VERIFYING GAS CHROMATOGRAPHS AT CUSTODY TRANSFER LOCATIONS

Daniel Tiller

ABB Inc. Totalflow Products
Bartlesville, Oklahoma

INTRODUCTION

Chromatography is one of the most widely used means of performing chemical analyses in the world. Russian botanist Mikhail Tswett is credited with discovering the technique of chromatography. Using alcohol as a mobile phase and chalk as a stationary phase, Tswett was able to separate various plant extracts.

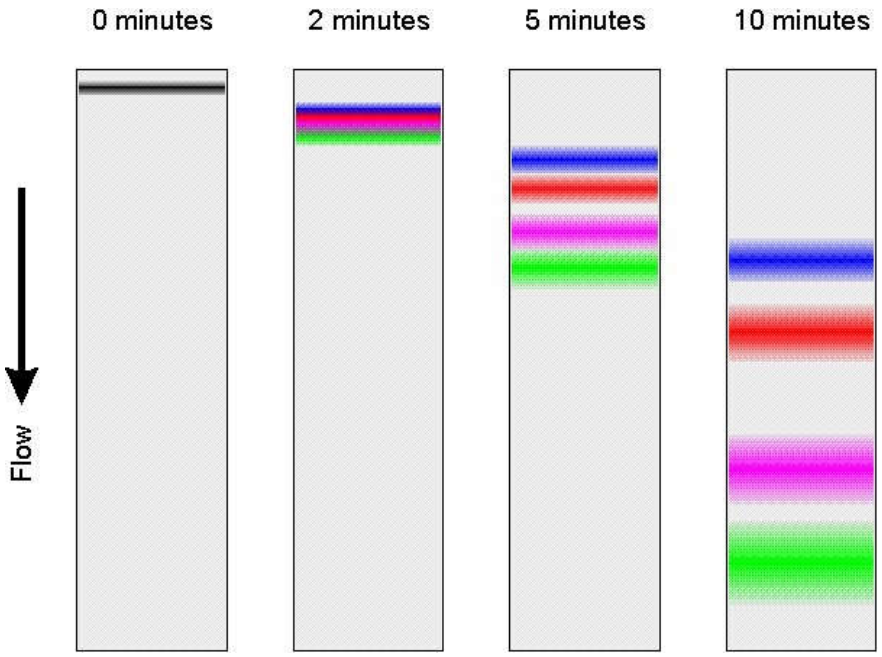

Figure 1. Example of Tswett's Experiment

Figure 1 shows how Tswett's experiment may have taken place. The vertical columns represent the chalk. At 0 minutes a mixture of plant extracts was placed at the top of the column. A steady rate of alcohol was then added to the top of the column. Over the next 10 minutes, as the extracts were pushed through the chalk by the alcohol, the extracts were separated into distinct bands.

A modern definition of the term chromatography is the ability to separate components based upon their affinities for separate phases. Several different types of chromatography exist including:

- Thin Layer Chromatography
- Liquid Chromatography
- Gas Chromatography

Gas chromatography is the preferred method for analyzing natural gas and will be the topic of this paper. This paper will discuss the general theory of gas chromatography. It will also discuss how to verify a chromatograph is operating satisfactorily at custody transfer locations.

THEORY

Reviewing the modern definition of chromatography, the ability to separate components based upon their affinities for two separate phases. These phases are known as the stationary phase and the mobile phase. In Tswett's experiments, the alcohol was the mobile phase, and the chalk was the stationary phase. In gas chromatography, the mobile phase is the carrier gas, and the stationary phase is the chromatograph column.

Separation of the analytes is achieved by placing a narrow band of the mixture on the tip of the column. The mixture is pushed through the column (stationary phase) by the carrier gas (mobile phase). As the components in the mixture interact with the stationary phase, they are separated into distinct bands which are detected as they exit the column. The primary mechanisms for separation by the stationary phase are surface adsorption, molecular size, and polarity.

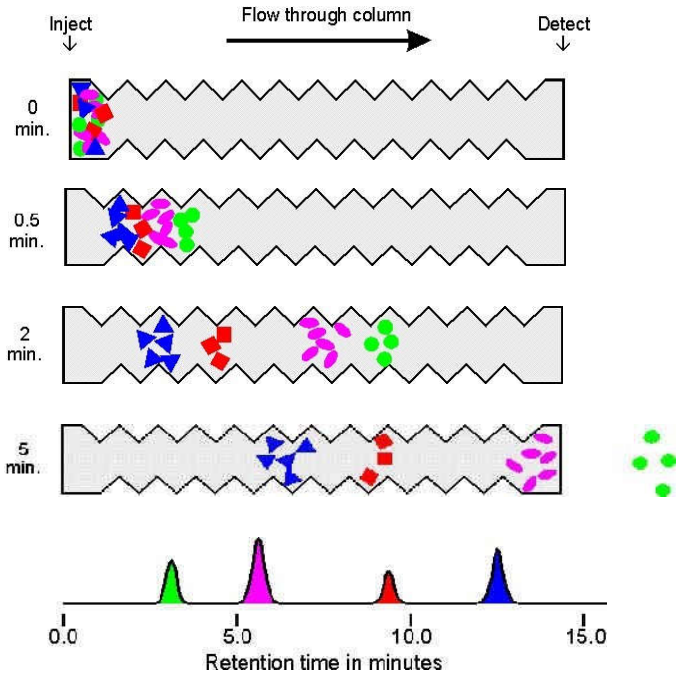

Figure 2. Example of Gas Chromatography

Figure 2 shows how a modern gas chromatograph mimics Tswett's experiment. At 0 minutes, a mixture of components is injected into the flowing carrier gas. The mixture is then carried onto the column. As the mixture is pushed through the column by the carrier gas, it is separated into individual components.

The trace generated by the detector signal is called the chromatogram. For natural gas analysis, the chromatogram is generated using a thermal conductivity detector (TCD). Thermal conductivity is the ability of a compound to conduct heat. In order to measure this property, most TCD's use thermistor beads arranged in a wheatstone bridge.

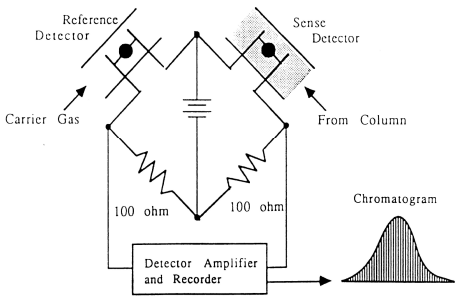

Figure 3. Wheatstone Bridge

One of the thermistors is the reference bead and is exposed to pure carrier gas. The other thermistor is the sense bead and is located at the end of the column. The beads are operated at a constant temperature. When a compound goes past the sensing bead, the bead either heats up or cools down, depending on the physical properties of the gas. This changes the resistance in the bridge and a detector signal is generated. Figure 4 is an example chromatogram.

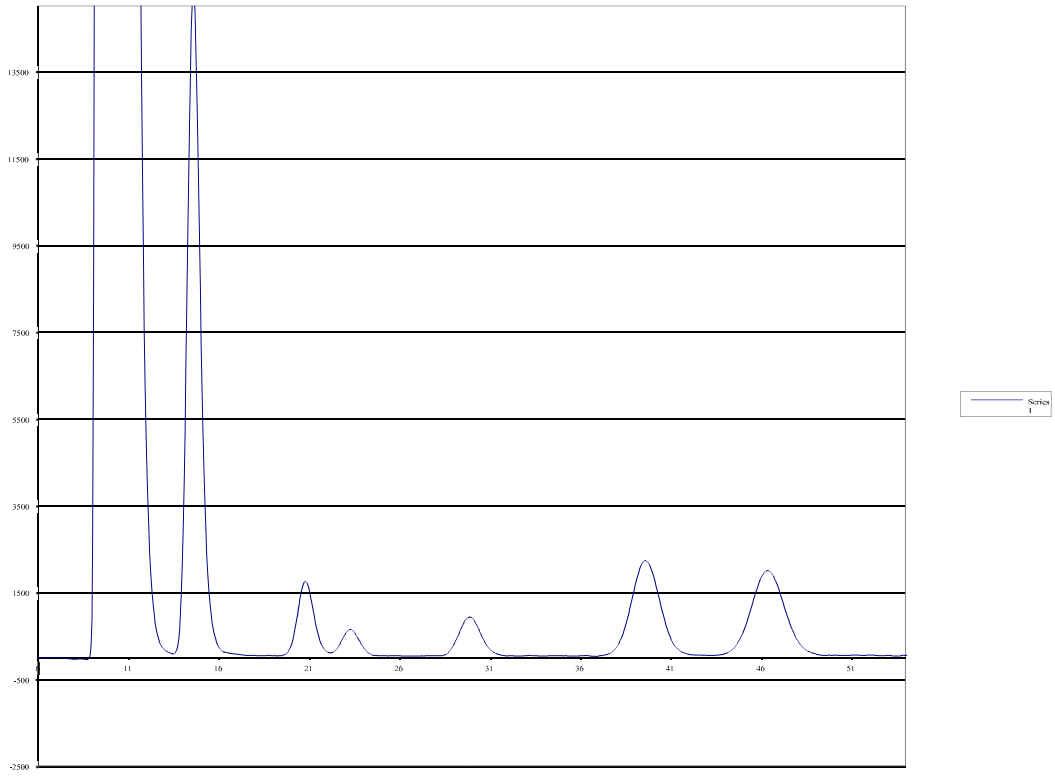

Figure 4. Example Chromatogram

In order to yield consistent chromatograms, the flow rate of the carrier gas (mobile phase) and the temperature of the column (stationary phase) must be carefully controlled.

It is necessary to control these parameters because components are identified by their retention time. The retention time is the amount of time from the beginning of the analysis until the component exits the column. If flow and temperature are held constant, the retention time is very repeatable. Retention time is the primary means of identification.

The concentration of the component is determined by comparing the peak area of the unknown to the peak area of a known standard. To calculate the amount of a given component, follow the equation:

$$C_{unk} = RF * PA_{unk} \qquad \text{(Equation 1)}$$

Where

C_{unk} = Concentration of unknown
RF = Response Factor
PA_{unk} = Peak Area of unknown

UNDERSTANDING RESPONSE FACTORS

The purpose of calibration is to represent the detector response curve for each component mathematically, thereby allowing the calculation of component values from individual component peak areas and component response factors. Comparing differences in response factors plays a vital role in determining the validity of the results of the gas chromatograph. There a several different ways to establish response factors for a GC, this section attempts to explain these differences and speak to their suitability in different situations. For the purpose of brevity, response factors will be classified as linear and non-linear.

Historically, linear response factors have been used to calculate concentrations, however, as technology changes, advanced non-linear response factors may be used with greater accuracy improving the linear dynamic range of the gas chromatograph.

Figure 5 is a representation of the actual methane response curve on a thermal conductivity detector.

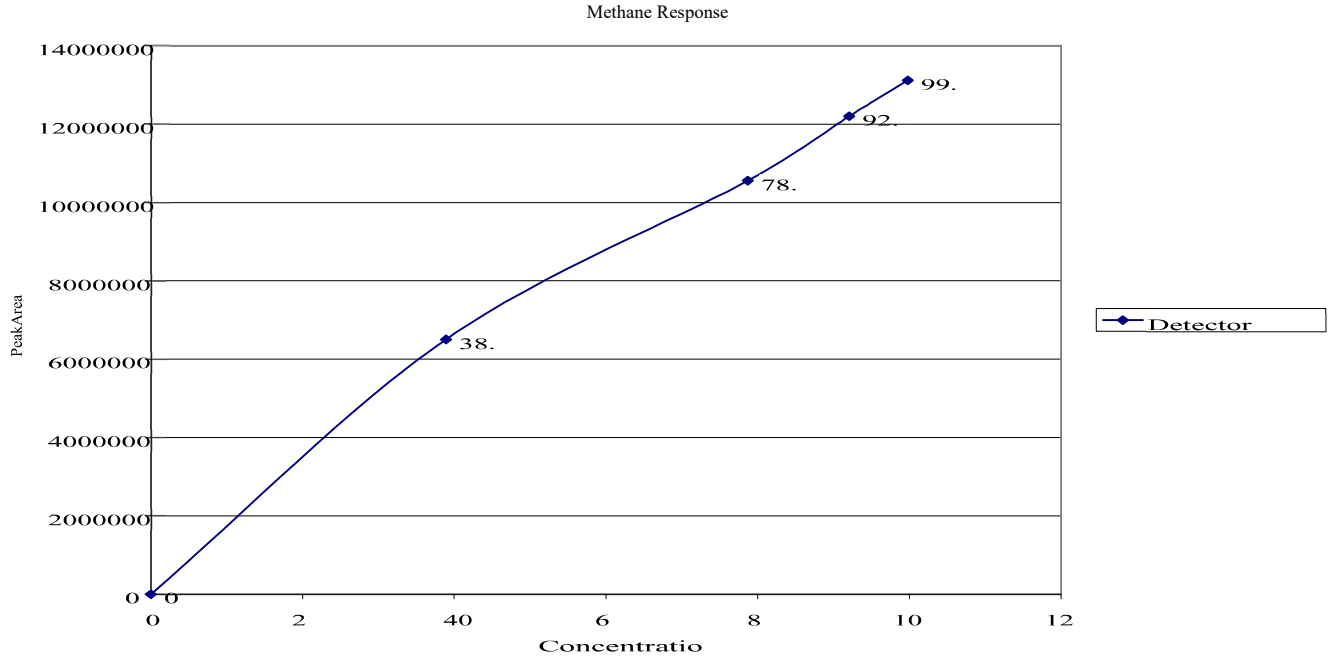

Figure 5 Detector Response Curve for Methane

Linear Response Factors (Linear Calibration)

Linear calibration uses a linear curve which is defined by the equation,

$$y = RF*x + b \quad \text{(Equation 2)}$$

Where y = mol% of component
RF = Response factor for given component
x = peak area
b = y intercept (offset)

The response factor is generated using equation 3.

$$RF = Conc_{std} / PA_{std} \quad \text{(Equation 3)}$$

Where RF= linear response factor for component

$Conc_{std}$= Certified concentration for component

PA_{std} = Peak Area for component of certified standard

A linear curve is often referred to as a single point calibration, but 2 points are actually required. This second point is the y intercept, typically zero is used as the y-intercept, this is known as force-thru zero.

Observe what happens when one does a linear calibration of methane at a concentration of 99.8 Mol%.

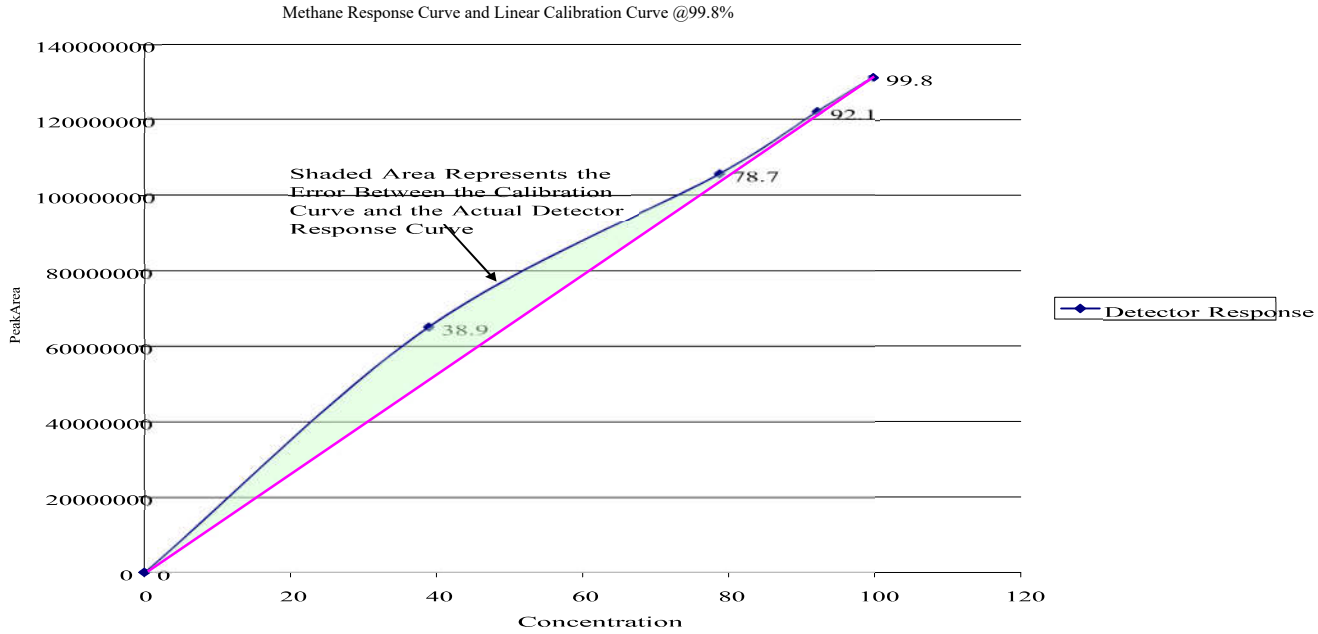

Figure 6 Methane linear calibration at 99.8%

The large shaded area represents the amount of error between the linear calibration and the actual detector response. At 99.8Mol% the readings are identical as one would suspect, but the farther away from the 2 calibration points one gets, the larger the amount of error. This is why many analyzers require that users must carefully choose a calibration blend which is analytically close to the process stream being measured.

Next consider Figure 7, if one calibrates at 78.7 Mol%.

Methane Response Curve and Linear Calibration Curve @ 78.7%

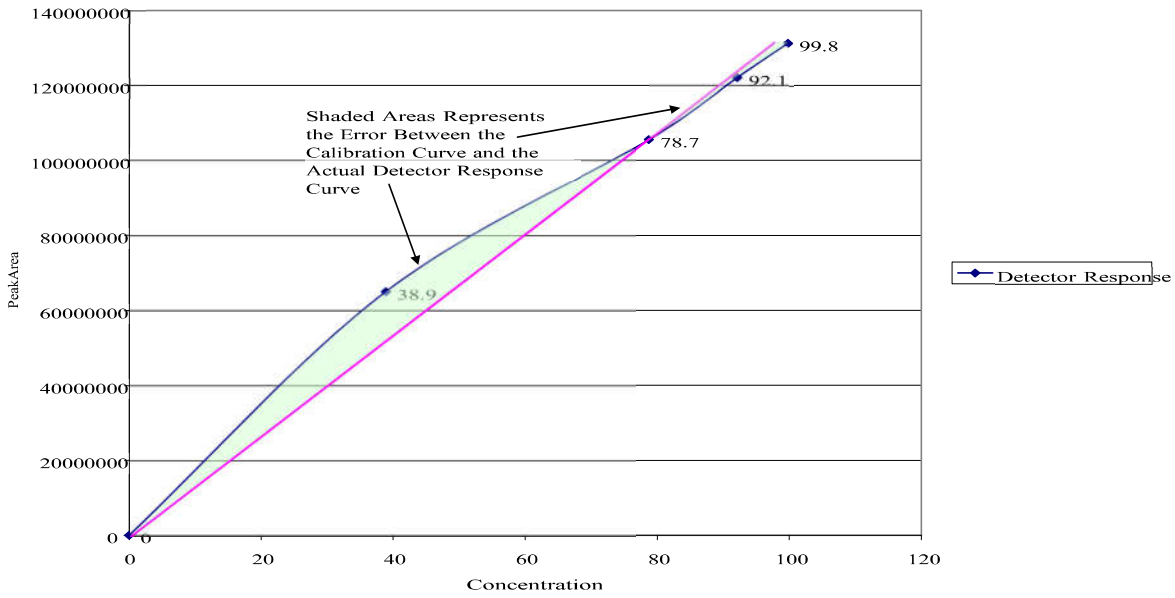

Figure 7 Methane Linear Calibration at 78.7%

Notice this time, it has 2 shaded areas represented the amount of error between the calibration curve and the detector response curve. The analysis will still be the most accurate the closer one is to the actual calibration point.
The next graph, Figure 8 was calibrated at 38.9 Mol%.

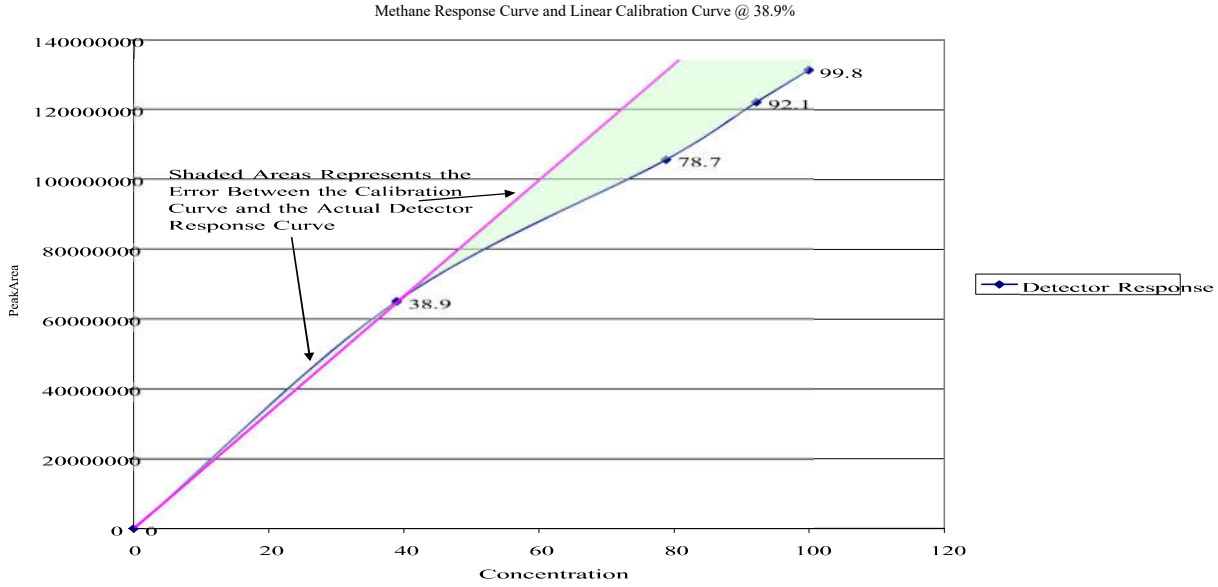

Figure 8 Methane Linear Calibration at 38.9%

Notice how relatively close the 2 curves are between 0 and 40%, and then the large amount of error over 40% because the actual detector response changes but the linear curve does not.

Next consider using a y intercept other than zero (Figure 9), one still need 2 points to plot our straight line. Using the 38.9% and 99.8%, one can calculate a y intercept as shown in the next graph.

Methane Response Curve and Linear Calibration Curve Using Y Intercept

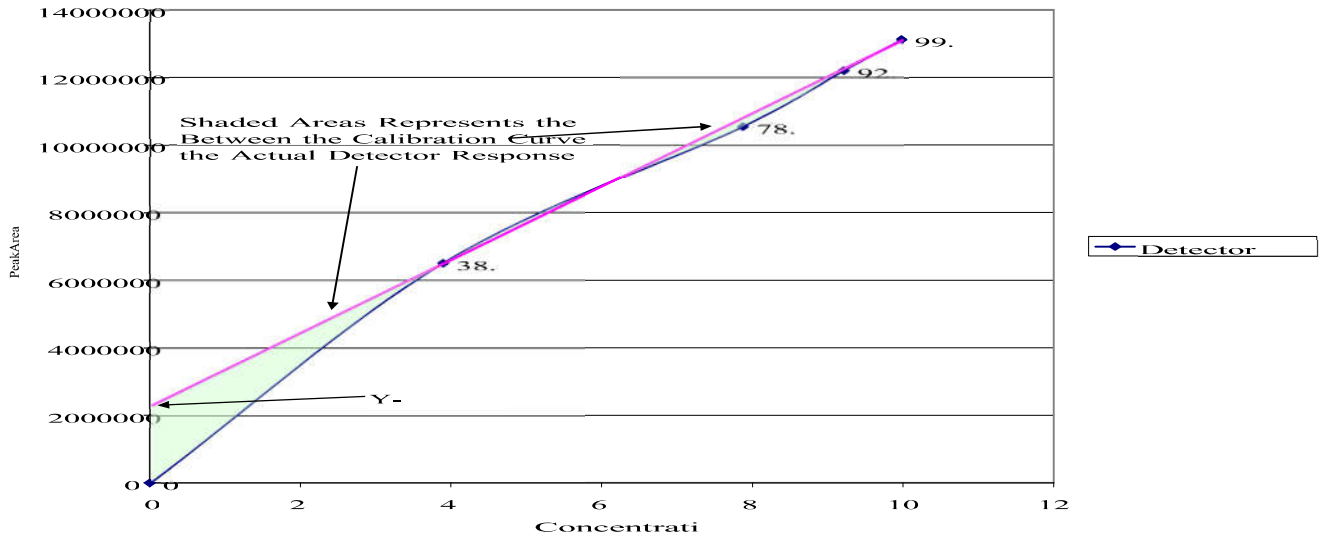

Figure 9 Methane Linear Calibration thru 38.9% and 99.8%

The error between the 2 calibration points has been greatly reduced using the y-intercept and the linear calculation. However, between 0 and 40% there is significant error.

It is clear that using a linear (single) point calibration reduces the linear dynamic range of the chromatograph. The operator must be very careful to make sure that he is calibrating within the range that he will be measuring to minimize the amount of error.

Non-Linear Response Factors (Exponential Calibration)

In order to maximize the linear dynamic range, the calibration curve needs to fit the actual detector response curve as closely as possible. This can be achieved by replacing the single point linear curve with a multipoint exponential curve.

Each component has its own non-linear curve. Each curve is defined by 3 coefficients, the multiplier, the response factor, and the offset. The concentration of each component is calculated as follows.

$$Y = a * e^{(b*x)} + c \quad \text{(Equation 4)}$$

Where Y = Concentration (Mol%)
a = the multiplier e = constant
b = response factor x = peak area
c= offset

The response factor term is generated using a curve fitting algorithm based upon peak area data generated from multiple certified calibration standards.

The following diagram (Figure 10) is a plot of the exponential calibration curve vs the actual detector response curve.

Methane Response Curve vs Exponential Response Curve

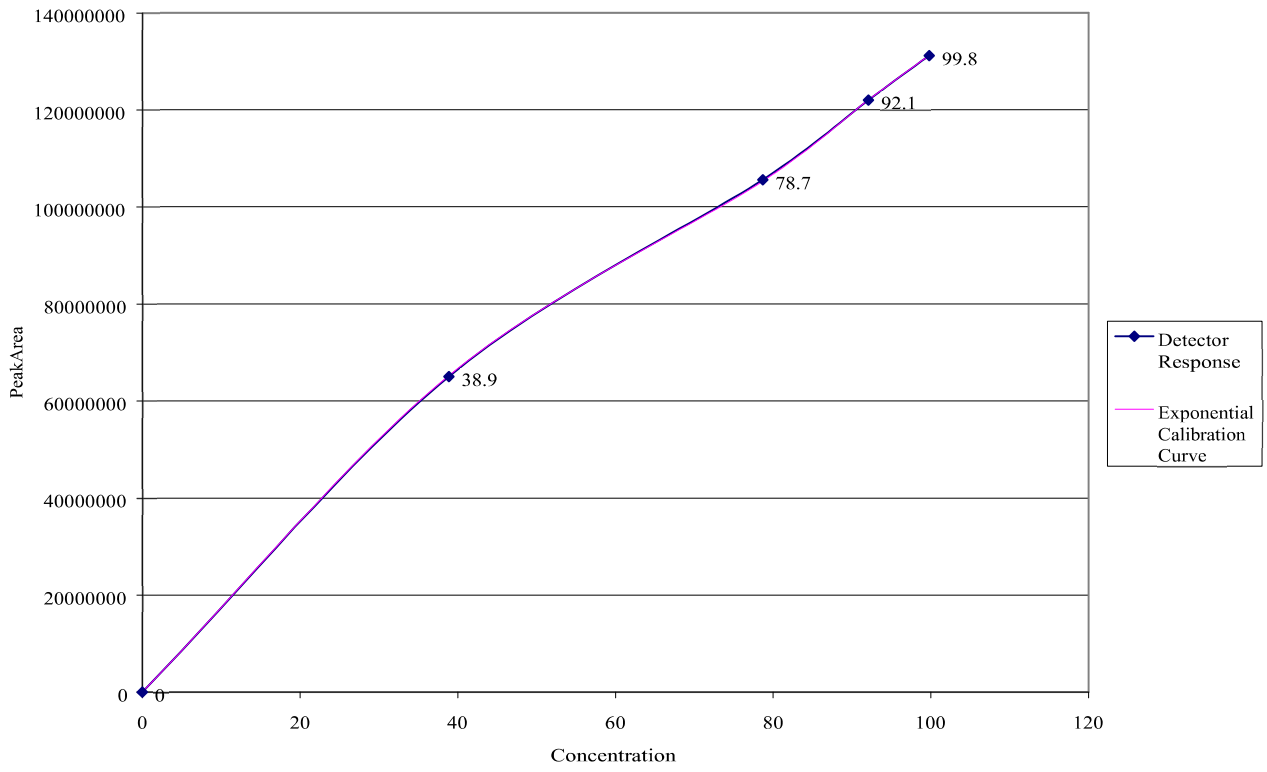

Figure 10 Methane Non-linear Calibration Curve

Notice how closely the calibration curve and the detector response mirror each other, greatly increasing the linear dynamic range of the analyzer.

GAS CHROMATOGRAPH VERIFICATION

Diagnostic Tools

There are several different types of available diagnostic information which is useful in determining the overall health of the analyzer system. These include:

- Alarm/Event Logs – Most analyzers generate and store a variety of alarms and events that can affect the performance of the analyzer. All alarms and events should be investigated and confirmed to not be adversely affecting the quality of the analysis.
- Unnormalized Totals – Unnormalized total has been used for years as an indication of how much an analyzer has drifted since the last calibration. Limits for this value are up to the individual user but are usually set between 97 and 103%.
- Response Factor Trends – Logging response factors can be useful in identifying how much response factors change from one calibration to the next. Response factors that change drastically can be an indication that the results should be scrutinized. As with unnormalized totals, acceptance limits are up to individual users, but in general response factors should not be changing more than 2% in a properly operating system.
- Retention Time Trends – Logging retention times of key components is also useful in determining a properly operating system. Under constant temperature and pressure, the retention time of components should be consistent to within 0.5 seconds. If retention times continue to drift, this could be a sign of a degrading column.
- On-Board Diagnostics – As mentioned earlier, two things that are necessary for repeatable results are constant temperature and constant carrier flow. As more analyzers move away from older analog designs to more modern and flexible digital control algorithms, it is now possible to monitor control variables. The control variable will give an indication of how well digital control algorithm is in control. Analyzers now have the ability to have on-board diagnostics which automatically monitor key performance indicators, such as control variables, as well as monitor the sample system for any signs of leakage. Figure 11 is an example of a diagnostics report.

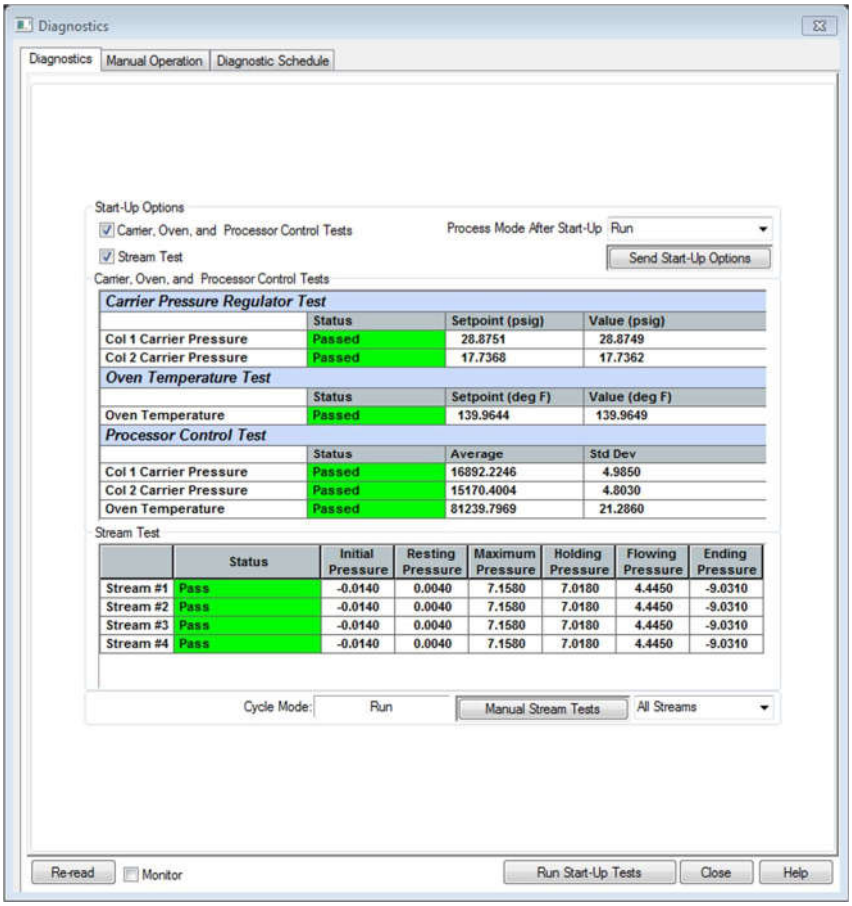

Figure 11 Diagnostics Report

- Fidelity Plots – There is a linear relationship between the molecular weight and the thermal conductivity of the nalkanes being analyzed. By plotting the molecular weight versus the linear response factors, one can get an indication of proper operation and setup. Figure 12 is typical example of this plot.

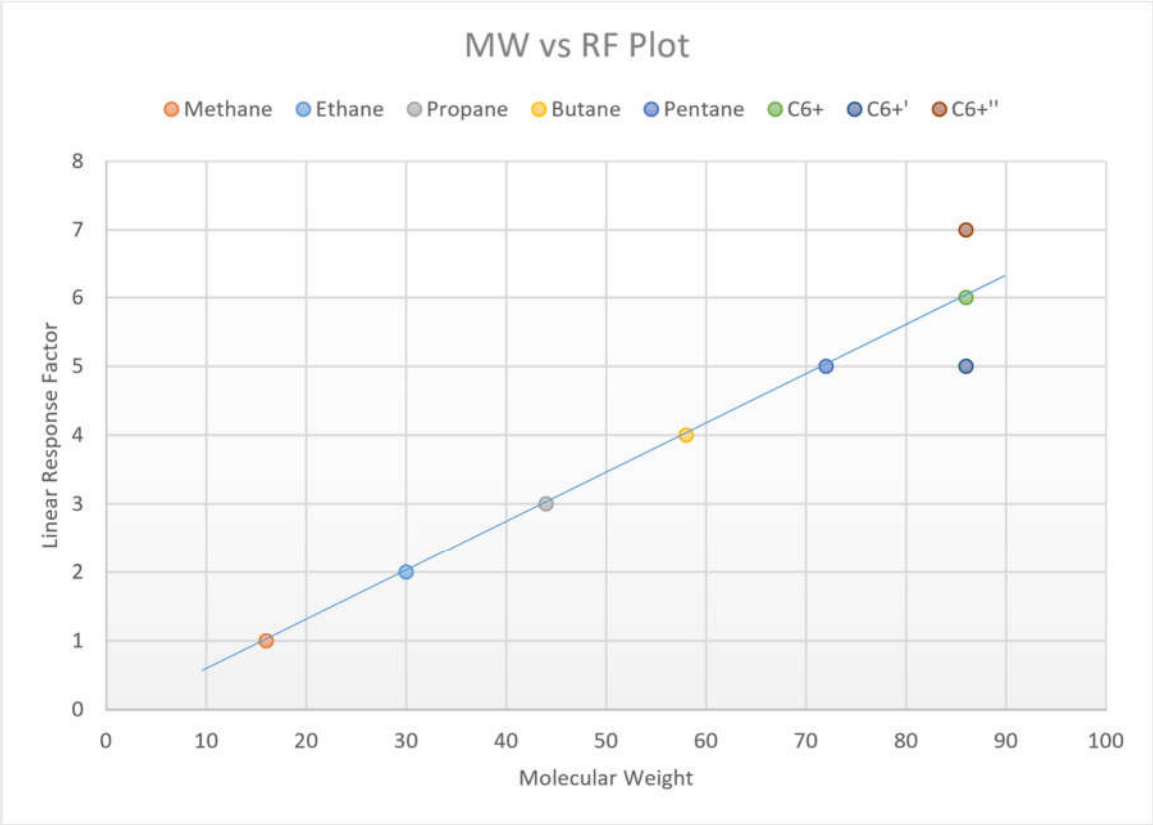

Figure 12 MW vs RF Plot

Notice on the graph there is a linear relationship between the molecular weight of n-alkanes and the thermal response on a TCD. If one has an outlier, particularly for n-hexane and n-pentane, more investigation is required. First, one should check the valve timing to make the sure the backflush is occurring at the proper time. If one is back-flushing part of n-pentane as well as n-hexane, C6+ will be falsely high. Conversely if part of n-hexane is not being back-flushed, the value will be falsely low. If the graph is still non-linear even after the user has assured themselves that the valve timing is correct, then the calibration gas standard should be investigated to make sure that none of the heavier components have condensed.

Verification Tools

While the previously mentioned diagnostic tools are useful in discovering a potential problem with the gas chromatograph, one should not automatically conclude that the analyzer is giving erroneous data. It is possible for the analyzer to be operating in less-than-ideal circumstances and still be generating correct reports.

The only way to truly validate the results from the GC is to perform an audit using certified calibration blends according to industry accepted standards. Generally in the US, audits are performed in accordance with GPA 2261. While internationally, standards such as ISO10723 are used. Typically, in the US, the data from the analyzer is considered suitable as long as it meets the performance criteria specified in section 10 of GPA2261-13.

GPA2261

Repeatability and reproducibility limits should be calculated as specified in section 10 of GPA2261-13. In simplest terms, repeatability is a measure of how well a set of data agrees when it is generated on the same instrument by the same user. Reproducibility has to do with how well a set of data agrees when it is generated on multiple instruments by multiple users.

The acceptance criteria (permissible error) can then be calculated from the reproducibility limit and the component blend uncertainty.

$$PE = CV \pm \sqrt{U^2+R^2}$$

(Equation 5)

Where PE = Permissible Error for each component
CV = Certified Value for each component in certified blend
U = Uncertainty for each component in certified blend
R= Reproducibility limit for each component

Once the permissible error limits have been calculated for each component, one can then compare the analyzer results to the acceptance criteria for suitability.

CERTIFIED BLENDS

Note that the permissible error calculation now takes into account the uncertainty of the certified blends being used for the audit. So, it may be necessary to use certified blends with lower degrees of uncertainty in order to achieve the permissible errors that might be required by end user.

The uncertainty of the analytical results is directly related to the uncertainty of the calibration blend. Figure 13 shows a Monte-carlo simulation comparing results generated using a calibration blend with low uncertainty and higher uncertainty. The data generated with the certified blend with lower uncertainty exhibited a much higher degree of precision.

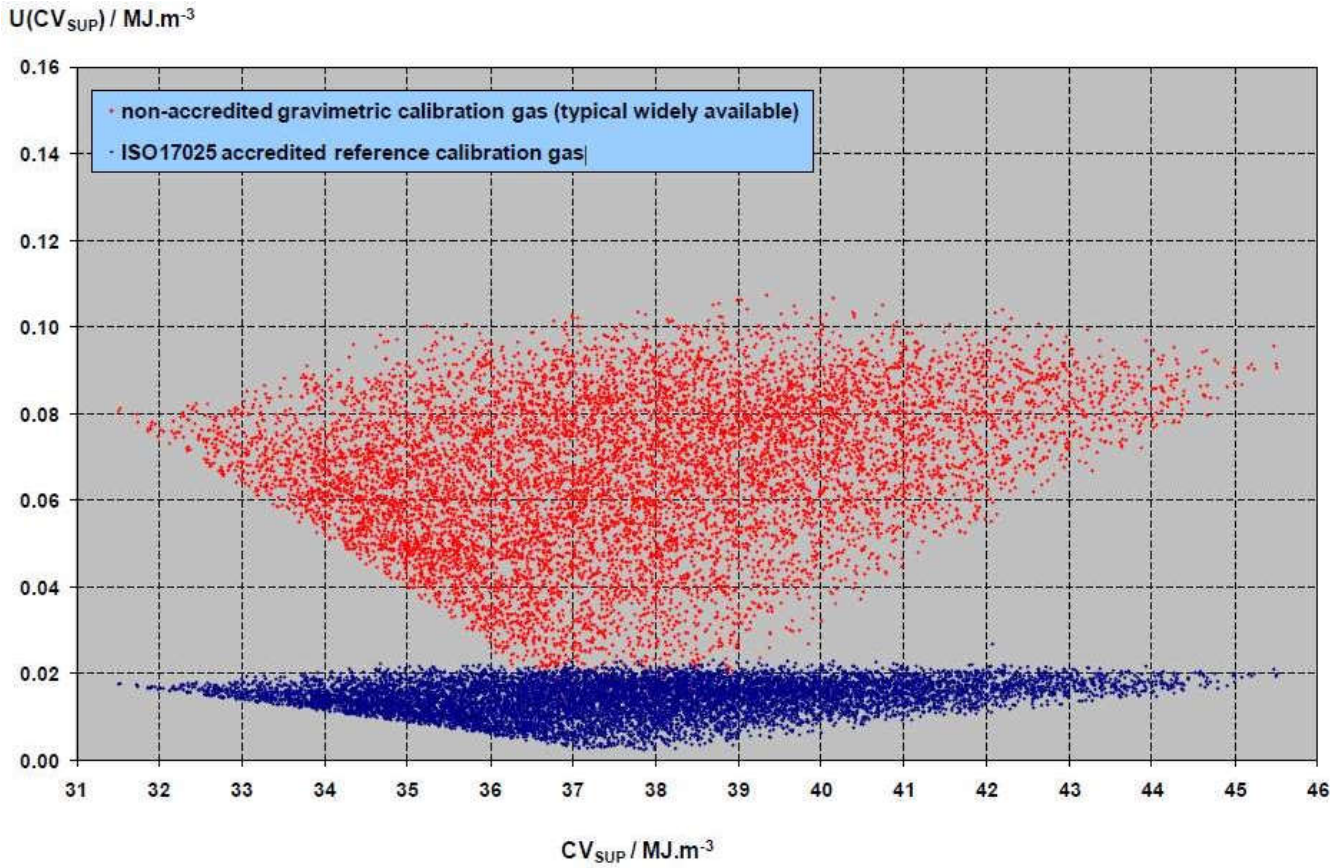

Figure 13– Uncertainty Effects Due to Blend Quality

CONCLUSION

There are many different factors that can contribute to properly verifying the operation of a gas chromatograph for custody transfer locations. There are a number of diagnostic tools that have been used for many years to verify the health of a chromatographic system. These include:

- Monitoring Alarms/Event Logs
- Monitoring Un-normalized Totals
- Tracking changes in Response Factor Values
- Tracking changes in the Retention Times of components
- Utilizing On-Board Diagnostics
- Use of Fidelity Plots

However, it should be noted that just because the instrument does not pass some of these historical tools, it does not mean that the analyzer is generating erroneous results.

One must understand the differences and potential advantages of using different types of response factors, in order to select the proper type of response factors for a given application.

Ultimately, the best way to verify a gas chromatograph is to perform an audit according to the guidelines specified in GPA2261. At the same time great care should be taken in selecting the calibration and audit blends in order to achieve the permissible errors that are satisfactory to each user's individual needs.