. It is important to ensure the initial health of the GC to avoid systematic error. Once it is determined that the GC is healthy, 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.

When GC is known to be healthy, sample pressure let down system performance can be validated by comparing the spot sample result against the GC analysis result. Combining GC conditional based monitoring tool and pressure let down system validation method will ensure that sample given to GC is representative and that it is measured by GC accurately.

5.0 Notation

GC	Gas Chromatograph
CBM	Conditional Based Monitoring
CV	Calorific Value
EUETS	European Union Emission Trading Scheme
k	Coverage Factor
a,b,c,d	Coefficients of linear regression of si on $xi*$
si	standard deviation
$xi*$	Un-normalised concentration of component i
xi	Normalised concentration of component i
$s(xi*)$	Standard deviation Un-normalised component xi
yis	Instrument responses to component i in the sample.
$yistd$	Instrument responses to component i in the Standard
$s(yis)$	Standard deviations of component i in the sample
$s(yistd)$	Standard deviations of component i in the standard
$s(xi)$	Standard deviation of the normalized mole fractions
q	Number of components analysed
CRM	Certified Reference Mixture Mixture which is used for the determination of the response curves of the measuring system.
WRM	Working Reference Mixture Mixture which is used as a working standard for regular calibration of the measuring system.
GUM	Guide to the expression of uncertainty in measurement.
RF i,FP	Foot-print response factor for component i

$RF_{i,cal}$	Calibration data response factor for component i
$x_{i,wrm}$	Mole fraction of component i in WRM
$R_{i,cal}$	Peak Area from calibration of component i
N	Number of calibrations that have been performed following the footprint calibration
$c(xi)$	Relative sensitivity coefficient of component i mole fraction
$U(xi)$	Relative uncertainty of component i mole fraction
mmscfd	Million standard cubic feet per day
MMBTU	Million British Thermal Unit
MJ	Mega Joules
GJ	Giga Joules

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Appendix 1. Lag Time Calculation

Example

Consider that there are pressure let down system with a sample stub, two pressure regulator and a GC with the following detail:

1.   Sample stub

- Input

- Line pressure (P2) = 50 Barg
- Line temperature (T2) = 60 ^{o}C
- Line compressibility (Z2) = 0.95
- Base compressibility (Z1) = 0.99
- Tubing inside diameter (d) = 10 mm
- Tubing length (l) = 1 m
- Normal pressure (P1) = 1.01325 Bara
- Normal temperature (T1) = 0 ^{o}C
- GC sample flow (qv)= 50 cc/min

- Intermediate result:

- Tubing volume (V2) = 78.54 ml
- Normal volume (V1) =

$$VI = \frac{P2V2T1Z1}{P1T2Z2} = 3378.54 \text{ ml}$$

- Result

Lag time = $\frac{v1}{qv}$ = 67.57 minutes = 1 hour 7 minutes and 34 seconds

2.   Between end of sample stub to first stage regulator

- Input:

- Line pressure (P2) = 50 Barg
- Line temperature (T2) = 60 oC
- Line compressibility (Z2) = 0.95
- Base compressibility (Z1) = 0.99
- Tubing inside diameter (d) = 4 mm
- Tubing length (l) = 1 m
- Normal pressure (P1) = 1.01325 Bara
- Normal temperature (T1) = 0 ^{o}C
- GC sample flow (qv)= 50 cc/min

- Intermediate result:

- Tubing volume (V2) = 12.57 ml
- Normal volume (V1) =

$$VI = \frac{P2V2T1Z1}{P1T2Z2} = 540.57 \text{ ml}$$

- Result

Lag time = $\frac{v1}{qv}$ = 10.81 minutes = 10 minutes and 48 seconds

3.   Between first stage regulator and second stage regulator

- Input:

- Line pressure (P2) = 10 Barg
- Line temperature (T2) = 40 ^{o}C
- Line compressibility (Z2) = 0.97
- Base compressibility (Z1) = 0.99
- Tubing inside diameter (d) = 4 mm
- Tubing length (l) = 1 m
- Normal pressure (P1) = 1.01325 Bara
- Normal temperature (T1) = 0 ^{o}C
- GC sample flow (qv)= 50 cc/min

- Intermediate result:
- Tubing volume (V2) = 12.57 ml
- Normal volume (V1) = 2 2 1 1 1 2 2 = 121.6 ml

- Result

Lag time = $\frac{v1}{qv}$ = 2.43 minutes = 2 minutes and 25 seconds

4.   Between second stage regulator and GC inlet

- Input:
- Line pressure (P2) = 1.5 Barg
- Line temperature (T2) = 35 ^{o}C
- Line compressibility (Z2) = 0.98
- Base compressibility (Z1) = 0.99
- Tubing inside diameter (d) = 4 mm
- Tubing length (l) = 1 m
- Normal pressure (P1) = 1.01325 Bara
- Normal temperature (T1) = 0 ^{o}C
- GC sample flow (qv)= 50 cc/min

- Intermediate result:

- Tubing volume (V2) = 12.57 ml
- Normal volume (V1) =

$$VI = \frac{P2V2T1Z1}{P1T2Z2} = 27.91 \text{ ml}$$

- Result

Lag time = $\frac{v1}{qv}$ = 0.56 minutes = 33 seconds

5.   GC cycle time: 240 seconds

6.   Total lag time = 1 hour 7 minutes and 34 seconds + 10 minutes and 48 seconds + 2 minutes and 25 seconds + 33 seconds + 240 seconds **= 1 hour 25 minutes and 20 seconds.**

Table 10. Combined relative uncertainty

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
CO_2	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
neo-pentane	WRM Relative Uncertainty	Repeatability Relative Uncertainty	0.0004	0.3456
iso-pentane	0.03305	0.0190	0.0006	0.2499
n-pentane	1	0.0778	0.0006	0.3280
n-hexane	0.3083	0.1314	0.0002	0.2182

Table 11. 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	- 0.1513	- 0.0062
Nitrogen	0.0050	0.0050	2.1067	2	1.0534	- 0.0050	- 0.0053
CO_2	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	1.000	0.0500
Combined Standard Uncertainty							0.0595
Coverage Factor (k)							2
Combined Expanded Uncertainty (%)							0.1190
CV absolute uncertainty (MJ/m3)							0.05620

Table 12. Standard density - 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