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Technical Paper

Are We Barking Up the Wrong Tree? Uncertainty vs Error and the Role of CBM to Measure Both

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1   INTRODUCTION

What is the best way to maintain a GC? Should we ensure that we have the best calibration gas? Should we measure calibration gas as unknown and compare the GC result against calibration gas certificate? Should we be worried about the non-linear effect of the detector, should we compare spot sample result against GC result?

Various different operators have different maintenance regime to ensure that their GC is maintained in the best way. As there are many ways of maintaining the GC, different operators perform their maintenance to comply with certain regulations or agreement. However, many times the type of maintenance adopted by operators may not be the one best suited for their pipeline conditions. Very often operators barking up the wrong tree trying to comply with certain regulations while completely overlooking the issue in hand which results in significant errors without operators even knowing or noticing that.

As an example, calibration gas is specified to be of highest accuracy with less than 1% uncertainty on each component. And operators have that. Surprisingly, quite often during the process of changing calibration gas, the new composition value is not updated in the GC. In one of the case study such error reached monetary value of more than £400,000 /month.

There are few other examples that will be shown throughout this paper. In many occasions, the fact that an operator wants to be in compliance with a certain method causes them to completely miss a bigger issue in their hands, and as a result their quest for higher accuracy will lead them to the wrong direction.

The aim of the paper is to firstly show that currently there exist no single method that can handle all possible issues with the GC, and secondly, how any chosen method when not combined with the other method can cause operators to overlook unpremeditatedly important things that may have big impact on the GC measurement accuracy.

The issues are that may bring bigger impact on the GC if the other issues are overlooked are currently known as follows:

1. Calibration gas quality
2. GC Calibration results
3. GC non-linearity
4. GC reproducibility
5. Sample let down system

This paper also offers a solution in a form of conditional based monitoring software tool for GC that takes into consideration all those methods within one program.

2   ARE WE BARKING UP THE WRONG TREE?

Selecting a certain maintenance method while overlooking some other methods can cause operators to, non-technically speaking, bark up the wrong tree. The following are a few possibilities of those wrong trees and recommendation on how to fix them.

2.1   Calibration Gas Quality

2015/2016 has been a tough year for oil and gas industry. Most operators are looking to cut cost in all possible avenues. One of the cost saving avenue is by ordering calibration gas of lower quality. From buyer point of view, this might be a good way to cut cost, however, from the measurement point of view the impact can be quite significant.

The following is an example of the impact of calibration gas quality in terms of CV. Table 1 shows calibration gas composition with low composition uncertainty.

Component	Mole percentage	±	Absolute uncertainty	Relative uncertainty
Methane	84.994	±	0.03	0.0352966
Nitrogen	5.522	±	0.018	0.3259689
Carbon dioxide	1.995	±	0.005	0.2506266
Ethane	4.283	±	0.012	0.2801774
Propane	1.803	±	0.006	0.3327787
i-Butane	0.2496	±	0.0008	0.3205128
n-Butane	0.3474	±	0.0013	0.3742084
Neopentane	0.1	±	0.001	1
i-Pentane	0.3006	±	0.002	0.665336
n-Pentane	0.1995	±	0.0011	0.5513784
Hexane	0.1007	±	0.0021	2.0854022
Heptane	0.1008	±	0.0027	2.6785714
Total	99.995600			

Table 1. Calibration gas with low composition uncertainty

On GC measurement, each individual component impacts measurement of other components as the result will be normalised. Therefore error in one component measurement will impact all components. The low uncertainty of calibration gas means low CV uncertainty. The impact of the above calibration gas uncertainty on the CV calculation uncertainty is shown in Table 2. It is to be noted that the value shown herein ignores the 0.1% additional uncertainty from the calculation standard.

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Component	Normalised mole fraction	U(cal gas)	S(cal gas) S(repro)	Standard uncertainty
Methane	0.849940	0.017648	-0.0197	0.000348
Nitrogen	0.055220	0.162984	-0.0554	0.009030
Carbon dioxide	0.019950	0.125313	-0.0199	0.002494
Ethane	0.042830	0.140089	0.0307	0.004300
Propane	0.018030	0.166389	0.0260	0.004330
i-Butane	0.002496	0.160256	0.0054	0.000864
n-Butane	0.003474	0.187104	0.0075	0.001411
Neopentane	0.001000	0.500000	0.0029	0.001436
i-Pentane	0.003006	0.332668	0.0087	0.002889
n-Pentane	0.001995	0.275689	0.0058	0.001595
Hexane	0.001007	1.042701	0.0037	0.003808
Heptane	0.001008	1.339286	0.0044	0.005881
	Combined standard uncertainty			0.013780
	Coverage factor (k)			2
	Combined expanded uncertainty			0.027561
	CV absolute uncertainty (MJ/m³)			**0.010660**

Table 2. CV uncertainty of gas with low composition uncertainty

From Table 2, it is demonstrated that the impact of uncertainty on CV is quite minimum. On the contrary, when calibration gas selected is of a lower quality, for example with compositional uncertainty of ±2%, then the impact on CV uncertainty can become quite significant. Table 3 shows the same gas as above, only it has 2% measurement uncertainty.

Component	Mole percentage	±	Absolute uncertainty	Relative uncertainty
Methane	84.995481	±	0.3	0.3529599
Nitrogen	5.521183	±	0.11042366	2
Carbon dioxide	1.996865	±	0.0399373	2
Ethane	4.283801	±	0.08567602	2
Propane	1.803683	±	0.03607366	2
i-Butane	0.249655	±	0.0049931	2
n-Butane	0.347397	±	0.00694794	2
Neopentane	0.100055	±	0.0020011	2
i-Pentane	0.300574	±	0.00601148	2
n-Pentane	0.199614	±	0.00399228	2
Hexane	0.20169	±	0.0040338	2
Total	99.999998			

Table 3. Calibration gas with high composition uncertainty

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The impact of the high composition uncertainty in CV can become quite significant. Table 4 shows the impact on CV uncertainty.

Component	Normalised mole fraction	U(cal gas)	S(cal gas) S(repro)	Standard uncertainty
Methane	0.849955	0.176480	-0.0191	0.003377
Nitrogen	0.055212	1.000000	-0.0554	0.055392
Carbon dioxide	0.019969	1.000000	-0.0199	0.019919
Ethane	0.042838	1.000000	0.0308	0.030755
Propane	0.018037	1.000000	0.0261	0.026063
i-Butane	0.002497	1.000000	0.0054	0.005397
n-Butane	0.003474	1.000000	0.0075	0.007548
Neopentane	0.001001	1.000000	0.0029	0.002876
i-Pentane	0.003006	1.000000	0.0087	0.008692
n-Pentane	0.001996	1.000000	0.0058	0.005793
Hexane	0.002017	1.000000	0.0073	0.007321
	Combined standard uncertainty			0.073203
	Coverage factor (k)			2
	Combined expanded uncertainty			0.146406
	CV absolute uncertainty (MJ/m^3)			**0.056586**

Table 4. Calibration gas with high composition uncertainty

Assumption is made on pipeline that is flowing gas with monetary value worth £30 million /month. 0.146% uncertainty means an uncertainty of £43,921 /month in comparison to uncertainty of 0.027% which only means an uncertainty of £8,268 /month. it is obvious to use calibration gas with lower uncertainty that may be more expensive than the alternative, however from operation point of view it might potentially save much more money through more accurate measurement.

2.2   Calibration Gas Storage and Dew Point Temperature

Ordering calibration gas that is of high quality is the first step. However, many operators make mistake by filling as much pressure as possible into the calibration gas. Considerations need to be made in term of storing the calibration gas. This is crucial for the areas where ambient temperature can become quite cold. If the calibration gas is stored lower than its dew point temperature, it can have condensation on its heavier end and the impact will be a faulty calibration result. An example of the calibration result from non-homogenous gas can be seen in Figure 1.
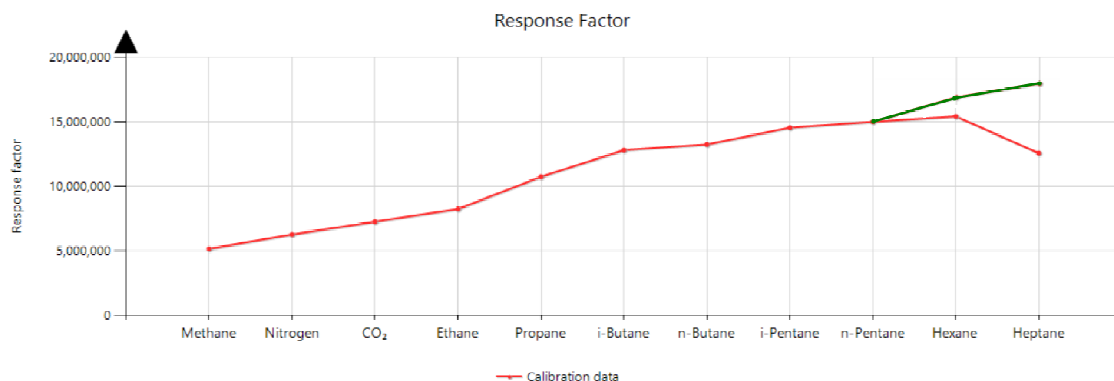
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Figure 1. Non homogenous calibration gas

Because the calibration gas certificate is always used as the basis for the calibration gas bottle concentration, when the gas is not homogeneous it will lead to a measurement error.

From the Figure 1, it can be seen that hexane and heptane response factor is lower than expected (green line is the expected RF for hexane and heptane). This is due to the gas being stored in the cold weather, lower than its dew point temperature. This issue if goes undetected can lead to quite significant mis-measurement.

However, this can be avoided by observing the response factor trend as well as the correlation chart.

Figure 2. RF trend and correlation chart of healthy GC

A healthy GC will have an ascending response factor trend and high correlation between the Response Factor and Molecular Weight as shown in Figure 2. The case where the heavy end sits at the bottom of the bottle can be overcome by re-heating the gas to a homogenous state and running the GC using calibration gas for several cycles. Test performed has shown that the detected gas return into its normal homogeneous state after 10 runs as shown in Figure 3.

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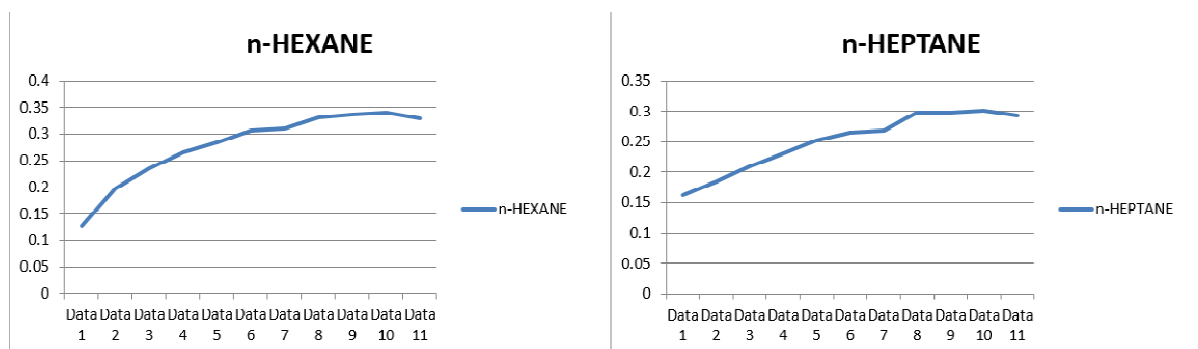
Figure 3. Runs of calibration gas prior to returning to homogenous state

Arguably after this process the composition within the bottle has been altered, however it can also be argued that normally the heavy end has low concentration with low sensitivity towards CV and density measurement and therefore the calibration gas will still be fit for purpose. Also the acceptability of calibration gas can be determined by the gas thermal conductivity property. Gas that flows through thermal conductivity detectors will follow consistent characteristic as shown in Figure 2 earlier. As long as the RF trend is ascending in the order of Methane – Nitrogen – CO2 – Ethane – Propane – iButane – nButane – neoPentane – iPentane – nPentane – Hexane – Heptane, and the correlation between RF and MW is high, it can be concluded that calibration gas is healthy as well as the valve and other time events in the GC are healthy too.

This principle can also be used to determine if a calibration gas is as per what stated in its calibration certificate. There are some occasions where errors occur in the making of calibration gas which results in the bottle composition not as per the bottle's certificate. This can be determined by checking the calibration result.

When goes undetected, this issue can cause systematic error despite the low uncertainty of the calibration gas composition.

2.3   Calibration Issue

Having good calibration gas is a good first step. However, in many occasion it has been seen that operators perform calibration with the wrong calibration gas composition entered into the GC. This can have a significant error on measurement. The following is an example that has been used in previous paper, however, it is a very useful example to show few things that can go wrong from a single calibration and how the calibration data information can become a very useful diagnostic tool to ensure GC correct measurement.

The GC in this case study had been offline for a while, and it was time to bring it back online again. A new calibration gas was installed and a calibration was done. Instead of checking the trend and the result of the calibration, a forced calibration was performed and GC was assumed to run correctly as it did not produce any alarm. However, because it was a new calibration gas, the composition of the new calibration gas and the composition of the old calibration gas that still existed in the GC were not the same. The initial calibration RF trend on this GC is as the following:
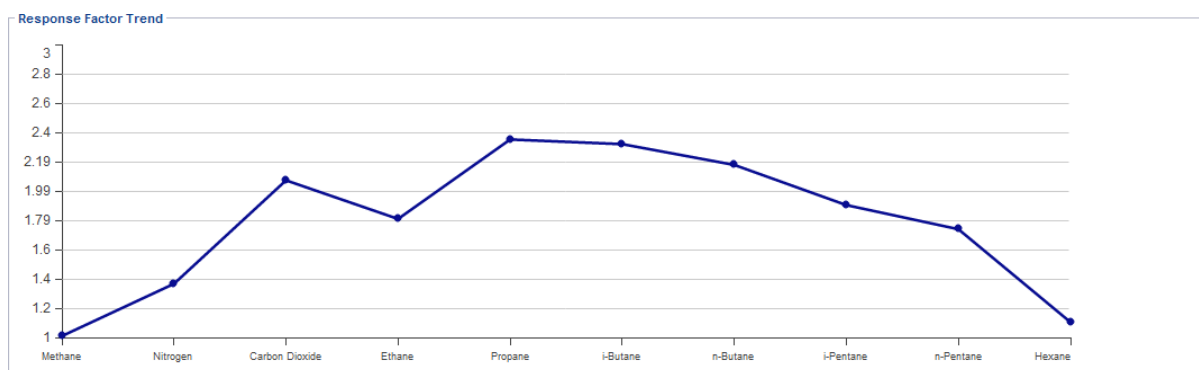
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Figure 4. RF trend due to wrong component concentration entered in GC data table

Following this, component data table within the GC was changed to match the calibration gas certificate and further calibration was performed. The result was a better response factor, with several minor issues as shown in Figure 5.
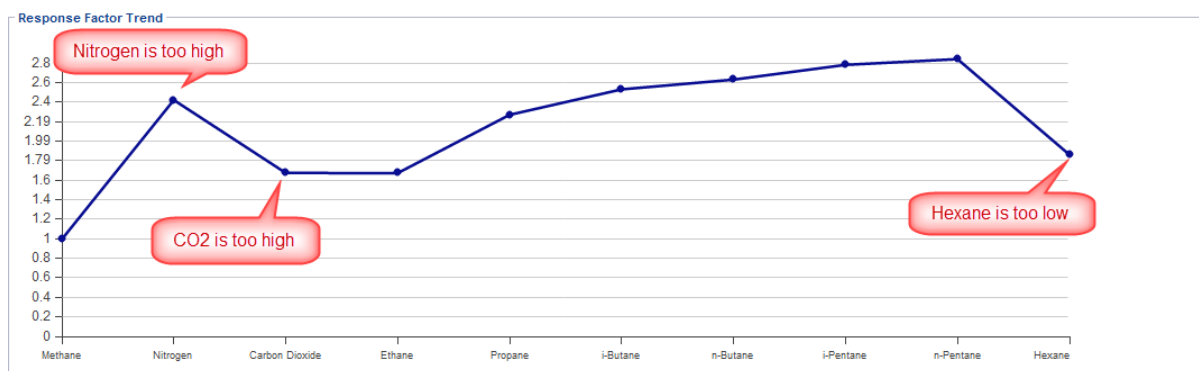

Figure 5. RF trend after component data table in GC was adjusted

From Figure 5, the trend shows that N2 level was too high and hexane level was too low. The N2 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 6.
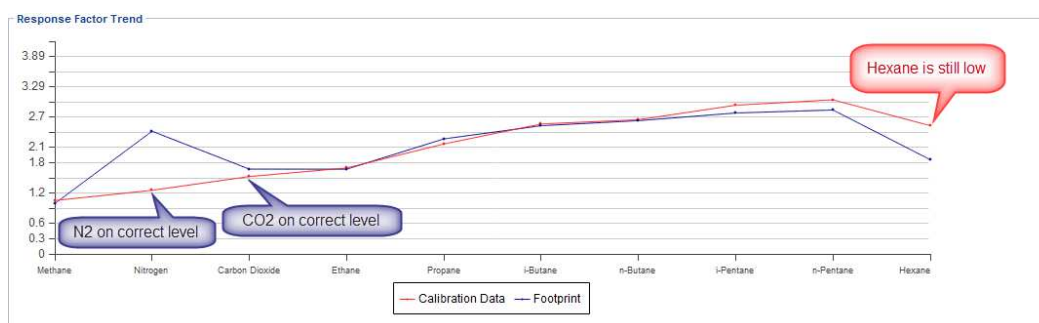
Figure 6. RF trend after calibration sample line has been purged

The blue line above shows the trend prior to purging, and the red line shows the trend after purging. The N2 is now at its expected level; however hexane RF was still lower than expected. Inspection of the correlation between MW and RF is then used to help determine the cause of the low Hexane RF as shown in Figure 7.
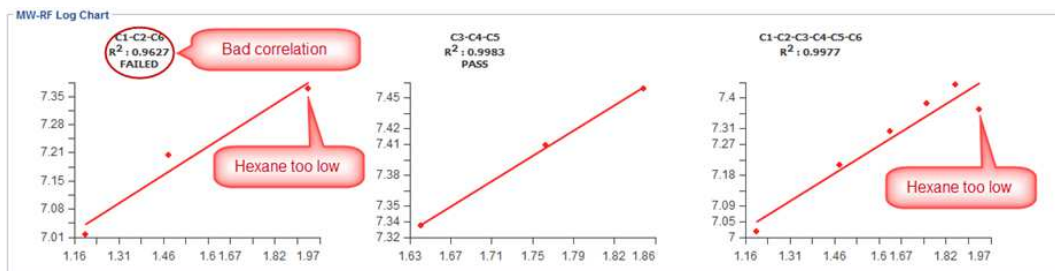
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Figure 7. MW-RF Log chart of calibration data

It was determined from the plot that based on the poor correlation of C1-C2-C6; the problem was caused by some of the heavy component (hexane) leaving column 1 to flow through column 2 instead of all of it being back-flushed due to incorrect valve timing. The result was not all hexane component being detected by the GC and the RF was low.

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 12.
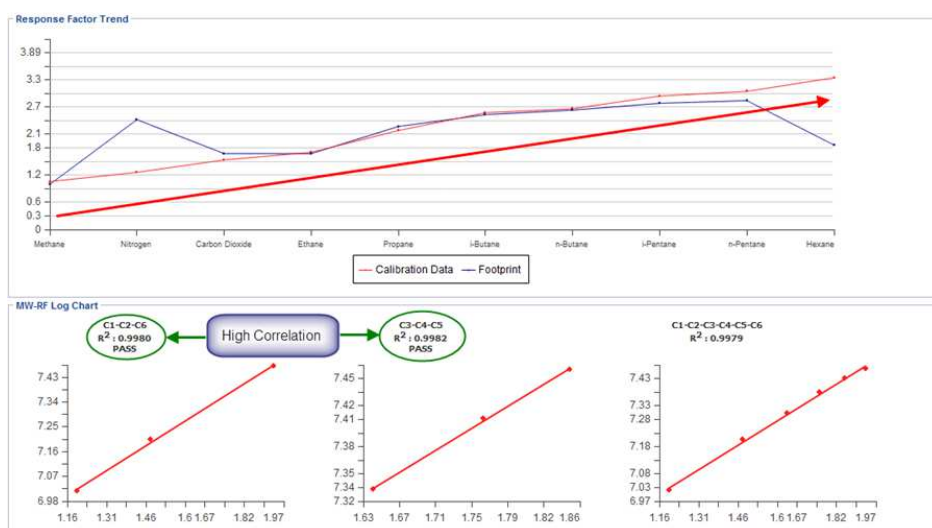
Figure 8. RF trend and MW-RF log chart of healthy GC

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 apparent at the individual component level, however analysis of the resultant calculated calorific values of the two calibrations clearly show the difference to be significant. The potential difference in the final output result is given in Table 5.

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Description	Wrong RF	Correct RF	Difference
CV	45.07	44.44	1.41%
Volume	100	100	
Volume	2,831,684	2,831,684	
Energy (MJ)	127,624	125,840	1,784
Energy (KWh)	35,451,330	34,958,311	493,019
Value per KWh	£0.02418	£0.02418	
Value /day	£857,213	£845,292	**£11,921**
Value /month	£25,716,394	£25,358,758	**£357,636**

Table 5. Unhealthy vs healthy result comparison, Value per KWh data is taken from Quarterly Energy Prices, June 2016

2.4   Dual Level Calibration to Reduce Non-Linear Bias

Calibration can be proven to be correct, calibration gas can be selected of the highest quality, however when the GC operates in the non-linear range, it will introduce bias that can also be quite significant. ISO 10723:2012 [3] specify how to perform GC performance evaluation test to understand the extent of non-linearity and how much impact the non-linearity has on overall measurement. This method requires 7 sets of different gas composition that covers the operational range of the GC. There are a lot of preparation prior to the performance evaluation test that can be quite impractical in case the test needed to be performed urgently.

Looking at the impracticality of performing ISO 10723, a new method was recently introduced in the UK and has received a letter of no objection from OGA (Oil and Gas Authority) as shown in 0. Dual Level Calibration is a middle ground between single point calibration using single set of gas compositions and multilevel calibration using 7 sets of gas compositions. The idea is to reduce the bias associated with single point calibration without exerting big efforts associated with performing evaluation test according to ISO 10723.

Single Point Calibration uses one set of calibration gas as compositions to get the GC response towards a certain component. Calibration result is calculated as a function of peak area generated by a certain mole%. This is illustrated in Figure 9.
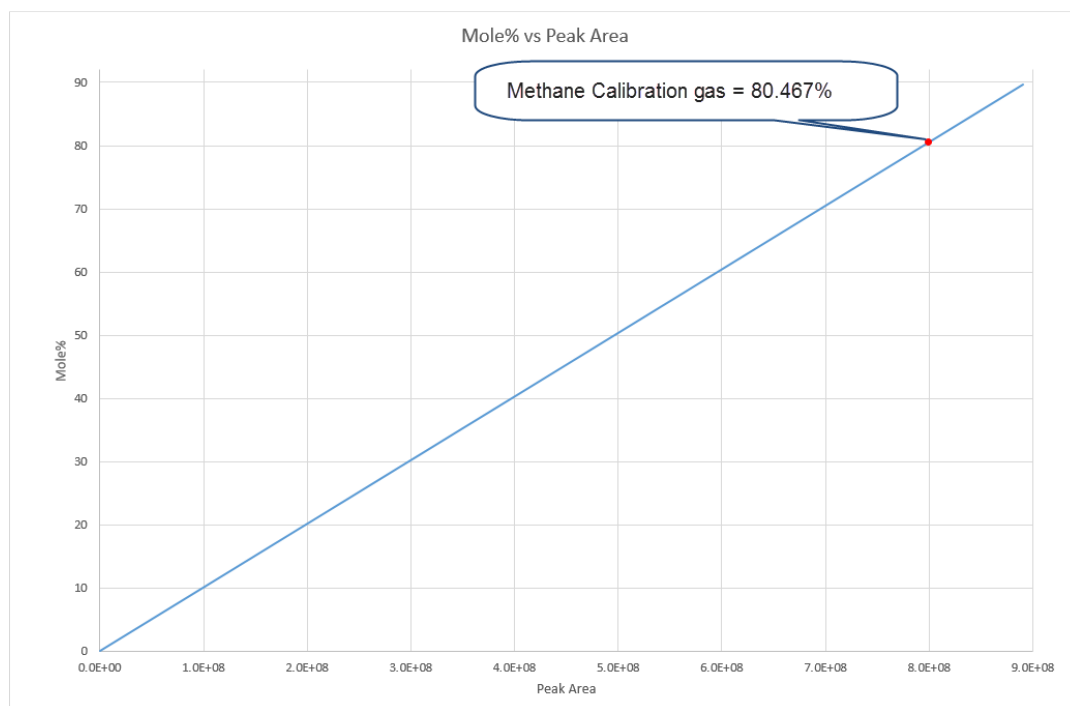
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Figure 9. Single point calibration

As shown in Figure 9 above, the mole composition measurement is proportional to the changes in peak area as shown in Figure 12 below.
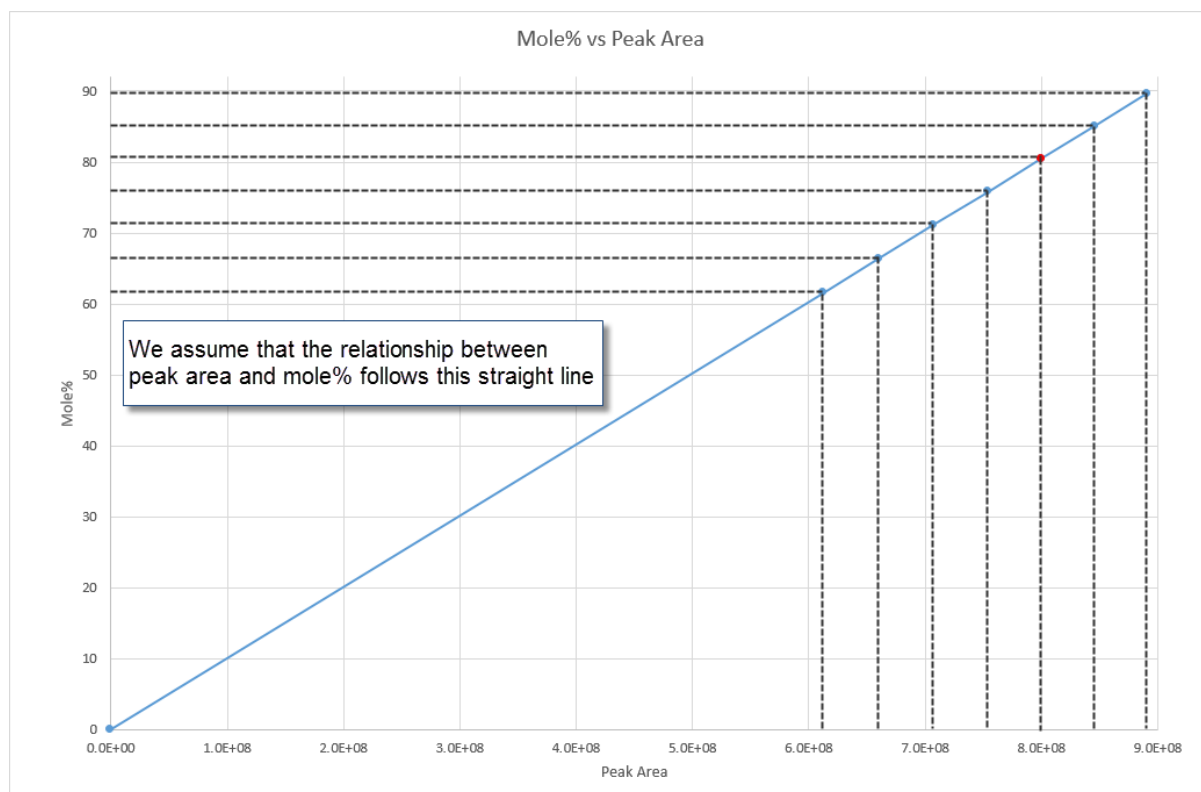

Figure 10. Peak Area – mole% relationship on a single point calibration

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By performing single point calibration, the GC is assumed to be linear. However, the true response function of the GC does not follow linear line as shown in a single point calibration. Figure 13 illustrate a real response function in comparison to single point calibration function on methane calibration results. The function on orange line (true function) is generated using 7 sets of gases with different composition.
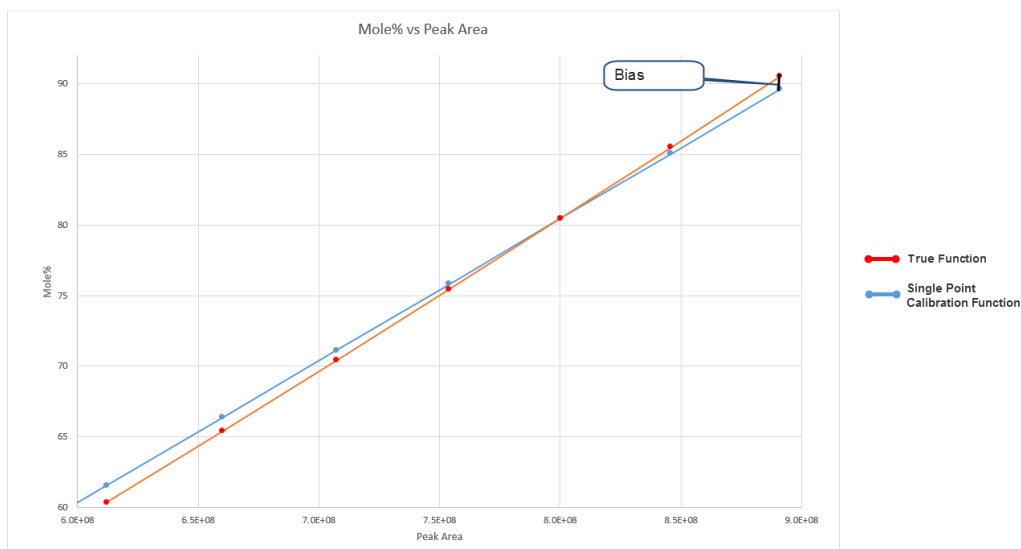

Figure 11. True function in comparison to single point calibration function

The impact of running single point calibration is bias where the measurement is not performed in the linear range of the gas. Figure 14 illustrates the bias of methane across range of measurement when calibrated using single point calibration in comparison to the true function.
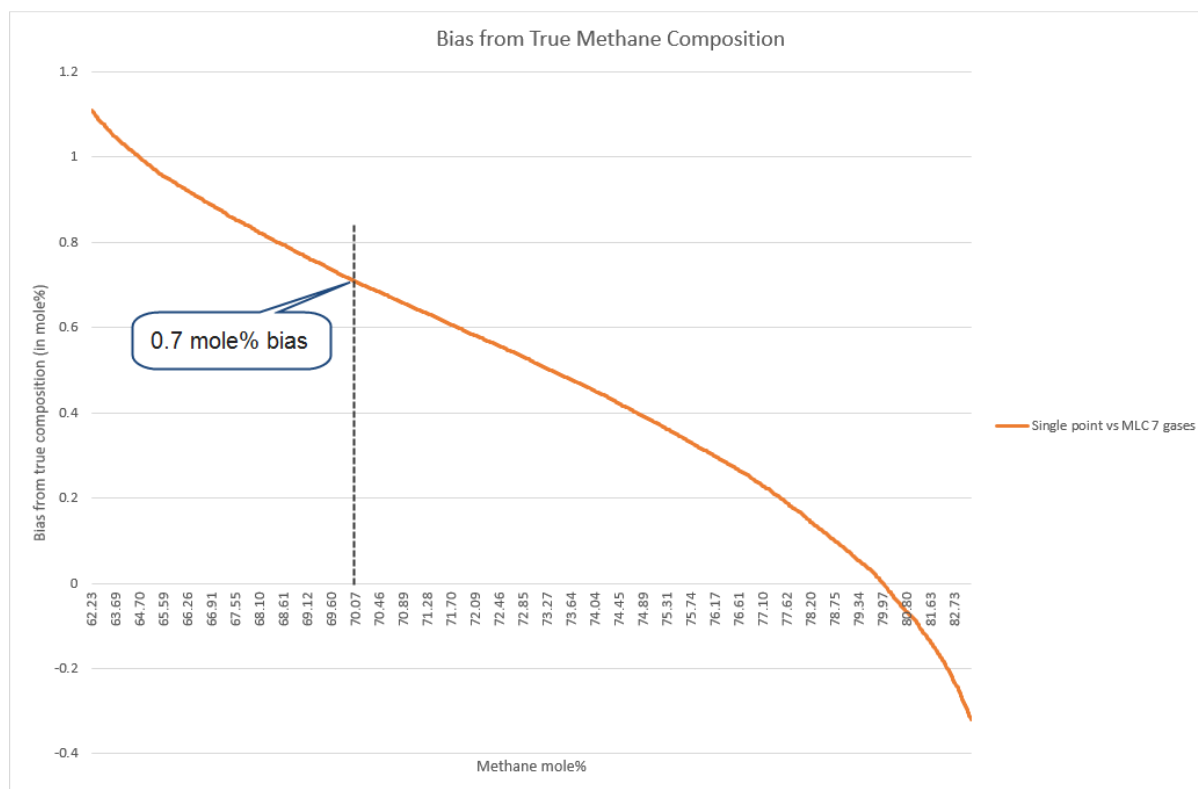
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Figure 12. Single point calibration bias when compared against true function

The above illustration is the reason why when measuring a stable gas composition, for instance stable gas that comes from a single well, it is recommended to design calibration gas composition as close to the process gas composition as possible. Doing so will minimise the measurement bias from detector non-linearity. Table 6 shows measurement from GC that has calibration gas that is non-representative of the process gas.

Description	Calibration Gas (mole%)	Actual value	GC measurement	Difference
Methane	69.5	84.9948	84.7366	-0.2582
Nitrogen	10	5.5195	5.6051	0.0856
CO_2	8	1.9973	2.0269	0.0296
Ethane	9	4.2856	4.3836	0.098
Propane	2	1.8035	1.829	0.0255
i-Butane	0.5	0.2497	0.2524	0.0027
n-Butane	0.5	0.3476	0.3527	0.0051
Neopentane	0.2	0.0999	0.1008	0.0009
i-Pentane	0.1	0.3007	0.3063	0.0056
n-Pentane	0.1	0.1996	0.2027	0.0031
Hexane	0.1	0.2017	0.2037	0.002
CV (MJ/m3)		38.6512	38.6704	0.0192
Difference (%)				0.0496%

Table 6. Big bias when calibration gas is non representative of process gas

This bias can easily be reduced to a negligible level when calibration gas is designed to be similar to the process gas composition. Table 7 shows the result between actual value and GC measurement when calibration gas is similar to the gas being measured.

Description	Calibration Gas (mole%)	Actual value	GC measurement	Difference
Methane	84.9955	84.9948	84.9944	-0.0004
Nitrogen	5.5212	5.5195	5.5197	0.0002
CO_2	1.9969	1.9973	1.9974	1E-04
Ethane	4.2838	4.2856	4.2857	0.0001
Propane	1.8037	1.8035	1.8035	0
i-Butane	0.2497	0.2497	0.2497	0
n-Butane	0.3474	0.3476	0.3476	0
Neopentane	0.1001	0.0999	0.0999	0
i-Pentane	0.3006	0.3007	0.3007	0
n-Pentane	0.1996	0.1996	0.1996	0
Hexane	0.2017	0.2017	0.2018	0.0001
CV (MJ/m3)		100	100	0
Difference (%)		38.65125	38.65127	0.00002
				0.00005

Table 7. Negligible bias when calibration gas is similar to process gas

This is however only useful when the process gas is stable with low variation over time. When the process gas variation is high, GC may be impacted by non-linearity. How big of a bias a GC has from non-linearity can be tested. This is specified in the ISO 10723:2012 standard [3].

In many occasions, selecting the correct calibration gas can ensure that the bias will be acceptable across a defined range of measurement. For example, if the range of measurement is between 70 to 75% on methane, running ISO 10723 will give us information what composition will be the best to use.

Figure 13 shows Monte Carlo simulation of methane bias between 60% to 90% measurement where calibration gas sits at 84%. From Figure 13 it is visible that bias is expected to increase as methane concentration reduces.
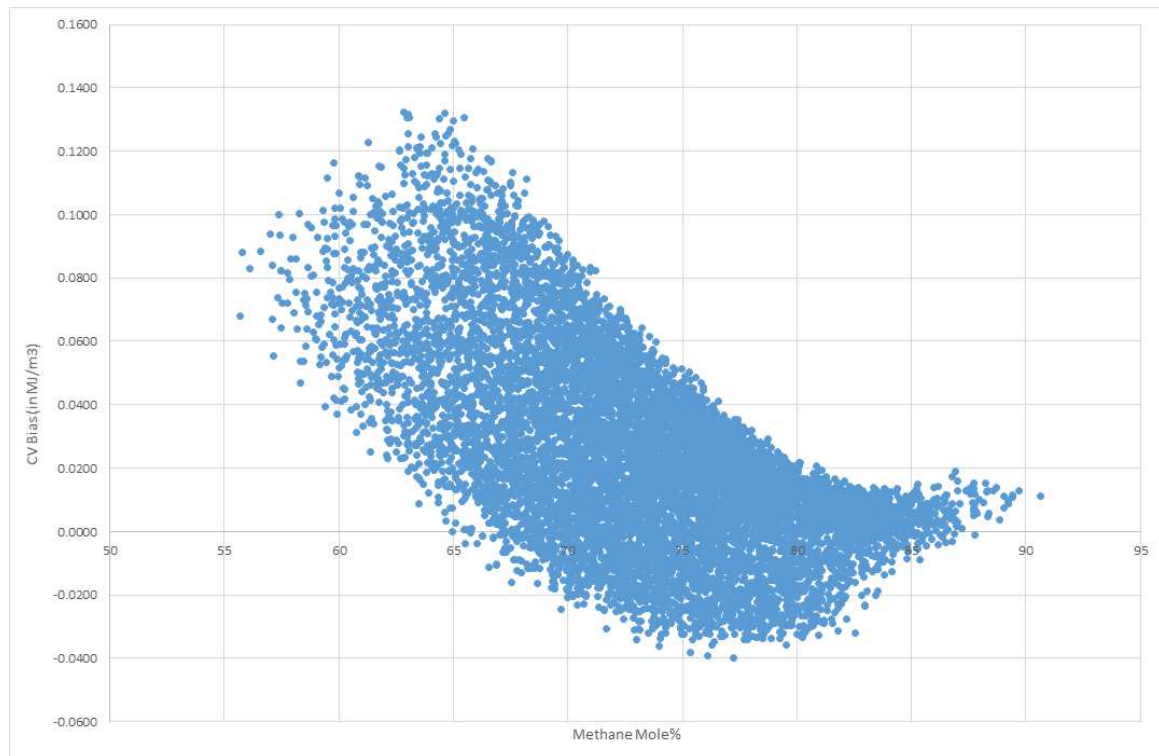
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Figure 13. Methane bias distribution when using 84% methane as calibration gas

The same simulation is done using calibration gas where methane sits at 70%. Figure 14 shows the result.
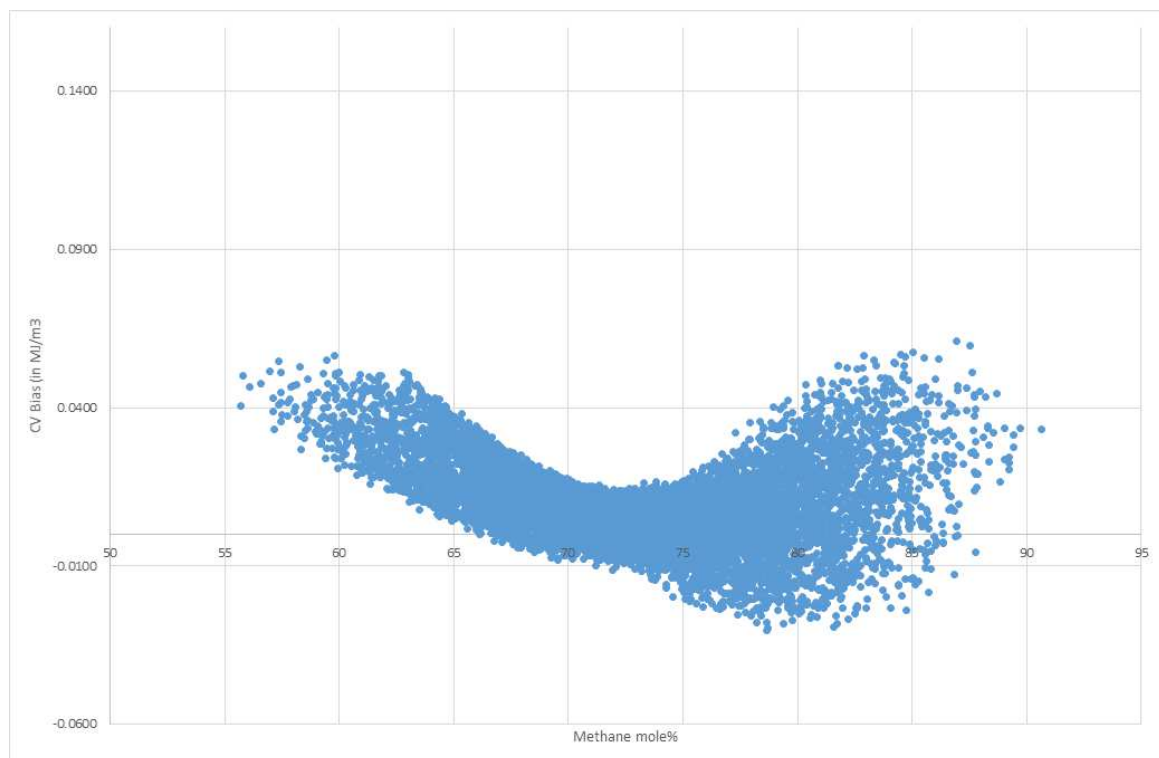

Figure 14. Methane bias distribution when using 70% methane as calibration gas

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It can be seen that selecting more suitable calibration gas reduces the bias significantly.

Although performing ISO 10723 performance evaluation test can be very useful, it is not very practical as it involves quite a significant preparation with the logistic to order and deliver 7 set of calibration gases. The following are some of the practical issues associated with preparation for and implementation of ISO 10723 performance evaluation test.

1. Logistic to deliver the 7 sets of gases
2. It can be costly. Cost – benefit analysis needs to be done. If process gas is stable, the cost may exceed the benefit.
3. When performed on a faulty GC, actual fault may be masked as non-linearity
4. Drifts may invalidate the constant generated during calibration
5. When constants are implemented in GC, RF will be close to 1. Log-log plot cannot be used when all RF is close to 1 and therefore checks to ensure if GC is healthy is not possible
6. If tested in the wrong range, failed result may give impression of faulty GC when if tested in the correct range the result may pass

Because of the logistical issue, test is normally done once a year, and it can become impractical when GC experience some issue and need to perform another performance evaluation test.

Dual Level Calibration eliminates the impracticality of ISO 10723 and reduces the bias of single point calibration to negligible level. Instead of using seven sets of gases, DLC uses 2 sets of gases of which both calibration gas can be stored on site. Where storage space permits, it is recommended to have two big bottles where both of them can be used as daily use calibration gas. However where storage space is limited, it is recommended to have one big bottle as daily calibration usage, and a small bottle for the use of performing DLC and monthly reproducibility check.

To perform DLC, the range of gas that is going to be measured need to be understood. The calibration gas is then designed to cover the range of the gas, one on the upper range, and the other one on the lower range as illustrated in Figure 15 below. On the below example, the methane measurement range will be between 70% - 80%.

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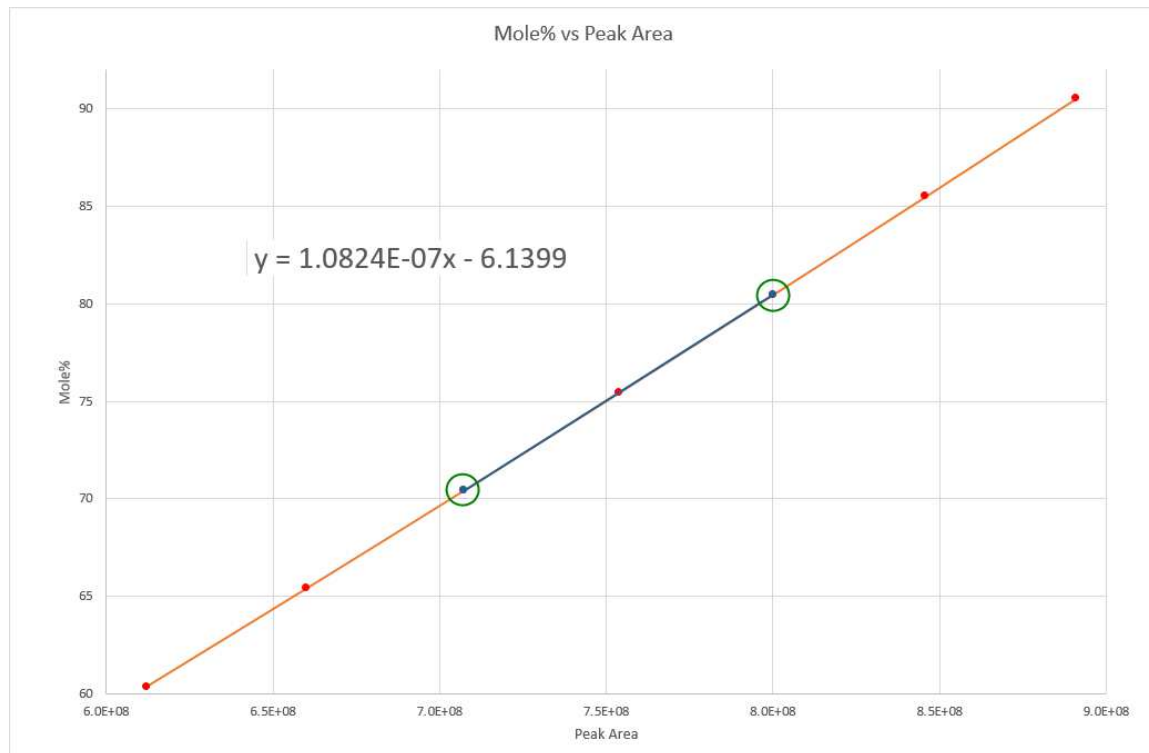

$$y = 1.0824E\text{-}07x - 6.1399$$

Figure 15. Dual Level Calibration Function

When this function is implemented on the GC, the bias on methane measurement on the range between 70%-80% is reduced to a negligible level as shown in Figure 16.
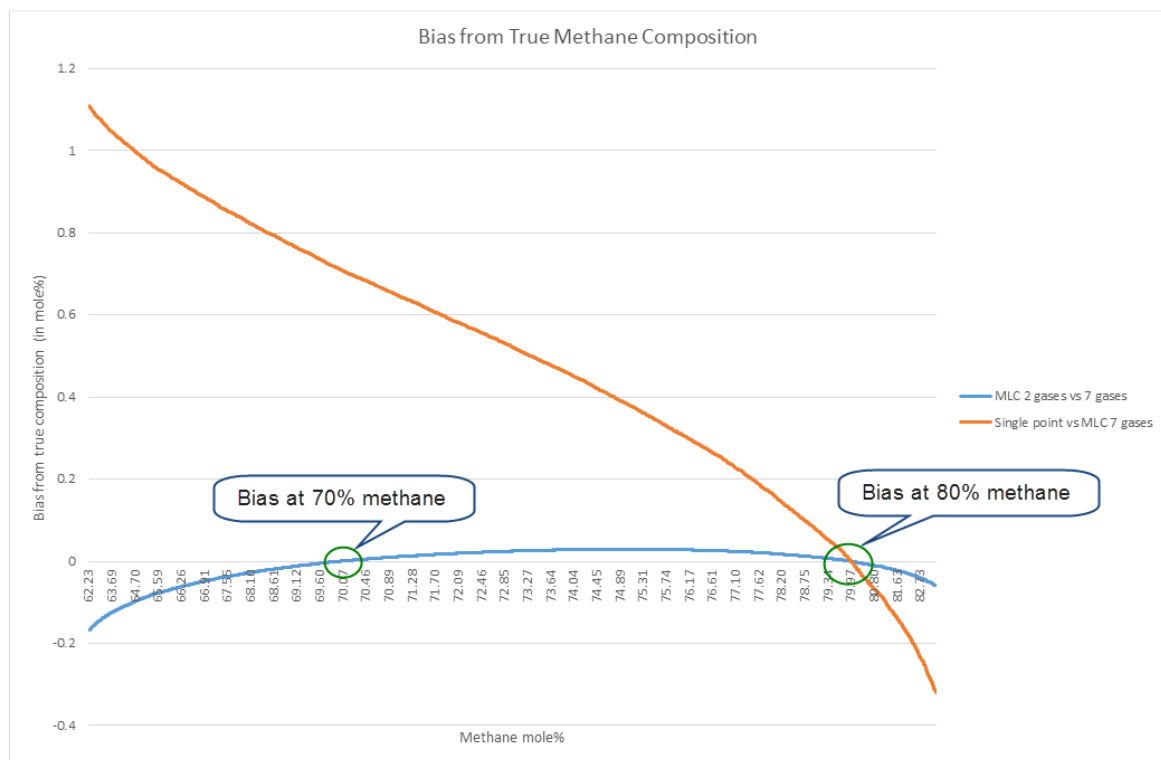

Figure 16. Bias reduced to negligible level

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The impact on the CV and line density bias is also reduced to significantly. Figure 17 and Figure 18 shows the bias on CV and density respectively from one of the case.
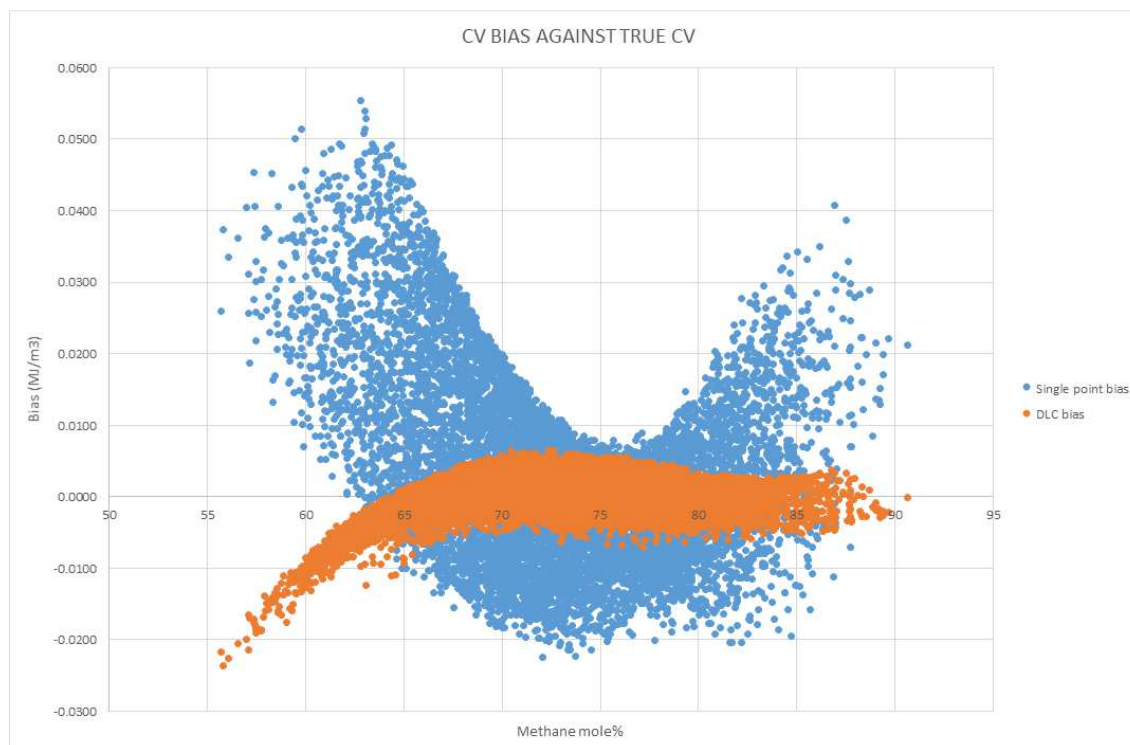

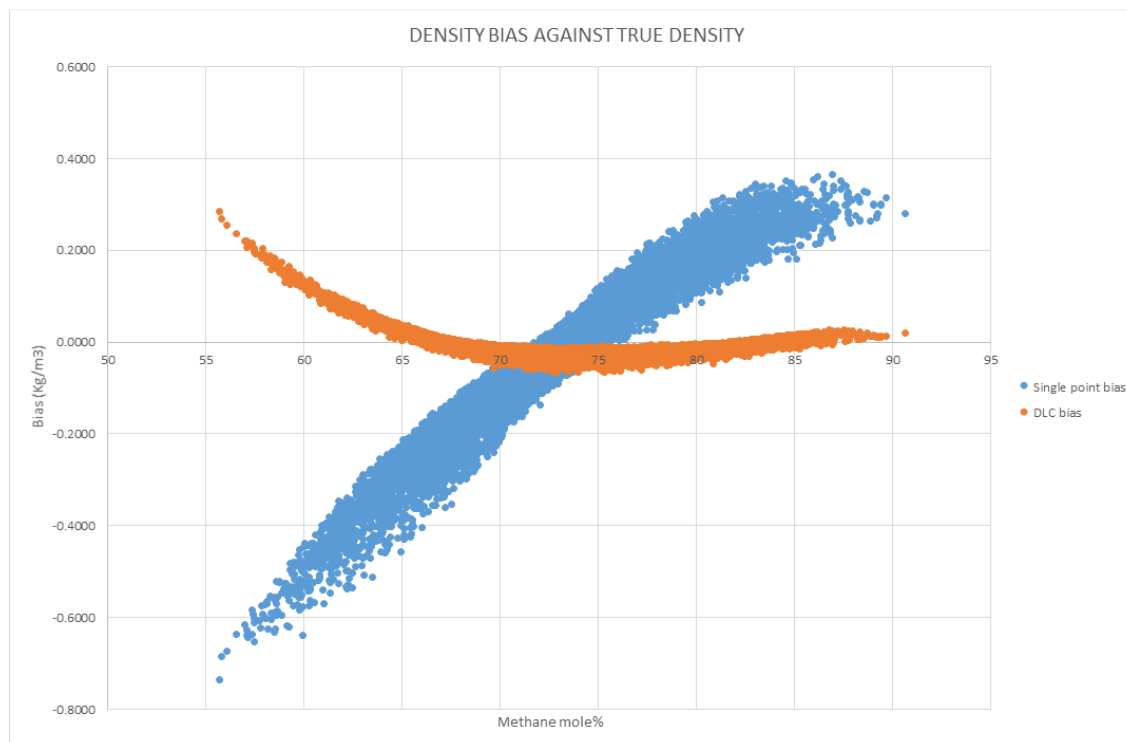
Figure 17. CV bias against true CV

Figure 18. Density bias against true density

From the Figure 17 and Figure 18 above it is clear that implementing dual level calibration constant can reduce the bias to a negligible level. Few other examples along with the procedure on how the DLC bias are calculated is included in 0.

2.4.1 DLC practicality

From the practicality point of view DLC can be performed without adding any significant cost to the operator. The only thing operators need is two sets of calibration gas that would cover the whole operational range. Both calibration gas can be used as daily calibration. Therefore when one bottle is depleted, the other composition can be used as calibration gas.

The spare calibration gas can then be used as reproducibility check. Rather than checking repeatability of GC using the same gas the GC was calibrated on, it is a very useful exercise to perform reproducibility test using another bottle that has completely different composition. In effect, this test performs a linearity test. Rather than performing the ISO 10723 test on yearly basis, this test can be done on monthly basis with no extra cost.

In the events where linearity test fails, one of the following can be checked and done:

1. If linearity check fails due to some failure on the GC, further troubleshooting can be done immediately and fault can be identified and rectified.
2. If there are drifts that causes bias, new constant can be generated using available calibration gas on site.

Tolerance for reproducibility limits can be taken for instance from ASTM D1945:2001 [1] or ISO 6974-5:2001 [2]. ISO 6974-5:2001 [2] shows a more stringent tolerance in comparison to ASTM D1945:2001 [1] and maybe more suitable to be used as tolerance.

2.4.2 Case study

The following case study is performed on two GC that measures export gas in one of the North Sea platform. The initial issue was identified where both GC shows low unnormalised total, however both GC shows good consistent calibration result. This indicates that both GC are affected by non-linearity.

Later it was found that the calibration gas composition is significantly different from process gas composition which were being measured. The comparison between calibration gas composition and process gas average is shown in Table 8.

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Description	Calibration Gas	Process Gas Average
Methane	69.476	82.196578
Nitrogen	2.65	1.259492
Carbon dioxide	5.634	1.68137
Ethane	12.941	8.397309
Propane	7.2172	4.082673
i-Butane	0.5234	0.499166
n-Butane	1.2489	1.134631
i-Pentane	0.1307	0.230733
n-Pentane	0.1366	0.280748
Hexane	0.0396	0.2373

Table 8. Calibration gas vs process gas average

Second calibration gas was then ordered to have quite a similar composition to the process gas.

Description	Calibration Gas	Process Gas Average
Methane	83.125	82.196578
Nitrogen	1.2085	1.259492
Carbon dioxide	1.2755	1.68137
Ethane	8.054	8.397309
Propane	3.864	4.082673
i-Butane	0.483	0.499166
n-Butane	1.087	1.134631
i-Pentane	0.231	0.230733
n-Pentane	0.3093	0.280748
Hexane	0.3578	0.2373

Table 9. Second calibration gas vs process gas average

Now that two calibration gases are available, a reproducibility test can be performed. Initial test was performed by having the GC single point calibrated using the first calibration gas, then the second calibration gas is measured as unknown. GC reading was then compared against calibration gas certificate. Result can be seen in Table 10.

Description	Calibration Gas	Repeatability test	Bias
Methane	83.12907332	82.935008	-0.194065
Nitrogen	1.208559219	1.22676	0.018201
Carbon dioxide	1.275562503	1.293297	0.017734
Ethane	8.054394665	8.071723	0.017328
Propane	3.864189345	3.950325	0.086136
i-Butane	0.483023668	0.489072	0.006048
n-Butane	1.087053266	1.099363	0.01231
i-Pentane	0.23101132	0.234153	0.003142
n-Pentane	0.309315156	0.314529	0.005214
Hexane	0.357817533	0.38577	0.027952
CV (% bias)	43.7879625	43.89291958	0.239694

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Table 10. Bias from reproducibility test of second calibration gas

As shown in Table 10, the bias from reproducibility test is very significant. This bias can amount to more than £50,000 per month on production of 100 mmsfcf/d.

After the reproducibility test, dual level calibration constant was generated and implemented in the GC. Then GC was calibrated again still using the same first calibration gas, but now with DLC constants implemented in the GC. Reproducibility test on second calibration gas was performed with result shown in Table 11.

Description	Calibration Gas	Repeatability test	Bias
Methane	83.12907332	83.145382	0.016309
Nitrogen	1.208559219	1.208111	-0.00045
Carbon dioxide	1.275562503	1.276249	0.000686
Ethane	8.054394665	8.035965	-0.01843
Propane	3.864189345	3.865698	0.001509
i-Butane	0.483023668	0.483918	0.000894
n-Butane	1.087053266	1.087583	0.00053
i-Pentane	0.23101132	0.230822	-0.00019
n-Pentane	0.309315156	0.30945	0.000135
Hexane	0.357817533	0.356823	-0.00099
CV (% bias)	43.7879625	43.78318356	-0.01091

Table 11. Bias from reproducibility test of second calibration gas using DLC constant

From Table 11, it is shown that implementing DLC constant reduces the bias from non-linearity to an acceptable level.

When DLC constants are not implemented, measurement using single point calibration can show result that can be seen as acceptable. On this particular case, both of the GC shows very similar result which gives the impression that the GC measures correctly. Figure 19 shows comparison between GC A and GC B when measurement was done using single point calibration.
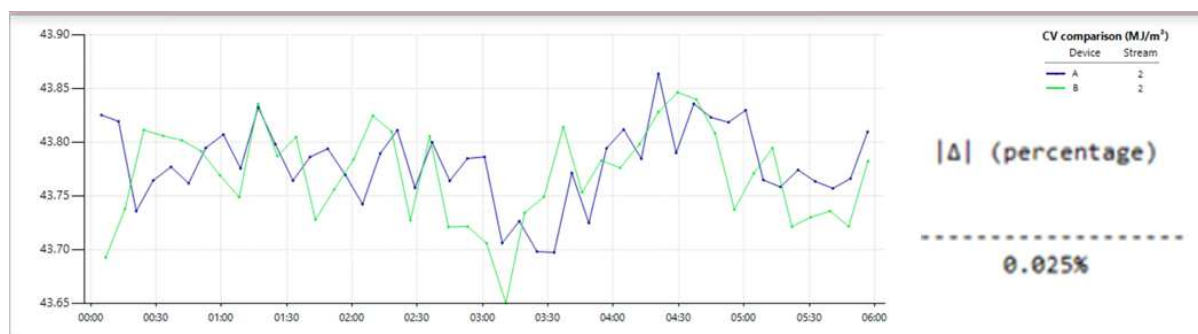

Figure 19. GC A vs GC B CV difference when measured using single point calibration

However, when DLC constants are implemented in the GC, it shows 0.2% of bias on both GC. Figure 20 shows the bias on GC A.
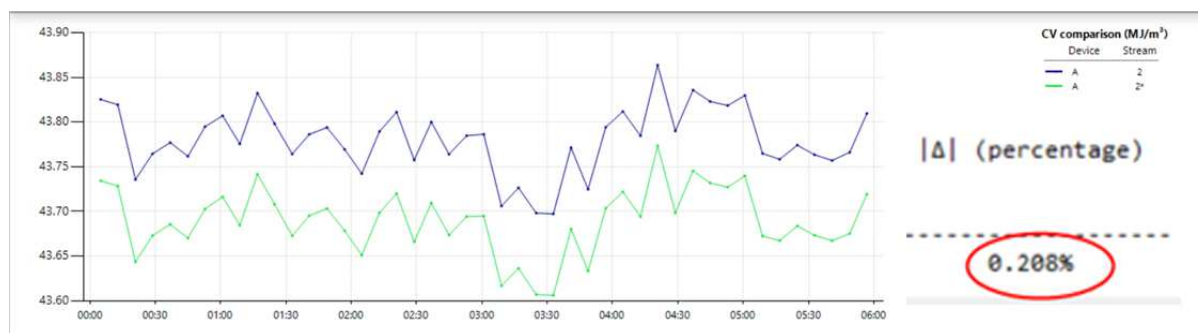
Technical Paper

Figure 20. GC A CV comparison between single point vs DLC measurement

2.5   GC "Live" Uncertainty

GC Live uncertainty is associated with the reproducibility of the GC from its daily / periodic calibration result. This should be performed after all methods above are utilised and GC health status is confirmed to be good. Failing to perform one or more methods described above may result in consistent systematic errors. While the methods above will ensure that GC works correctly on an instantaneous basis, the live uncertainty method will ensure that the GC works in reproducible manner over a long period of time. It may also predict future failure that may not be identified by methods described earlier on this paper.

Uncertainty of GC parameter quantifies GC performance derived from response factor control charts. The monitoring of the GC response factor not only ensures the health of the GC throughout the year, but also provides early indication of deterioration of GC performance as it will be revealed by increment of the GC uncertainty value.

Figure 21 shows respond factor trends of a healthy GC. Visually from the trend, many stories can be told. From Figure 21 it can be seen that there was a shutdown between August 2013 and October 2013. There was also change in calibration gas in April 2015 and some parameter changes were done on GC in June 2014. Also it can be seen visually that all response factor trends were up and down in harmonious way.
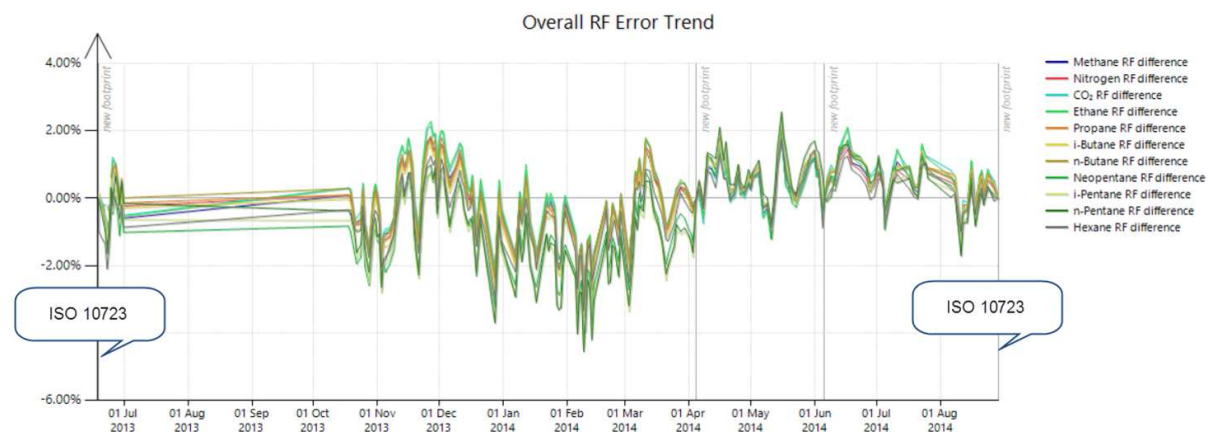

Figure 21. 1 year RF trend of healthy GC

Uncertainty trend is one way to quantify these parameters. Uncertainty trend of the GC associated with Figure 21 is shown in Figure 22 below.
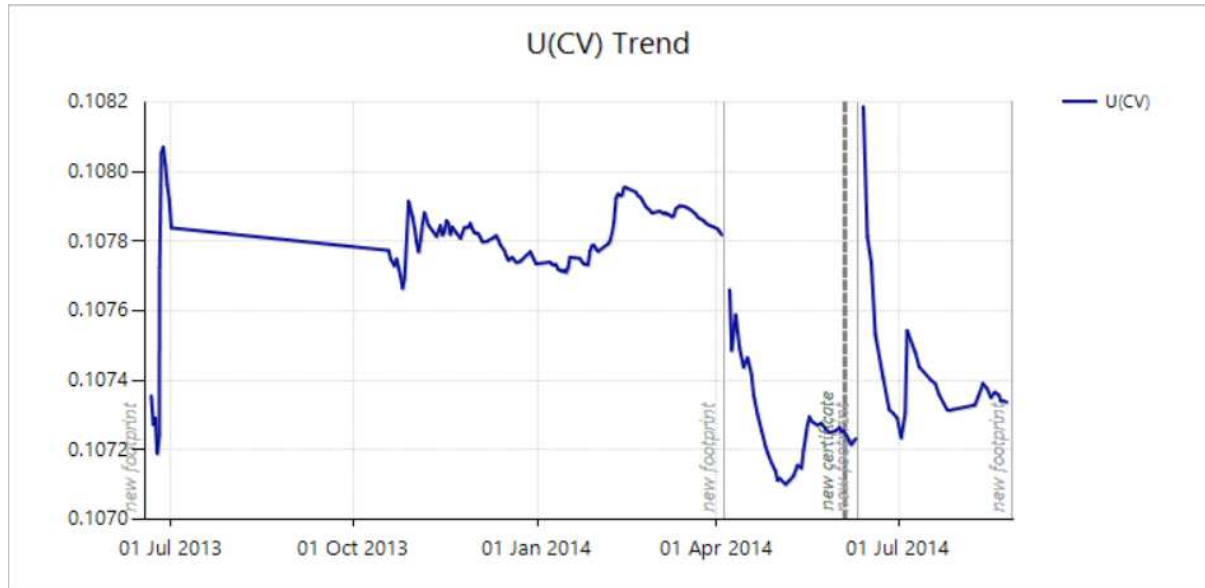

Figure 22. Uncertainty of CV associated with Figure 21

From here uncertainty limits can be set and alarm flagged at any time the uncertainty value exceeds the limit. Figure 23 shows an example where uncertainty limit is set at 0.12%. This limit is very useful to catch issues with GC before the issue becomes significant.
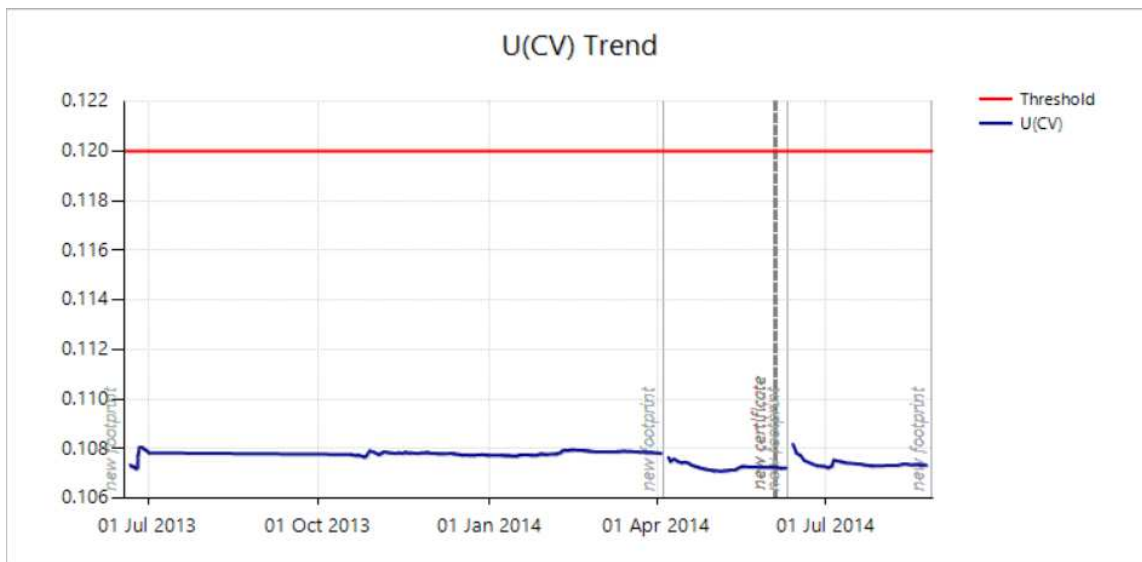

Figure 23. Uncertainty with set limit of 0.12%

The uncertainty method can also predict future failure that may otherwise be undetected using any other method. Figure 24 shows uncertainty trend that predicted GC failure two months prior to actual failure. This gives opportunity for the operator to order the required spare parts before the actual failure happens in the GC without losing much of down time.
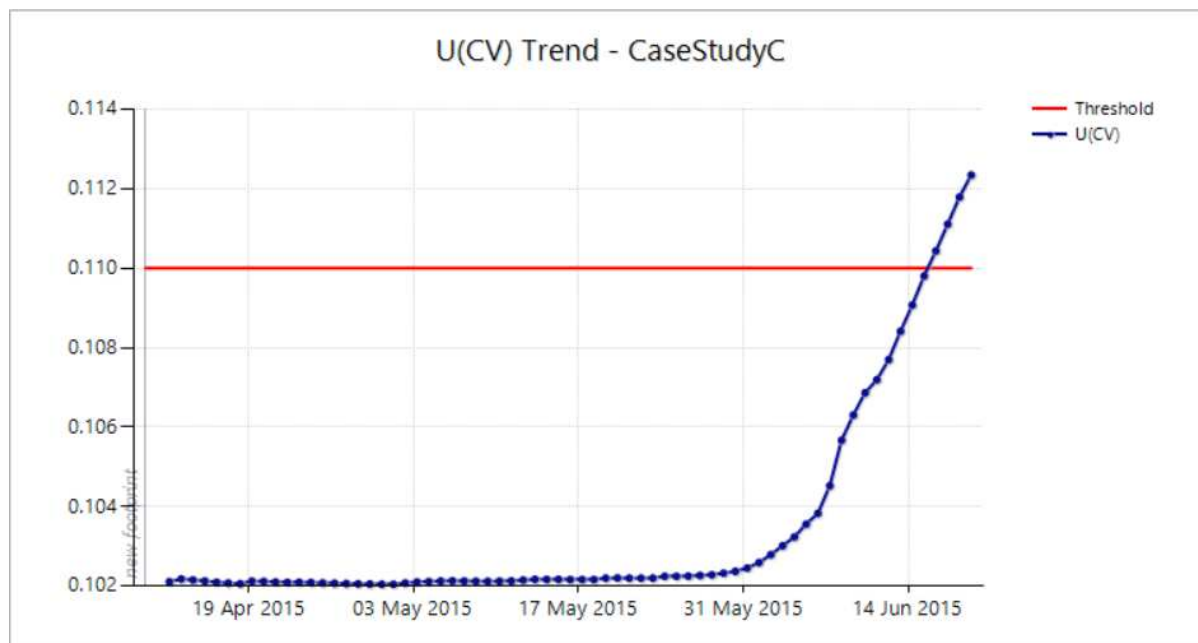
Figure 24. Increment in uncertainty predicted future failure

Ultimately when the GC is configured correctly and calibrated with high quality of calibration gas, the live uncertainty method can ensure that the GC provides accurate measurement at all time. Should error arises on the GC, the live uncertainty method will highlight the errors before the error become significant. Tools on the conditional based monitoring tool can be used to ensure correct operation during and after troubleshooting.

3   CONCLUSION AND RECOMMENDATION

There are many ways to perform GC maintenance. Current maintenance regime splits the maintenance into two categories, yearly health check and daily / periodic calibration. When a certain maintenance method is employed and some others are overlooked it may cause the operator to oversee some of the issue in hand which may result in significant systematic error.

This paper has discussed some of the available methods to ensure accurate GC measurement which involves the selection of good calibration gas quality with the correct range, procedure of performing calibration and the checking of the calibration result parameters, the handling of non-linear property of the GC, and finally the monitoring of historical performance of calibration result.

This can be quite a significant task to perform all this activities. However, considering the potential errors a GC can contribute to measurement, it is worthwhile to ensure correct measurement of a GC. It is recommended to use GC conditional monitoring tool that covers all these with minimum effort.

GCAS is designed to capture all the necessary data automatically from GC and provide all the analysis automatically. It removes the need for data entry as data is gathered automatically from the GC. This will then be presented in a dashboard showing alarm in

case any failure or potential failure is detected. In essence it will ensure that the GC provides accurate measurement at all time.

4   REFERENCES

[1]   ASTM D1945. Standard test method for analysis of natural gas by gas chromatography. *ASTM*, 2001.

[2]   BS EN ISO 6974-5. Natural gas - Determination of composition with defined uncertainty by gas chromatography - Part 5: Determination of nitrogen, carbon dioxide and C1 to C5 and C6+ hydrocarbons for a laboratory and on-line process application using three columns. *BS EN ISO*, 2001.

[3]   ISO 10723. Natural Gas – Performance evaluation for Analytical Systems. *ISO*, 2012.

Appendix 1.   OGA Letter of No Objection

From:	Arnould Patrick (Oil and Gas Authority) <patrick.arnould@oga.gsi.gov.uk>
Sent:	29 June 2016 11:48
To:	Anwar Sutan
Cc:	Griffin Douglas (Oil and Gas Authority); Mankin Alan (Oil and Gas Authority); OGA Petroleum Measurement and Allocation Team
Subject:	RE: Dual Level Calibration

Hi Anwar,

Thank you for your email, I confirm OGA are content with the summary below with the following proviso:

In the case where either:

The simulations using the ISO-10723 results show the bias to be excessive and the associated non-linearity cannot be removed by changes to the GC configuration
or
The reproducibility test on the 3rd gas continually fails indicating non-linearity and this non-linearity cannot be removed by changes to the GC configuration
then
OGA may still require the ISO-10723 evaluation to be performed.

Please do not hesitate to contact me if you wish to discuss further.

Best regards,
Patrick

Patrick Arnould
Snr. Petroleum Measurement & Allocation Inspector
Oil & Gas Authority
AB1, 48 Huntly Street, Aberdeen AB10 1SH:
patrick.arnould@oga.gsi.gov.uk T: 0300 020 1011

From: Anwar Sutan [mailto:anwar.sutan@i-Vigilant.com]
Sent: 28 June 2016 21:05
To: Arnould Patrick (Oil and Gas Authority)
Cc: Griffin Douglas (Oil and Gas Authority); Mankin Alan (Oil and Gas Authority); OGA Petroleum Measurement and Allocation Team
Subject: RE: Dual Level Calibration

Hi Patrick,

Thank you very much for your email. I would like to summarise the effect of your email below in terms of the practicality of the method in the industry. I really appreciate if you can confirm the following summary:

Technical Paper

1. OGA Guideline:
    7.5.8 Evaluation of Linearity and Repeatability– ISO 10723
    A procedure for determining the linearity and repeatability of gas chromatograph response on 7 different test gases is set out in an International Standard [ISO 10723: 2012].
    OGA may require operators of relevant systems to quantify at regular intervals the linearity and repeatability of fiscal gas chromatographs

    Effect of the no objection to the use of Dual Level Calibration for GC's:
    OGA has no objection to operators using a Dual Level Calibration. Using 7 gases is not necessary where operators can define two calibration gas compositions to cover the process conditions. The Dual Level Calibration will suffice and by implementing the dual level calibration function in the GC this will (as has been proven in several test cases) significantly reduce the associated bias.

2. Practicality of the method
    To make the method practical the following will be recommended to operators planning to implement the method:
    - 2 gases covering the operation range to be made available as calibration gas
    - Based on the actual range of the gas composition and potential of the bias the following monthly test will be recommended:
      - Reproducibility test of the cal gas that is not being used for calibration → This is to be done if the actual range is narrow enough. Examples:
        - A site has export gas composition that has 69% methane, but when it takes import gas methane will go to 82%. The gas will be operating at 69% ± 2 mole% or 82% ± 2 mole%. In this particular case, it will not be necessary to run reproducibility test using test gas of 75% as the actual gas does not go to that range. In this case we can do reproducibility test using the second calibration gas.
        - A site has process gas range between 88 – 92%. If Tests against true function of ISO 10723 shows negligible bias then reproducibility test can be done using the second calibration gas.
      - Reproducibility test using test gas that sits in middle of operation range → this is to be done if the actual range is quite wide. Here are two examples of wide range:
        - A site has gas that have high variation (let's say 70% to 85%). The two cal gas will have 70% methane and 85% methane. It will be recommended to have the third cal gas that has around 77% methane so that reproducibility test can be done using this test gas to see if we have significant bias.
      - When reproducibility test fails:
        - Check if there is any issue with the GC. If there is issue with the GC, actions to be taken to fix the GC, then if need be new dual level calibration constant to be generated.
        - If there is no issue on the GC, and it is a natural drift, a new constant can then be generated.
    - We will make procedure available on how to generate the constants. Based on this, it will also be recommended that operators have auditable trail of the constant generation on the GC and reproducibility tests being done.

Based on our discussion, I have come to the above conclusion. Can you confirm that you are in agreement with the above and please add any comments if you think I have missed something from our initial discussion. Thanks again for your time in reviewing the method and I look forward to be promoting and implementing the method in various operators that operates under OGA measurement guidelines.

Thanks and regards,
Anwar

Anwar Sutan CEng MInstMC | Director
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GCAS – Gas Chomatograph Condition Based Monitoring

From: Arnould Patrick (Oil and Gas Authority) [mailto:patrick.arnould@oga.gsi.gov.uk]
Sent: 27 June 2016 12:13
To: Anwar Sutan <anwar.sutan@i-Vigilant.com>
Cc: Griffin Douglas (Oil and Gas Authority) <Douglas.Griffin@oga.gsi.gov.uk>; Mankin Alan (Oil and Gas Authority) <alan.mankin@oga.gsi.gov.uk>; OGA Petroleum Measurement and Allocation Team <metering@oga.gsi.gov.uk>
Subject: Dual Level Calibration

Anwar,

Thank you for explaining the new Dual Level Calibration method for use with GCs.

I have completed a technical review of the method itself and the method used for comparing it against conventional single point calibration and multi-level calibration. I have seen the evidence from numerous tests using the above methodology including one example of implementation in the field and agree the results show an improvement over single point calibration and can, depending on the operational range and the extent of non-linearity present in the GC, offer similar performance to a multi-level calibration.

Based on the above I confirm that OGA have no objection to the use of Dual Level Calibration for GCs used in measurement systems which are operating under our Measurement Guidelines.

Best regards,
Patrick

Patrick Arnould
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Appendix 2.   DLC Results

Below are 5 case studies showing the comparison on bias when using 2 sets of gases (Dual Level Calibration) and single gas (Single Point Calibration) in comparison to 7 sets of gases Multilevel Calibration (MLC).

The data is generated as follows:

1. Generate 10,000 data points of MLC mole composition over a defined range.
2. Convert the data to the corresponding 'Single Point' data using the MLC functions for that GC (use calibration gas composition of either the high range or the low range of the range of interest and assume MLC RF of 1).
3. Generate the DLC linear curve for each component as follows:
    a. Get the peak area of low range mole% of calibration gas used for 2 gases linearization using 7 gases MLC functions
    b. Get the peak area of high range mole% of calibration gas used for 2 gases linearization using 7 gases MLC functions
    c. Generate a linear function based on these two peak areas and mole%
    d. Do this for every component
4. Convert the single point mole composition using the DLC functions to get the mole composition if we were to use the DLC linear functions
5. Convert the 7 gases MLC mole composition to single point mole composition, but this time using calibration gas that is used on the ISO 10723 performance report
6. Calculate the bias as follows:
    a. Single point CV bias = Single point CV – 7 gases MLC CV
    b. DLC CV bias = 2 gases DLC CV – 7 gases MLC CV
    c. Single point density bias = Single point density – 7 gases MLC density
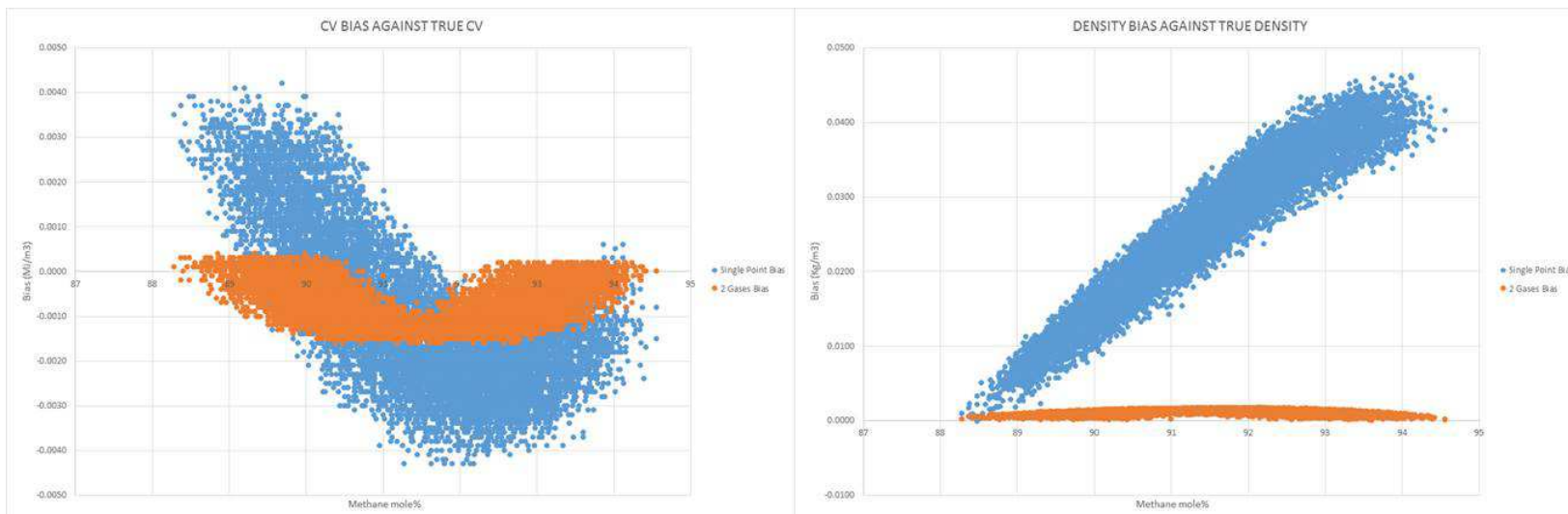   d. DLC density bias = 2 gases DLC density – 7 gases MLC density

Below is the resulting bias in both CV and density for 5 different GCs and composition ranges.

1. Case study 1 (area of interest between 70%-80% methane):
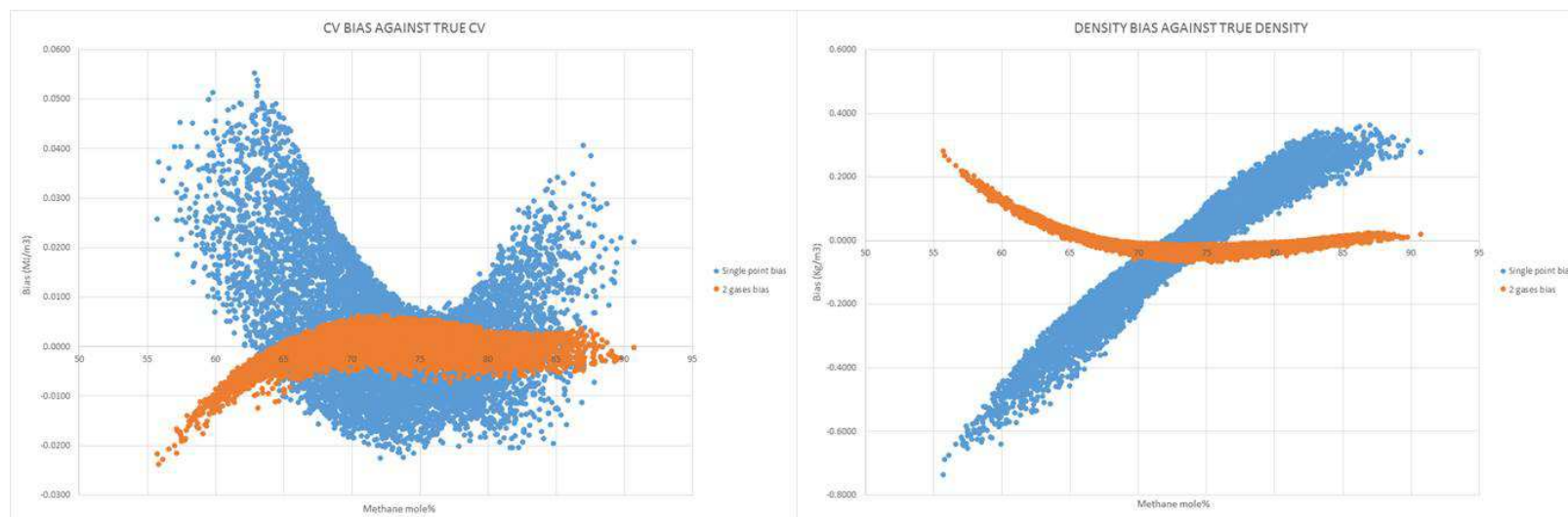
2. Case study 2 (area of interest between 89%-94% methane)

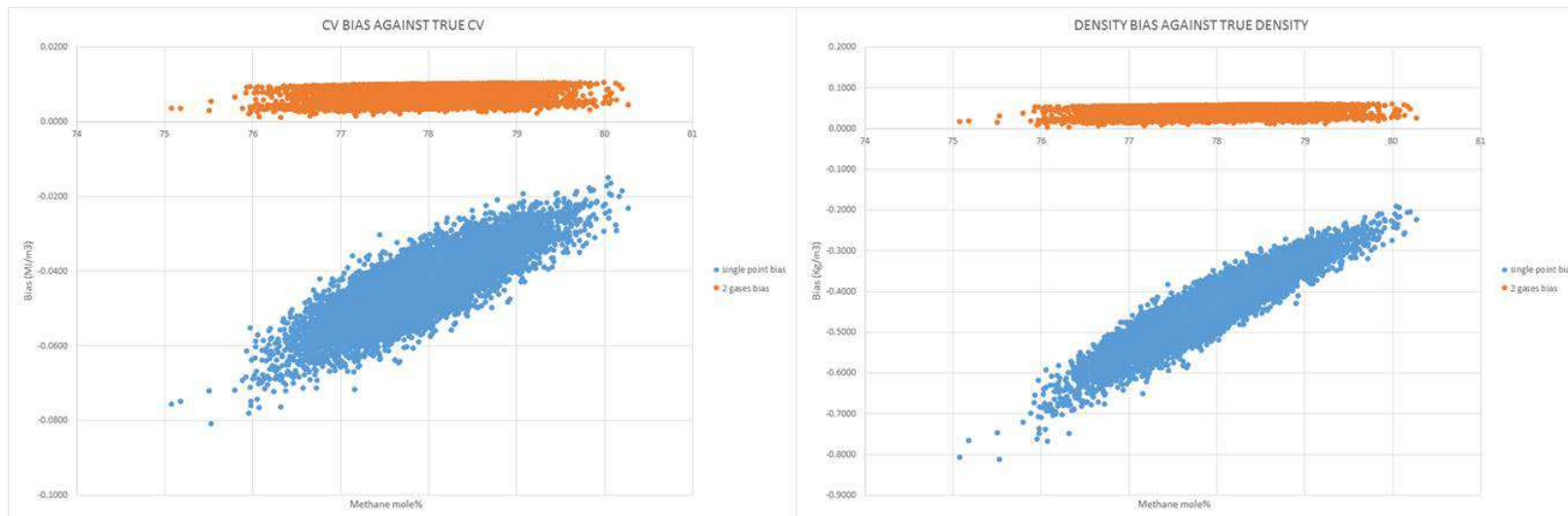3. Case study 3 (area of interest between 84%-86% methane):
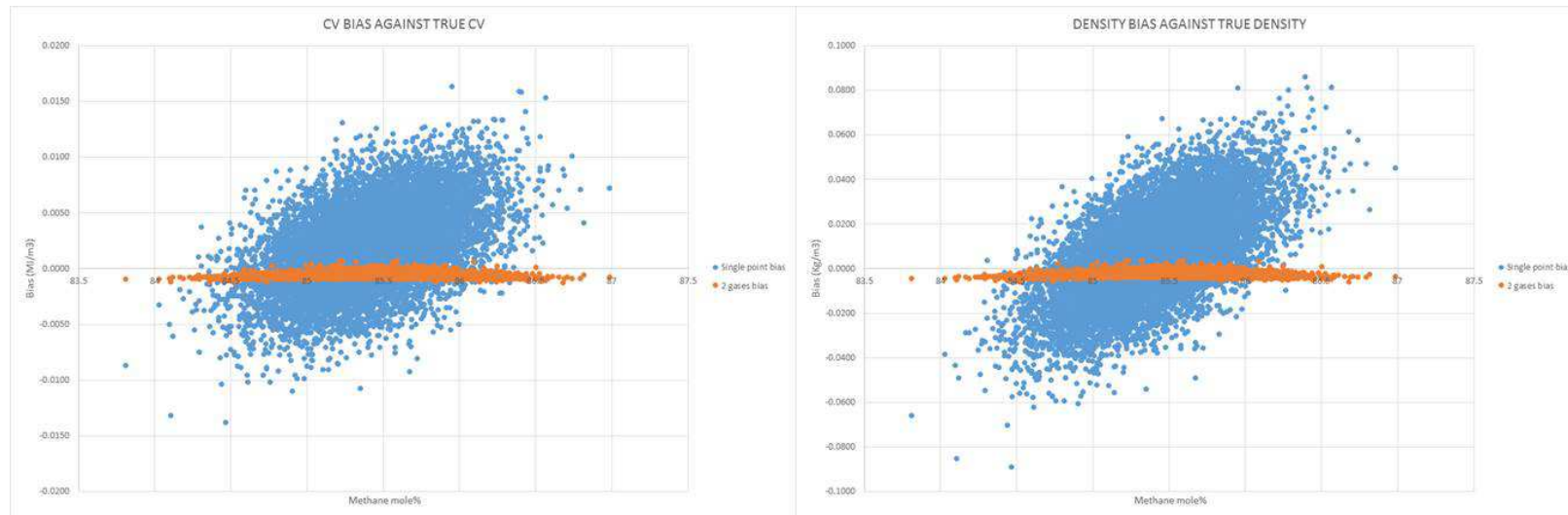
4. Case study 4 (area of interest between 76%-80% methane):

5. Case study 5 (area of interest between 76%-84% methane):