

Three Columns Gas Chromatograph Analysis Using Correlation between Component's Molecular Weight and Its Response Factor

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1 Introduction

Gas Chromatographs (GCs) are delivered from factory with a multilevel calibration already programmed. While this is an effective method to handle the linearity of the detector, it requires many sets of gases at varying concentrations to obtain the multi level calibration parameters. On site when component parts of the GC are changed such as columns, diaphragm, detectors, etc. the GC may require a new set of multilevel calibration parameters. For a number of reasons this is not always practical to do on site or in the field.

Other calibration issues on site can result in the systematic drift of the response factor. This sometimes cannot be detected by the GC automatically as the response factor shift can remain within the tolerance limit from the previous response factor set in the GC controller. Even with the wrong calibration result, the Gas Chromatograph still can give repeatable results, however the results will not be accurate and can increase the uncertainty of the measurement.

The repeatability and reproducibility tests are good to prove that a GC is working within limits which are specified in ASTM D1945:1996 [3] or GPA 2261:1995 [5]. However, due to the wide tolerance on some compounds these tests do not guarantee that the GC is working as intended. Using these tests does not ensure that each of the components goes through its intended column and further it does not confirm that all the valve timings are correct. A further analysis is required to check this functionality and this can be done by analyzing the response factor of each components.

This paper describes a practical method that can be used to overcome these issues by looking at the correlation between component's molecular weight and its response factor, and by looking at the historical response factor data for each component.

2 Chromatograph Design and Operation

In order to get a 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, a multi column separation technique is required.

The three columns GC design is consistent with ISO 6974-5:2000 [6]. It uses three 6-port chromatograph valves, three columns, a restrictor, reference detector and measuring detector in a controlled temperature chamber. The detectors are thermistors, where resistance changes depend on the temperature. The reference and measuring detectors form a balanced Wheatstone Bridge. Helium is the preferred carrier gas because it has high thermo-conductivity, Nitrogen, Hydrogen and Argon can also be used in special circumstances. With

only carrier gas flowing across the two detectors, the Wheatstone bridge is in balance. In the measuring detector, the sample gases passing across the thermistor causes thermo-conductivity changes resulting in a change of thermistor heat exchange rate, this in turn results in an increase of the temperature of the thermistor. The change of temperature results in a change of resistance in the measuring detector and unbalances the Wheatstone Bridge. The magnitude of the voltage created by Unbalance Bridge and the time taken to pass through the detector then 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 mole % of component being measured.

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

The GC tested was configured such that C1, C2 and C6+ went through measurement detector with the same flow rate, and C3, iC4, nC4, iC5, nC5 went through measurement detector with another flow rate. Figure 1 shows flow path for C1, C2 and C6+ where the flow went through column 3.

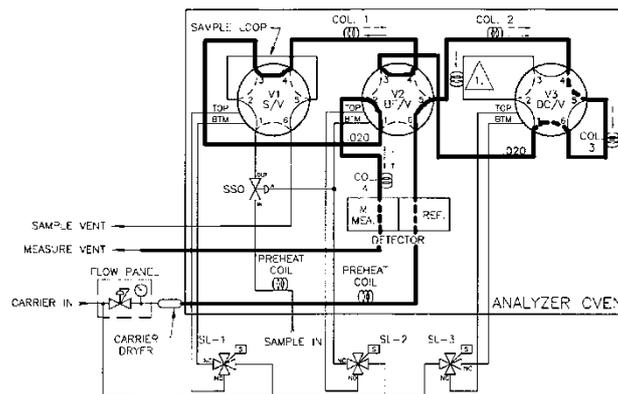


Figure 1. Danalyzer / 2350A Gas Chromatograph, Hardware Reference Manual [1], Three-column GC flow path of C1, C2 and C6+

Figure 2 shows flow path for C3, through nC5 where the flow goes through restrictor tubing.

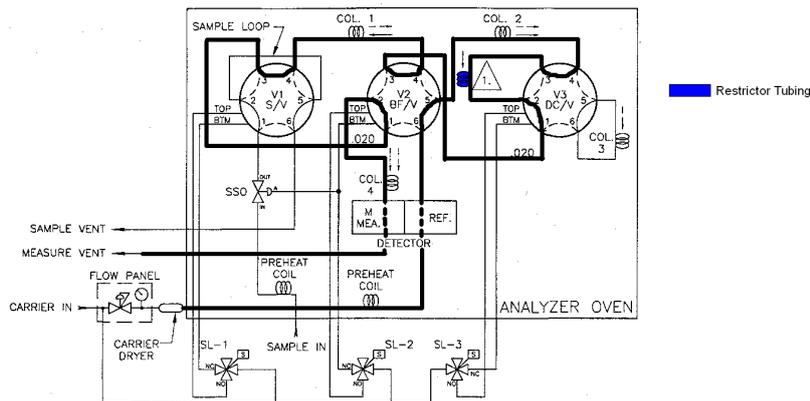


Figure 2. Danalyzer / 2350A Gas Chromatograph, Hardware Reference Manual [1], Three-column GC flow path of C3, C4 and C5

3 Verification Procedures

There are some well established procedures available and used to verify Gas Chromatograph operation on site. These procedures ensure that GC is working within the limits specified in the standard. A daily or periodic auto calibration is normally done. The repeatability criteria in D1945:1996 [3] or GPA 2261:1995 [5], is used to ensure that the calibration is valid.

Other periodic checks that are usually carried out are:

- Reproducibility test
- Detector bridge balance;
- Oven and detector temperature check;
- Carrier gas pressure check;
- Calibration gas pressure check;
- and flow rate check for both sample and measurement detector vent.

3.1 Periodic Auto Calibration

A periodic auto calibration is performed to ensure that the GC is functioning within a defined specification. These periods are determined by the stability of the GC calibration and can be daily, weekly or monthly. A calibration report is generated after each calibration cycle. In the report, there are old response factors from the previous calibration and new response factors from the current calibration. A slight shift in the response factor is acceptable as defined in ASTM D7146-05 [4]. This auto calibration however is not designed to detect systematic shift in these factors and this must be reviewed manually over time and historical calibrations. If the response factor increases or decreases consistently after every calibration, and the response factor deviation from the previous response factor is still within the deviation limit set, the GC will not generate any alarm and will function without reporting any faults.

3.2 Repeatability Test

Repeatability stated by D1945:1996 [3] section 10.1.1 is the difference between two successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials should be considered suspect if they differ by more than the following amounts:

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

Table 1. D1945:1996 [3] section 10.1.1

Repeatability stated by GPA 2261:1995 [5] section 9 is the expected precision within a laboratory using the same equipment and the same analyst. It should be considered suspect if they differ by more than the following amounts:

Component	Mol % Range	Tolerance (Percent relative)
Nitrogen	1 to 7.7	2
CO ₂	0.14 to 7.9	3
Methane	71.6 to 86.4	0.2
Ethane	4.9 to 9.7	1
Propane	2.3 to 4.3	1
Isobutane	0.26 to 1	2
n-Butane	0.6 to 1.9	2
Isopentane	0.12 to 0.45	3
n-Pentane	0.14 to 0.42	3
C6+	0.1 to 0.35	10

Table 2. GPA 2261:1995 [5] section 9

Repeatability test on an on-line GC is performed by analyzing a gas of known composition. A calibration gas that has a known composition gas is used and analyzed a number of times. The analysis result of the sample gas is compared with the gases' calibration certificate. By carrying out this type of repeatability test, the GC is confirmed to work within the standard specification. If the repeatability test fails, the data can be used as a troubleshooting tool.

There are two sets of criteria to be checked when performing the repeatability test range and precision. Range is the difference between maximum value and minimum value of the measured gas during the test. Precision is the difference between the value measured by GC and the value stated in calibration gases' certificate. Both have to fall within the stated tolerance (Table1, Table 2).

3.3 Reproducibility Test

Reproducibility stated by D1945:1996 [3] section 10.1.2 is The difference between two results obtained by different operators in different laboratories on identical test materials should be considered suspect if they differ by more than the following amounts:

Mol % Lookup	Tolerance %
0 to 0.1 Mol%	0.02 %
0.1 to 1 Mol%	0.07 %
1 to 5 Mol%	0.10 %
5 to 10 Mol%	0.12 %
Over 10 Mol%	0.15 %

Table 3. ASTM D1945:1996 [3] section 10.1.2

Reproducibility stated by GPA 2261:1995 [5] section 9 is the expected precision when the same method is used by different laboratories using different equipment and different analyst. It should be considered suspect if they differ more than the following amounts:

Component	Mol % Range	Tolerance (Percent relative)
Nitrogen	1 to 7.7	7
CO ₂	0.14 to 7.9	12
Methane	71.6 to 86.4	0.7
Ethane	4.9 to 9.7	2
Propane	2.3 to 4.3	2
Isobutane	0.26 to 1	4
n-Butane	0.6 to 1.9	4
Isopentane	0.12 to 0.45	6
n-Pentane	0.14 to 0.42	6
C6+	0.1 to 0.35	30

Table 4. GPA 2261:1995 [5] section 9

On site or in the field , this is normally achieved by comparing the result obtained from the online GC with a Laboratory GC result.

4 Gas Thermal-Conductivity vs Response Factor

The relationship between Thermal Conductivity and Molecular weight in Hydrocarbon and inert gases is well known. The larger the molecular weight the smaller the Thermal Conductivity. The thermal conductivity detector's resistance changes as the temperature changes. The temperature on the detector changes whenever gas with different thermal conductivity property flows through it. The higher thermal conductivity difference between carrier gas and the component being measured, the more temperature change will occur, and the more change on the thermal conductivity resistance. Therefore the higher the thermal conductivity property of a component, the lower the peak area generated by detector, and the lower response factor for that component ($RF = PA/mol\%$).Applying this to the thermal-conductivity detector, because of the high Thermal Conductivity property of the carrier gas,

the higher the thermal conductivity of a component being measured the lower difference on carrier gas – measured component gas thermal conductivity, the lower peak area generated by the detector and the lower the response factor for that component ($RF = PA/mol\%$). The three column gas chromatograph measures components, in order from high thermal-conductivity to low thermal conductivity, Methane; Nitrogen; Ethane; CO₂; Propane; i-Butane; n-Butane; neo-Pentane; i-Pentane; n-Pentane; Hexane+; and Heptane+ etc.

As a first verification step the calibration result can be analyzed by monitoring the response factor data. Response factor of methane will be lowest, followed by Nitrogen; Ethane; CO₂; Propane; i-Butane; n-Butane; neo-Pentane; i-Pentane; n-Pentane; Hexane+; and Heptane+. If this sequence is not evident, then this would point to some form of incorrect setting, or if everything is ok with GC, the calibration gas could be considered suspect. Typical graphical representation of components response factor is shown in figure 3.

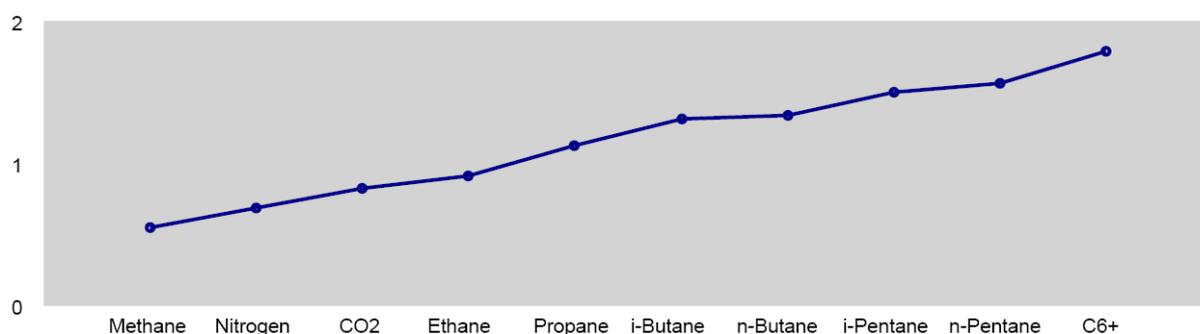


Figure 3. Typical response factor graphic of gas components response factor

5 Flow Rate Effect on Response Factor

The Author performed a test on a C7+ GC where there were significance differences with flow rate when valve 3 was on and when valve 3 was off. The initial test had flow a rate of 13.3 cc/min when valve 3 was on (flow through column 3), and it had flow rate of 10.4 cc/min when valve 3 was off (flow through restrictor tubing). The result of the test was as follow:

Comp	MW	RF	Log(MW)	Log(RF)
C1	16.04	7.91733E+06	1.20520	6.89858
C2	30.07	1.22268E+07	1.47813	7.08731
C3	44.09	1.30256E+07	1.64434	7.11480
nC4	58.12	1.56587E+07	1.76433	7.19476
nC5	72.15	1.78403E+07	1.85824	7.25140
C6	86.18	2.01611E+07	1.93541	7.30451
C7	100.21	4.12349E+07	2.00091	7.61526

Table 5. Calibration result of GC with different restrictor-column3 flow rate

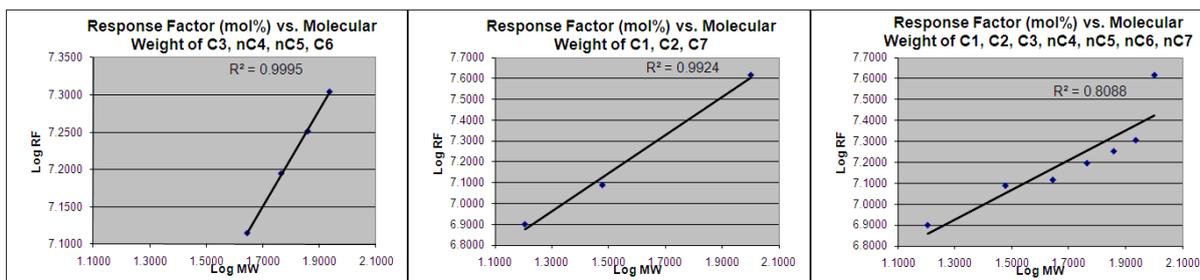


Figure 4. Correlation between Response factor and Molecular weight with different flowrate when valve 3 is on and when valve 3 is off

An adjustment was made to the restrictor tubing to achieve a similar flow rate between the condition when valve 3 is on and when valve 3 is off. The final test had flow rate of 12.9 cc/min when valve 3 was on (flow through column 3), and it had flow rate of 12.7 cc/min when valve 3 was off (flow through restrictor tubing). And the result was as follows:

Comp	MW	RF	Log(MW)	Log(RF)
C1	16.04	7.59792E+06	1.20520	6.88069
C2	30.07	1.18068E+07	1.47813	7.07213
C3	44.09	1.51142E+07	1.64434	7.17939
nc4	58.12	1.72937E+07	1.76433	7.23789
nc5	72.15	1.96312E+07	1.85824	7.29295
c6	86.18	2.20184E+07	1.93541	7.34279
c7	100.21	2.82900E+07	2.00091	7.45163

Table 6. Calibration result of GC with similar restrictor-column3 flow rate

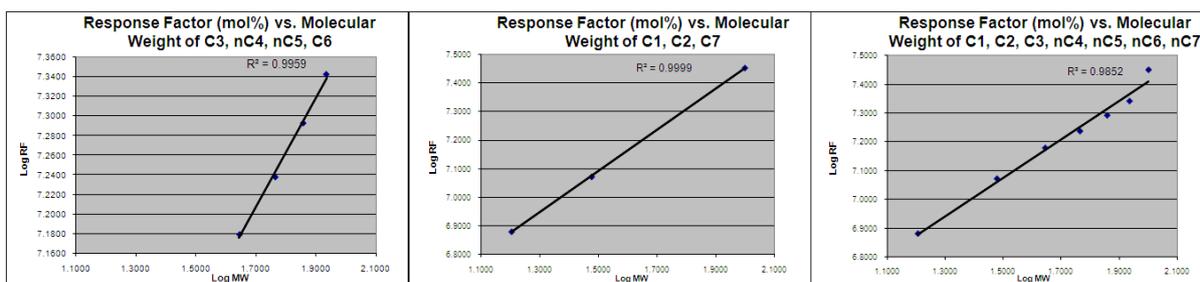


Figure 5. Correlation between Response factor and Molecular weight with similar flow rate when valve 3 is on and when valve 3 is off

From the graphic of correlation (R^2) for all components there is a big discrepancy in terms of correlation when the flow rates were similar and when the flow rates were significantly different. There was no significant difference in correlation of components where the flow rates were similar, e.g. (C3, nC4, nC5, nC6) and (C1, C2, C7) however there was a significant divergence in components where the flow rates were different.

The restrictor column arrangement makes it very rare to have an absolute match on flow rate through all the columns. Therefore it is difficult to get a high correlation on all components. Good correlation is achievable for each group of components when the flow from valve 3 is either through the column or the restrictor when the component passes the measurement detector.

6 Chromatograph Valve Timing

There are 3 critical valve timings on the 3 column chromatograph:

1. Back-flush the heaviest component (C6+ on C6+ GC and C7+ on C7+ GC). Back flush is initiated after C5 and lighter (on C6+ GC) or after C6 and lighter (on C7+ GC) 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 ethane is eluted into column 3, but before any propane 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

In GC operation, valve-timing errors can result in:

1. Some of heavy components leave column one and flow through column 2
2. Some of the middle components are back-flushed together with the heavy component
3. Some ethane left in column 2 after the valve 3 actuation to trap the lights
4. Some propane goes in to column 3 before valve 3 actuation to trap the lights
5. Splitting of the first and last components on the column resulting in extraneous peaks on the chromatogram
6. If extraneous peaks are within the peak window of calibrated peaks they may be recognized as the calibrated peak,

The impact of these valve timing issues will affect correlation of the components. The more valve timing issues, the less correlation between components. Using the chromatogram we can analyze what has occurred with regard to the valve timing.

Before checking the correlation of components a few criteria have to be met.

- Carrier gas pressure must be stable,
- Oven temperature must be stable,
- Flow rate to be noted and stable when valve 3 on and when valve 3 off,
- Detector-bridge must be balanced,
- And repeatability must be within specified standard.

After all these criteria are fulfilled, the next calibration result can be analyzed based on its component correlation.

7 Components Correlation Analysis

To analyze the correlation between components, both graphs need to be utilized. The cause and effect of the valve timing faults are as follow:

1. Some of heavy components leave column 1 and flow through column 2. The effect is smaller response factor of heavy component. We can see it from graphical presentation, the heavy component will be lower than it should be and result in bad R^2 .

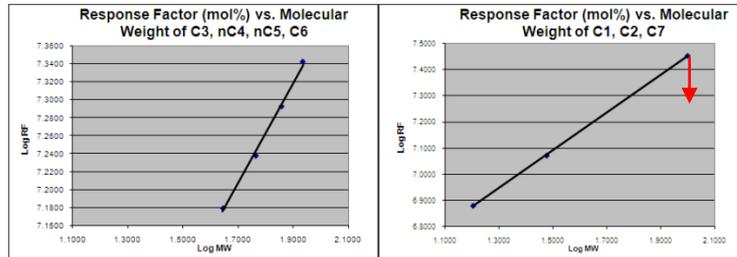


Figure 6. RF – MW Correlation Graphical presentation

2. Some of the middle components are back-flushed together with the heavy component. The effect is smaller response factor on the heaviest middle component and bigger response factor on the heaviest component. From the graphical presentation we are able to see that the heaviest component response factor is higher than expected, and heaviest of the middle component is lower than expected, both graphs have bad R^2 .

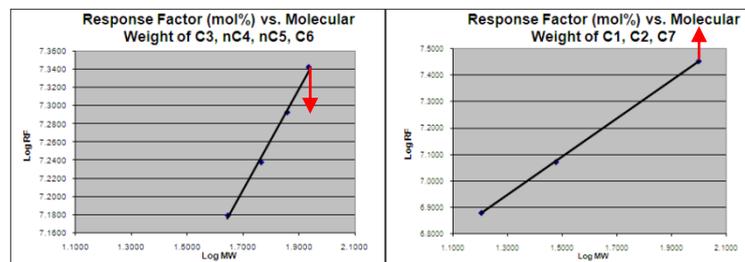


Figure 7. RF – MW Correlation Graphical presentation

3. Some ethane left in column 2 after the valve 3 actuation to trap the lights. The effect is a smaller response factor of Ethane. From graphical presentation it can be shown that the ethane will be lower than the line of C1 and the heaviest component. This results in bad R^2 .

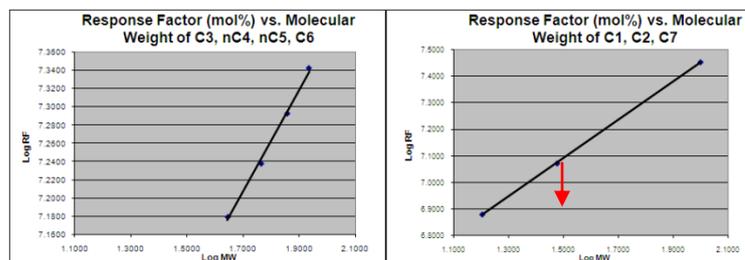


Figure 8. RF – MW Correlation Graphical presentation

- Some propane goes in to column 3 before valve 3 actuation to trap the lights. The effect is smaller response factor of propane. From graphical presentation it can be shown that the propane is lower than expected, results in bad R^2 .

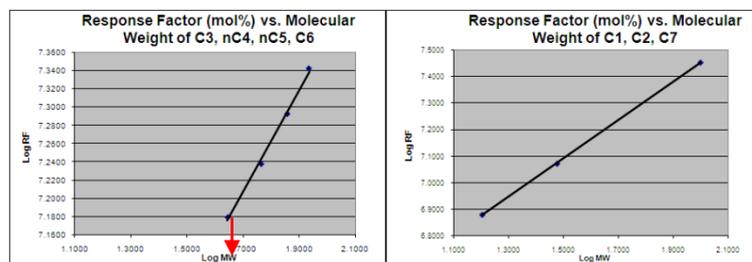


Figure 9. RF – MW Correlation Graphical presentation

Based on these analyses, the valve timing can be adjusted, and the effect of adjustment can be seen after another calibration.

8 Footprint and Historical Data

The correlation method can be utilized more effectively if a footprint of the GC is taken when the conditions and operations were stable and the GC was freshly calibrated. At this time historical data of calibration reports and chromatograms could be acquired. A live test case of the use of correlation method, footprint and historical data is detailed below:

A chromatograph valve diaphragm was changed on a C6+ GC on 24 July 2007. A chromatogram and a calibration report were taken as a footprint on 26 July 2007. The chromatogram below shows data from 26 July 2007, 28 August 2008, and 16 September 2008. On analysis there were a number of issues that could be taken from these chromatograms, these are discussed in detail.

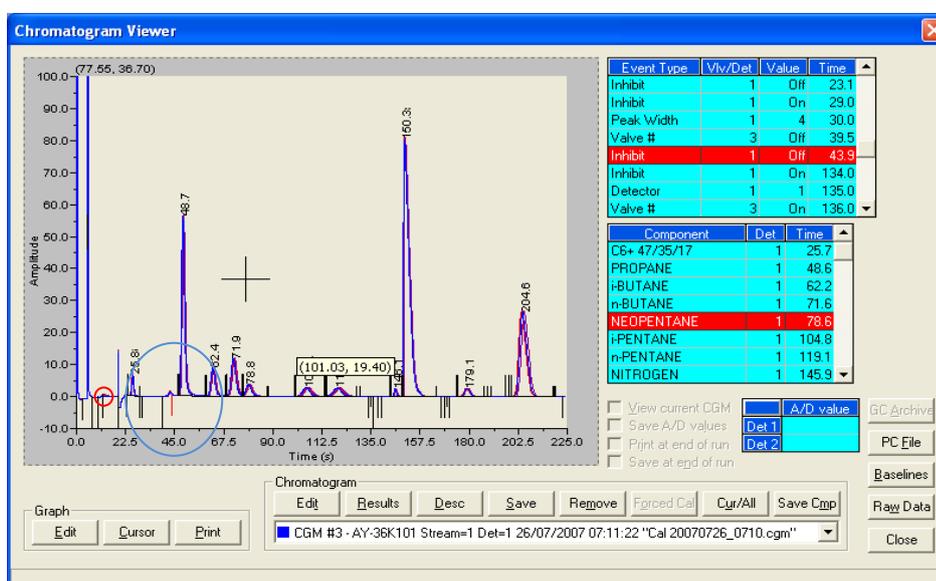


Figure 10. Daniel MON2000 Interface [2], Chromatogram of 26 Jul 2007 (blue), 21 Aug 2008 (red), 16 Sep 2008 (Magenta)

Figure 10 shows the chromatogram for the analysis and footprint of the GC tested. The red circle and blue circle is where we can see the detail of the error and they are zoomed in on figure 11 for the red circle and figure 12 for the blue circle.

From the chromatogram (figure 11), the analysis (red) when compared against the footprint (blue), we can see that there were some deviations. This was caused by a port to port leak on the valve 2 diaphragm. The retention times of components were slower (relative move right) than they should have been (figure 12) from the calibration report if the results were compared with the footprint calibration report. The RF of components generally went up, with C6 having the highest shift of RF (figure 15), this was caused by a change of the carrier gas flow rate which changed the response of the TCD to each component. Even with this deviation and slower retention times, the correlation analysis was still good. However, the increase of response factors of some components and the shift of retention times suggested that the GC was moving from being in a healthy to an unhealthy state. By analysing this information, it can be shown when to intervene and perform maintenance before the GC enters an unhealthy state.

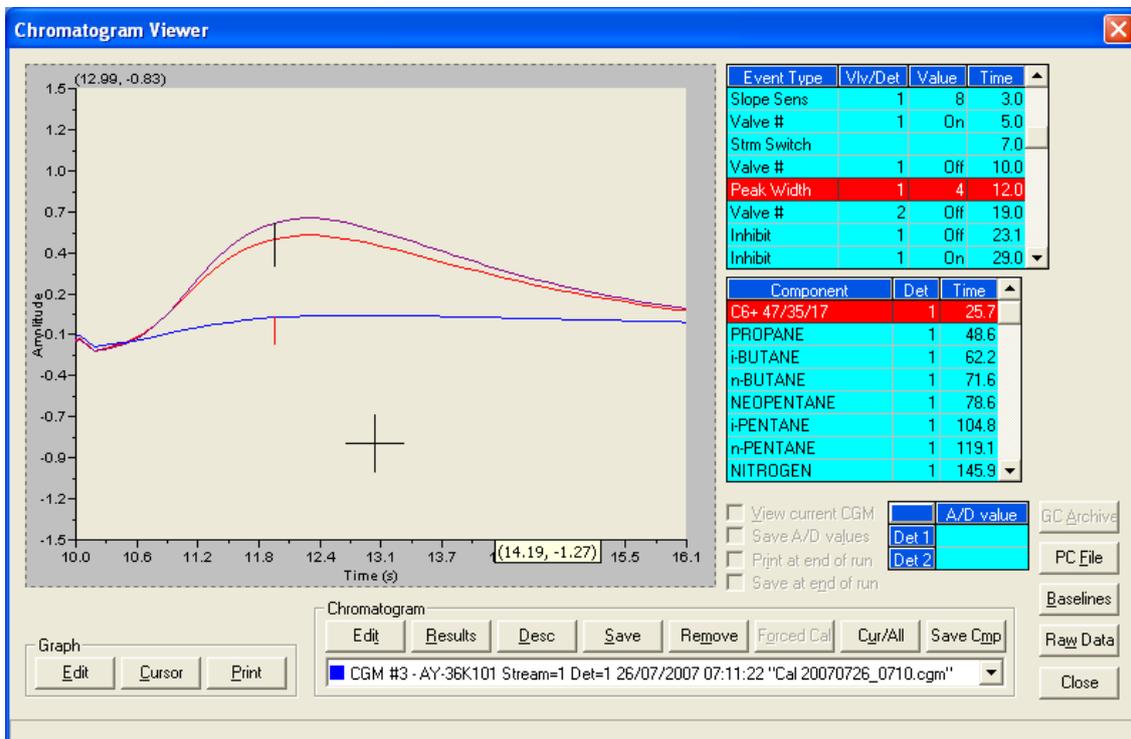


Figure 11. Daniel MON2000 Interface [2], Bumps caused by leaking chromatograph valve 2

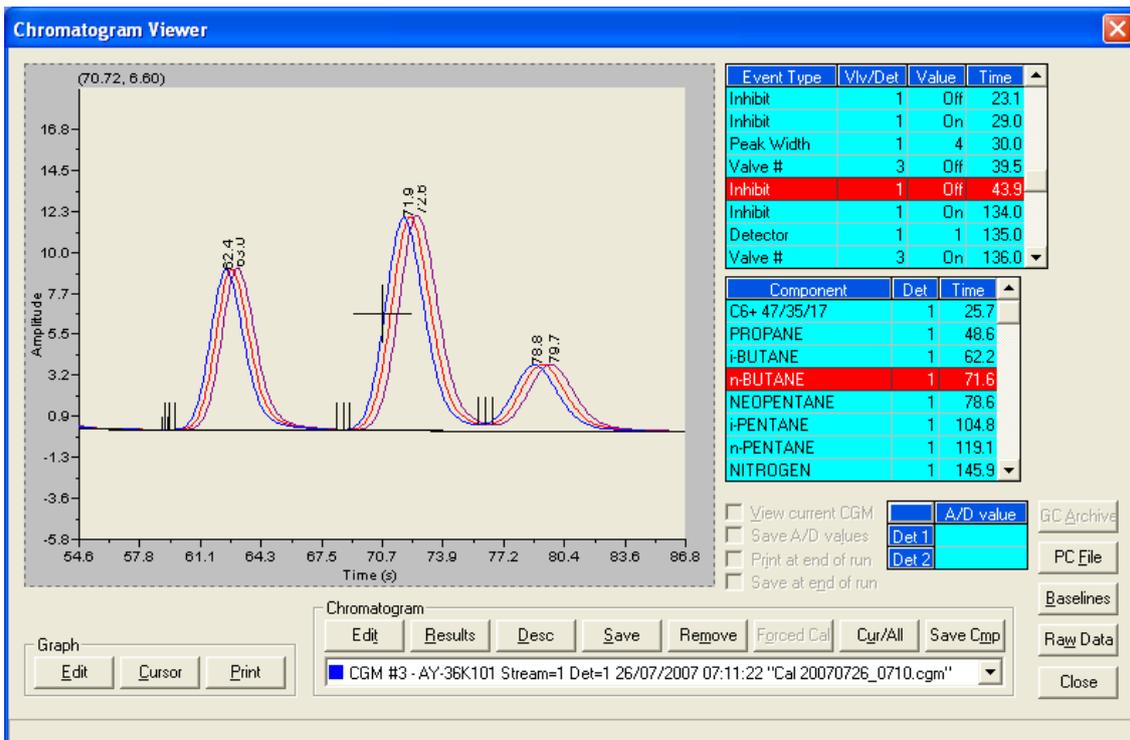


Figure 12. Daniel MON2000 Interface [2], Shift in retention time

A software package is available which can be used to analyze a GC in the way described in this paper. The software uses the footprint information generated when the GC is known to be functioning correctly. Data such as oven temperature, carrier gas pressure, carrier gas flow rate, response factor etc. are recorded and the response factor and correlation between response factor and molecular weight is plotted. These footprint values can be used as a tool to analyze day to day calibration results. This can be used in contrast to comparing calibration data on day to day basis, which has some limitations as described earlier..

The report generated by the software uses the footprint data as the initial configuration. The report compares the current calibration data to the footprint by overlaying plots of the data from the footprint, with the plot from current calibration. With the graphic representation, a drift in response factor from the footprint data can be seen. There are tables for repeatability tests either based on D1945:1996 [3] or on GPA 2261:1995 [5].

A trend is generated of the error between each component response factors for selected dates and the footprint data. Based on this error analysis, the drift in response factor can be trended. Further statistical methods can be used to analyze the error data.

A report generated for example above is as follows.

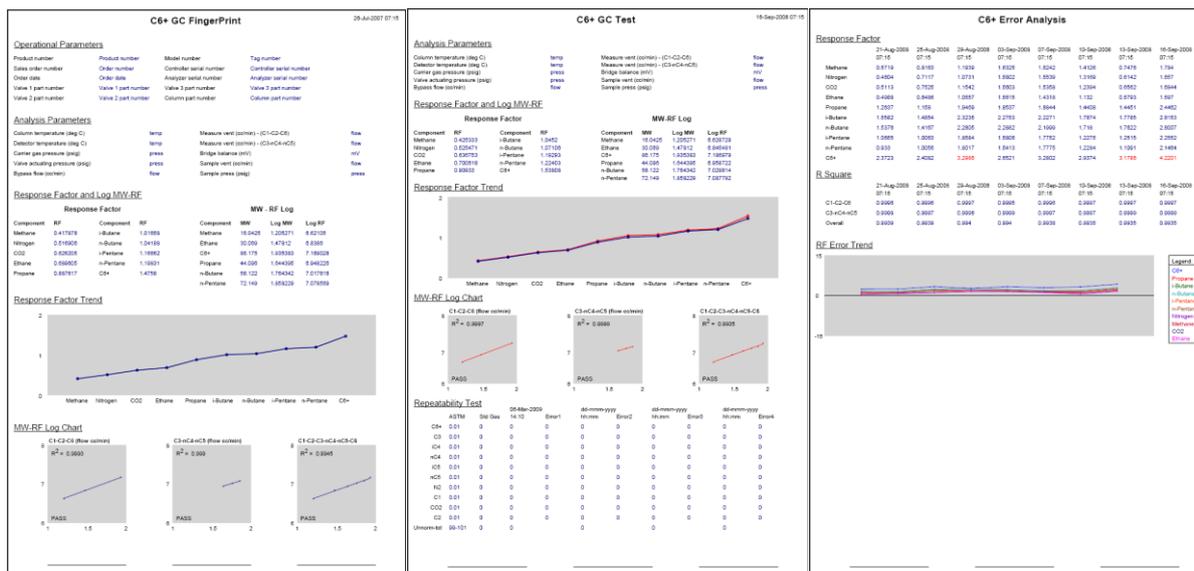


Figure 13. Footprint page, Current test page, and Error analysis page of GC analysis report

9 Correlation Method Application on Calibration Gas Replacement

A further example of the use of the correlation method described above is when a calibration gas is to be replaced. The footprint and the historical data can be used to make sure that the certificate and calibration for the new reference is correct. Before a new calibration or reference gas bottle is replaced, the last calibration data of the GC needs to be checked. When the calibration data is good, then the calibration gas to be changed should be analyzed to ensure that the composition determined by the GC is within acceptable deviation limits of the calibration gas certificate. Once the reading has stabilized, a calibration can be performed using the new calibration gas.

The calibration results, the shifts from the footprint data, and the shifts from the last calibration result can be used in the correlation software to confirm the validity of the new calibration. Further investigation can be done based on the analysis of this data if the calibration result is not satisfactory.

10 Summary

This section summarizes the conclusions from Correlation Method.

10.1 Parameters affecting GC Response Factor

There are 3 parameters that must be kept constant in order to get good repeatability on GC Response Factor. They are Pressure, Temperature, and Carrier gas Flow rate. All these parameters affect the response of thermal conductivity detectors to each component. A correct pressure, temperature and flow rate must be maintained to get good separation of components and good repeatability of GC.

10.2 Correlation Method

A correlation between Molecular weight and response factor has been developed to demonstrate the representivity of the compositions from the GC. The correlation can be used, to troubleshoot GC errors associated with valve timings, flow inconsistencies and calibration drift. A high correlation of Molecular Weight and Response Factor can be achieved when a GC maintains a constant pressure, temperature, and flow rate. Two sets of Correlation data are required on three column GC to compensate the un-avoidable slight difference in flow rate caused by difference of restrictor tubing and column-3.

10.3 Footprint and Historical Data

Footprint and historical GC data can be important to analyze and identify symptoms of GC health. This information can be used as a continuous monitoring tool to detect and act on GC symptoms before failure.

10.4 Calibration Gas Replacement

The footprint, historical data, and correlation method can be used to confirm the certification of the calibration gas and make sure that the calibration gas composition is as stated on the certificate. It is also an effective double check to ensure that the first calibration after the calibration gas replacement is correct.

11 References

- [1] Danalyzer / 2350A Gas Chromatograph, Hardware Reference Manual, Part Number 3-9000-537 Revision F, December 2002
- [2] Daniel MON2000 Version 2.46 Interface
- [3] ASTM D1945, Standard Test Method for Analysis of Natural Gas by Gas Chromatography, 1996
- [4] ASTM D7164-05, Standard Practice for On-line/At-line Heating Value Determination of Gaseous Fuels by Gas Chromatography, 2005
- [5] GPA 2261, Analysis of Natural Gas and Similar Gaseous Mixtures by Gas Chromatography, 1995
- [6] 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, 2000