Conditional Based Monitoring of a Three Column Gas Chromatograph

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Abstract

Chromatography is an analytical technique which facilitates the separation of components in a mixture for subsequent use or analysis. On-line Gas Chromatography is frequently used within the oil and gas sector to obtain the composition of natural gas for the purposes of such things as allocation, fiscal reporting and sales/custody transfer. The composition measured by the Gas Chromatograph (GC) is therefore likely to come under the direct scrutiny of the buyer(s), the seller(s) and the regulator.

The GC is widely known as a device that conducts its measuring functions recurrently and it is imperative that the instrument remains stable and repeatable. The requirement for high repeatability makes the setting of the GC valve timing fundamentally important to accurate chromatography and hence there is a requirement to detect the presence of potential drift before the measurement becomes compromised.

The composition measured by the GC may be used to calculate various parameters, however, the gas calorific value is commonly used as the basis for financial transactions and as such the accuracy of this measurement is critically important. The author has performed a live test, which, in the absence of condition based monitoring, would have resulted in an undetected problem with the GC settings that would have caused an error of up to 1.4% in the calorific value. For the case in question, the monetary value of this error would have been in excess of £300,000 per month.

It is very clear that failure to calibrate and operate a GC to its full potential can be very costly and result in significant financial exposure for all the parties involved. This paper presents a condition based monitoring strategy aimed at ensuring that the GC performance is maintained and that any potential problems are identified early to prevent erroneous measurement.


### Glossary

Table 1 presents a list of abbreviations and definitions.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>C1</td>
<td>Methane</td>
<td>N2</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>C2</td>
<td>Ethane</td>
<td>CO2</td>
<td>Carbon Dioxide</td>
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<tr>
<td>C3</td>
<td>Propane</td>
<td>GC</td>
<td>Gas Chromatograph</td>
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<td>iC4</td>
<td>Iso Butane</td>
<td>CV</td>
<td>Calorific Value</td>
</tr>
<tr>
<td>nC4</td>
<td>Normal Butane</td>
<td>K</td>
<td>Coverage factor</td>
</tr>
<tr>
<td>neoC5</td>
<td>Neo Pentane</td>
<td>Δ</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>iC5</td>
<td>Iso Pentane</td>
<td>R²</td>
<td>Coefficient of determination</td>
</tr>
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<td>nC5</td>
<td>Normal Pentane</td>
<td>RF</td>
<td>Response Factor</td>
</tr>
<tr>
<td>C6's</td>
<td>Hexanes</td>
<td>RT</td>
<td>Retention Time</td>
</tr>
<tr>
<td>C6+</td>
<td>Hexane and heavier</td>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>C7+</td>
<td>Heptane and heavier</td>
<td>DECC</td>
<td>Department of Energy and Climate Control</td>
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### 1 Introduction

Gas Chromatography is defined as a process in which a sample mixture is vaporised and injected into a stream of carrier gas (typically nitrogen or helium) moving through a column containing a stationary phase composed of a liquid or particulate solid and is separated into its component compounds according to their affinity for the stationary phase [1]. The Oil and Gas Industry commonly use GCs to measure the components of a gas stream which is then used to calculate, among other things, the calorific value, molecular weight, density, and compressibility. These important parameters are required for various calculations performed in custody or fiscal transfer measurement systems and gas allocation methodologies; therefore, it is critical to have accurate measurement of the gas composition.

To ensure that the GC performance is acceptable, there exist various routine tests. Repeatability and reproducibility tests prove that a GC is working within limits specified in ASTM D1945:1996 [2] or GPA 2261:1995 [3]. However, due to the wide tolerance on some compounds, these tests do not guarantee that the GC is always working as intended. These tests are not able to determine that each of the components goes through the intended column or that all of the valve timings are correct. Only by conducting further analysis of the response factor of each of the components can such functionality be shown with suitable confidence and precision.

This paper describes a practical method that can be used to overcome some of the current testing limitations by analysing the response factor trend, the correlation between the component’s molecular weight and its response factor, and by looking at the historical data for each component.
2 Gas Chromatograph Design and Operation

A multi-column separation technique 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 [4]. 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, Figure 1 shows the GC flow tubing path configuration for C1, N2, CO2, C2 and C7+. Similarly Figure 2 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.
3 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. However, 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/m³ 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.

Application of some fundamental methodologies and utilization of Gas Chromatography Analysis Software (GCAS™) can assist not only in identifying the 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 the GCAS™ will allow the industry to achieve the obvious advantages and 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

4 The method

The method has 3 main features: Footprint; Calibration Data, and Data Analysis.

4.1 Footprint

The ‘Footprint’ contains data from a GC where the GC is known to be healthy. The Footprint is then used as reference for comparison of every future calibration data. The Footprint page of GCAS is shown in Figure 3.
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 Figure 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 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 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 Figure 4.

MW – RF Log Chart

There are 3 critical valve timings within a 3 column chromatograph:

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 done 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 Figure 5.

![Figure 5: MW – RF Log Chart](image)

Figure 5a shows the correlation between C1, C2, and the heaviest component where the measurements are performed when carrier gas flow through column 3. Figure 5b shows the correlation among the middle components where the measurements are performed while carrier gas flows through the restrictor. Figure 5c shows the correlation among all components. The correlation obtained from the first two graphs are 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 (Figure 6) 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.

![Figure 6: RF – MW correlation case 1](image)
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 (Figure 7) 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.

![Figure 7: RF – MW correlation case 2](image)

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 (Figure 8) 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.

![Figure 8: RF – MW correlation case 3](image)

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 (Figure 9) it can be seen that C3 is lower than expected, which results in a poor correlation between C1, C2 and the heavy component.

![Figure 9: RF – MW correlation case 4](image)
RetentionPolicy

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 [5]. 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 Figure 3.

4.2 Calibration Data

The calibration data page is shown in Figure 10.
The layout of the calibration data page is exactly the same as that of the footprint page. On the calibration data page, both the footprint and the selected calibration data are shown for comparison.

4.3 **Data Analysis**

Historical data trending is important when trying to analyse the GC performance over time. Within the data analysis trend, along with the variable being reviewed, ± 2 standard
deviations \((2\delta)\) \(k=2\) are also plotted as tracking action limits. To calculate the mean and \(\delta\) the first 25 data points are used following a footprint. If the trend begins to shift outside the action limit, then it would indicate a possible problem with the GC.

There are five types of data trended within GCAS. These are Response Factor, Response Factor – Error, Retention Time, Retention Time – Error and \(R^2\). Figure 11 shows an example of the Response Factor – Error trend.

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5 Case Studies

Several case studies 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.

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, Figure 12, clearly indicated that the GC was not healthy.
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 Figure 13.

![Figure 13: RF trend after component data table was adjusted](image)

From Figure 13, 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 Figure 14.

![Figure 14: RF trend after calibration sample line was purged](image)

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 Figure 15.
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 Figure 16.

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>
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<th></th>
<th>Wrong RF</th>
<th>Correct RF</th>
<th>Difference</th>
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<tbody>
<tr>
<td>CV</td>
<td>45.07 MJ/sm³</td>
<td>44.44 MJ/Sm³</td>
<td>1.41%</td>
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<tr>
<td>Volume</td>
<td>100 mmScf</td>
<td>100 mmScf</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>2,831,684 m³</td>
<td>2,831,684 m³</td>
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</tr>
<tr>
<td>Energy (MJ)</td>
<td>127,624 GJ</td>
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</table>

Table 2: Unhealthy vs Healthy result comparison, Value per KWh data is taken from Quarterly Energy Prices, September 2011 [6]

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.

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 Figure 17.
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 also to ensure that other potential causes leading to non-homogeneity of the stated gas mixture are avoided.

6 Conclusions

The studies described above show that with the application of condition based monitoring as described, the accuracy of the GC can be maintained throughout the year. Creating a fully auditable database of the GC performance, eliminating unnecessary errors, predicting future failures, and providing the necessary course of action to prevent failures should guarantee the accuracy of the GC and promote prolonged reliable performance.

As the GC conditional based monitoring method is performed by offshore technicians, its utilization will help to increase the competency level of technicians and therefore reduce unnecessary specialist cost to solve GC issues.

With the data presently available, further studies will allow the determination of a live uncertainty calculation to be performed for each GC.
7 References


