

Verifying Gas Chromatographs at Custody Transfer Locations

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Introduction

Chromatography is the separation of a mixture by passing it in solution or suspension or as a vapor (as in gas chromatography) through a medium in which the components move at different rates. Russian botanist Mikhail Tswett is credited with discovering the technique of chromatography. He used chalk and alcohol to determine plant extract properties.

Verifying gas chromatographs at custody transfer locations is one of the most critical measurement procedures there is today. Not knowing exactly what the Gc is reading and how accurate the results are could cost the company hundreds of thousands of dollars depending on flow rates and time between verifications. Calibrations are not always a fool proof way making sure that the Gc is working correctly since minor human errors can occur.

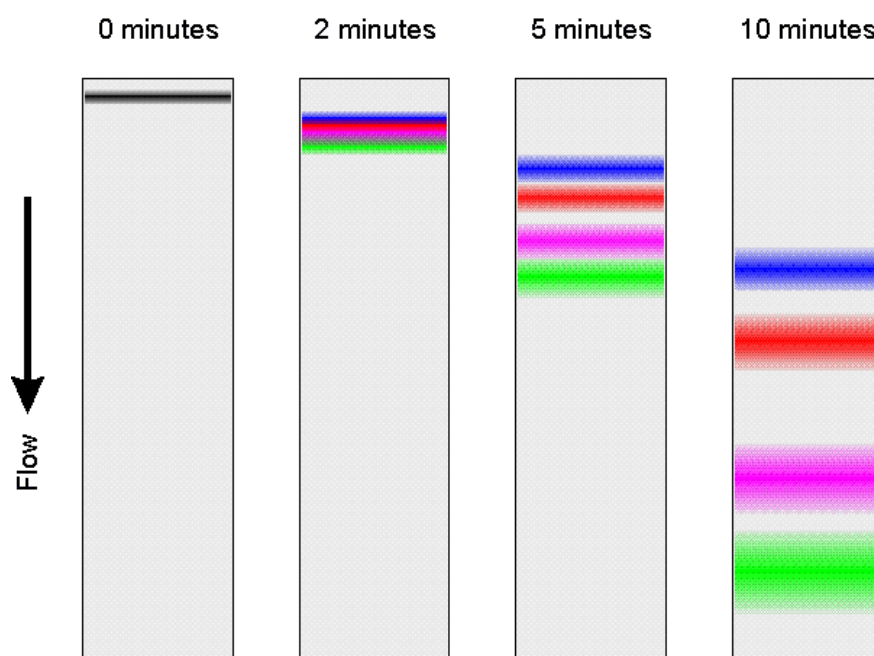


Figure 1. Tswett's Theory of Chromatography

Figure 1 shows the theory of chromatography. The vertical columns represent the chalk. After placing the plant extract on top of the column alcohol was added to push the extract down the column at a steady rate. After ten minutes the extracts were then separated into distinct bands.

Gas Chromatography is the preferred method of analyzing natural gas. This paper will discuss the general theory of chromatography and how to verify a chromatograph at custody transfer locations.

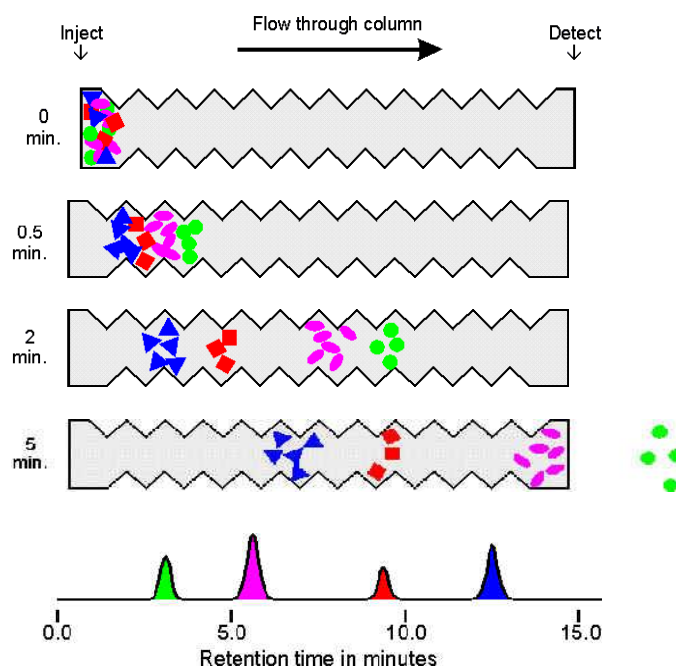


Figure 2. Example of Gas Chromatography

Figure 2 shows the theory of modern chromatography. A sample is injected into the flow of carrier gas at a specified rate. The sample then travels into the column which is then separated out by molecule size. The smaller the molecule, the faster it will travel through the column. The larger molecules will travel slower and pass through at a longer time. This is called retention time which will be covered later in the paper. The primary mechanisms for separation by the stationary phase are surface adsorption, molecular size and polarity

Theory

Reviewing the modern definition of chromatography is the ability to separate components based upon their affinities for two separate phases. The two phases would be the mobile phase and stationary phase. The mobile phase is the carrier gas and the stationary phase would be the columns.

Separation of the gas components takes place in the columns. This occurs when the carrier gas pushes the components through the column which has material in it designed to allow different size molecules of each component to pass through at different times. Once each component has passed through the column it then reaches a detector. There are two detectors, one that reads pure carrier gas and the other that reads the gas sample. The detector that is reading the carrier gas is known as the reference. The detector that reads the sample is known as the sense detector. Once the sample reaches the sense detector, it will heat up and cool down as each component passes by.

Gas Chromatography uses a TCD. This stands for Thermal Conductivity Detector. Thermal conductivity is where the compound conducts heat when a component passes by the detector. Most TCD's use thermistor beads arranged in a Wheatstone Bridge. The beads are operated at a constant temperature and will heat up or cool down depending on each component's physical properties. This will change the resistance in the bridge and give a reading of how much of each component there is. The TCD also needs a consistent flow of carrier gas and stable temperature to accurately produce consistent chromatograms.

The necessity of the temperature, pressure and flow to be consistent is so the components will move through the columns the same speed each time a sample is injected into the column. This will ensure that each component is within the given retention time allotted for that component. Retention time is measured from the start of the component going across the detector to the end of the component leaving the detector. If the flow and pressure are held constant, the retention time is very repeatable. Retention time is the primary of identification.

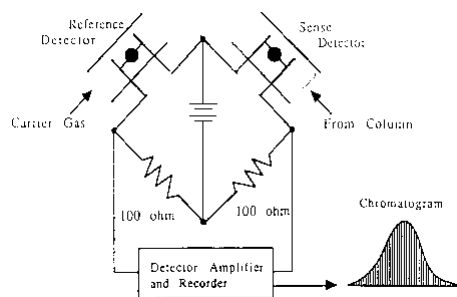


Figure 3. Wheatstone Bridge

Figure 3 shows a Wheatstone Bridge which detects each component as it passes through the sense detector along with the reference detector with pure carrier traveling through it. This will provide the data needed for a chromatogram.

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:

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

Where

C_{unk} = Concentration of unknown

RF = Response Factor

PA_{unk} = Peak Area of unknown

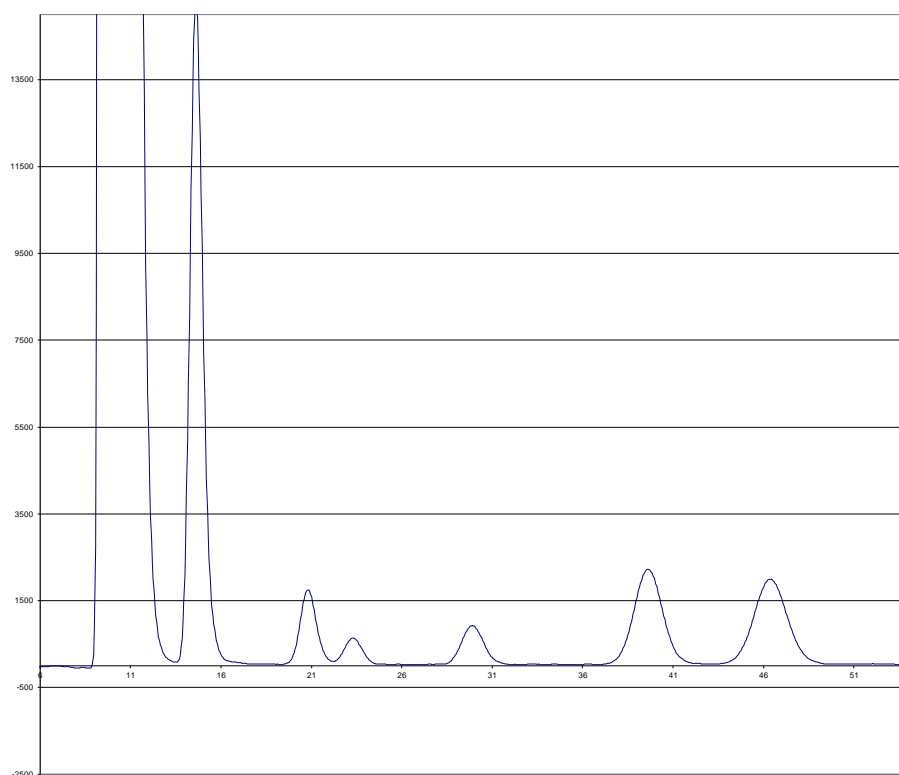


Figure 4. Example Chromatogram

Troubleshooting

There are many different areas that a gas chromatograph could be reading inaccurately. A few of the ways could be, too little or too much sample flow, high or low carrier pressure, Gc is not correctly calibrated, retention times are not correct, or temperatures are not correct. There are also several diagnostic tools to use to troubleshoot certain problems. These could include Alarm/Event logs, unnormalized totals, response factor trends, retention time trends and on-board diagnostics.

Sample flow could be deviation could be caused by several problems. These could include plugged filters on sample probe, dirty or plugged filters on sample conditioning panel, improperly adjusted regulator or having the incorrect regulator installed.

As talked about earlier the carrier pressure flow should be kept at the same flow and pressure to ensure proper analysis. This should be checked each time the GC is looked at.

Gc calibration is very important to complete thoroughly and precisely. Entering the components in the component data table correctly will ensure the Gc knows how much of each component there is in the calibration standard. By incorrectly calibrating the Gc will certainly cause improper readings of the stream gas. This will also give an incorrect BTU reading.

Diagnostic Tools

Retention times: When retention times are reading incorrectly, this will mean that some of the component's peak may not be incorporated into the total. If the retention is off by more than .5 seconds this could mean a degrading column.

The Gc needs to have a very constant temperature to work properly. If the temperatures are not at the required setting, this could cause a couple of different problems. One is that the sample will move through the columns at different speeds than what was calibrated at. The second is that if the temperature is too low the sample could condense and liquid could get into the columns and start degrading them.

Alarm/Event Log: This tool will give a list of alarms that the Gc has encountered. Looking through this will allow troubleshooting practices to have a starting point in determining what went wrong. The event log will provide answers to what and when control changes were made.

Unnormalized Total: Unnormalized total is an indication of how far the Gc has drifted from calibration and if the sample size is consistent with calibration.

Response Factors: When trending response factors, take into consideration that it should not change by more than 2% in a normally operating system. Response factors that change drastically should be investigated deeper.

On-Board Diagnostics: With analyzers getting more and more advanced in technology, the on-board diagnostic capabilities are expanding. With this technology the analyzers are moving away from old analog designs and implementing digital control processes that can monitor control variables.

The screenshot shows the 'Diagnostics' window with three tabs: 'Diagnostics', 'Manual Operation', and 'Diagnostic Schedule'. The 'Diagnostics' tab is active, displaying 'Start-Up Options' and test results.

Start-Up Options

- ☒ Carrier, Oven, and Processor Control Tests
- ☒ Stream Test
- Process Mode After Start-Up: Run
- Send Start-Up Options

Carrier, Oven, and Processor Control Tests

Carrier Pressure Regulator Test

	Status	Setpoint (psig)	Value (psig)
Col 1 Carrier Pressure	Passed	28.8751	28.8749
Col 2 Carrier Pressure	Passed	17.7368	17.7362

Oven Temperature Test

	Status	Setpoint (deg F)	Value (deg F)
Oven Temperature	Passed	139.9644	139.9649

Processor Control Test

	Status	Average	Std Dev
Col 1 Carrier Pressure	Passed	16892.2246	4.9850
Col 2 Carrier Pressure	Passed	15170.4004	4.8030
Oven Temperature	Passed	81239.7969	21.2860

Stream Test

	Status	Initial Pressure	Resting Pressure	Maximum Pressure	Holding Pressure	Flowing Pressure	Ending Pressure
Stream #1	Pass	-0.0140	0.0040	7.1580	7.0180	4.4450	-9.0310
Stream #2	Pass	-0.0140	0.0040	7.1580	7.0180	4.4450	-9.0310
Stream #3	Pass	-0.0140	0.0040	7.1580	7.0180	4.4450	-9.0310
Stream #4	Pass	-0.0140	0.0040	7.1580	7.0180	4.4450	-9.0310

Cycle Mode: Run Manual Stream Tests All Streams

Re-read Monitor Run Start-Up Tests Close Help

Figure 5. Diagnostic Report

Fidelity Plots: There is a linear relationship between the molecular weight and the thermal conductivity of the n-alkanes being analyzed. By plotting the molecular weight versus the linear response factors, one can get an indication of proper operation and setup. Figure 6 is an example of this.

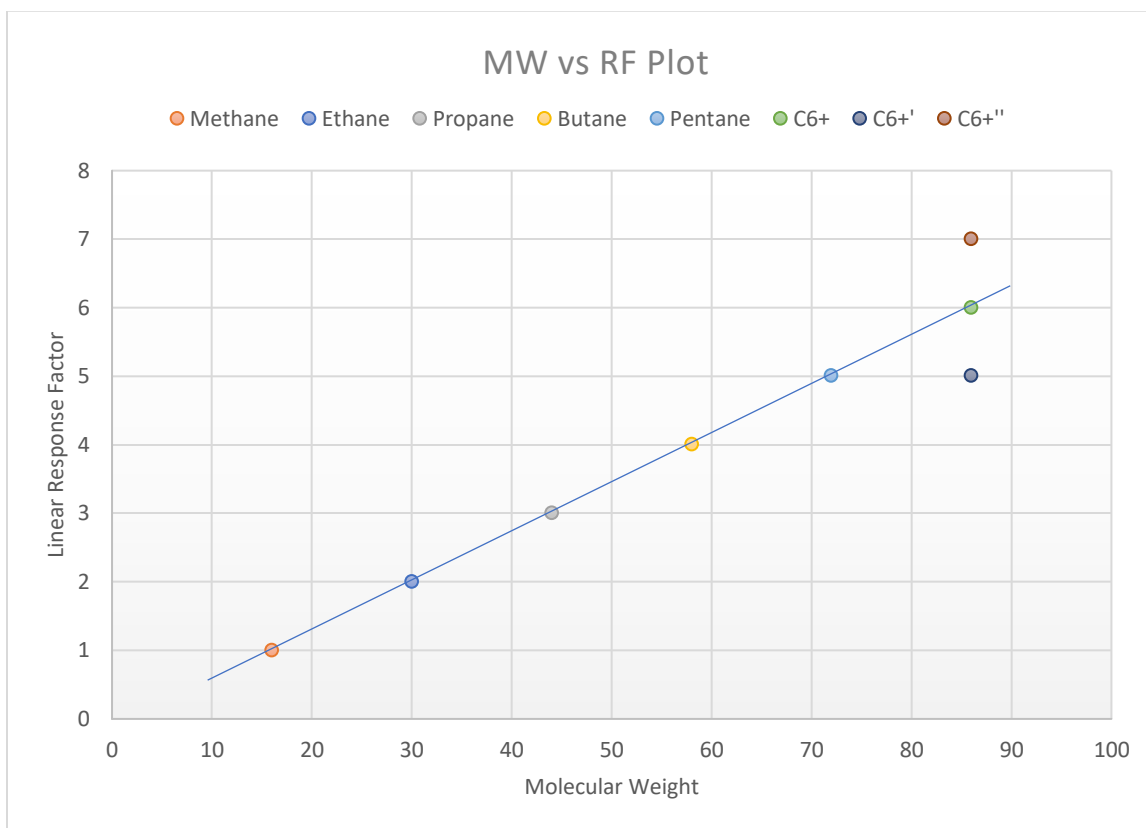


Figure 6. MW vs RF Plot

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 sure the back-flush 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

After the troubleshooting has been done and the analyzer is running correctly, now is the time to check to make sure that the calibrations are spot on. This can be done by auditing the analyzer semi-annually with a completely different cal standard. This will be run as an unknown. There are several key steps to take to ensure the process is done correctly and accurately.

First off, make sure the audit standard is different than the stream gas and cal standard currently in place. Ideally this should be done with high btu and low btu standards to test the analyzers operating ranges. This will ensure that the analyzer will pick up any upset conditions that may occur with the process.

The next step would be to make sure the bottles are at a proper temperature. The standard is 30 degrees above hydrocarbon dewpoint. A heated sample line along with the correct regulator will allow a representative sample to flow to the analyzer.

Run the calibration as an unknown a few times to make sure the analysis is the same every time. This will ensure that sample line has been completely purged. Once the sample is repeating accurately each run make sure the components are reading the correct amount. If not make the necessary adjustments to the analyzer to correct this issue. There will need to be a before and after analysis saved to show how far off the equipment was off. This will make troubleshooting easier later.

	As Found Conditions						
Active Alarms:	<input type="checkbox"/> Yes	<input checked="" type="checkbox"/> No		Analysis Temp:		#1	#2
				<i>Deg. F</i>			
Helium Pressure:	Bottle 1	Bottle 2					
<i>Primary PSI</i>				PreAmp		As Found	As Left
<i>Delivery PSI</i>				<i>mV</i>			
Carrier Pressure:							
				120	Deg F Audit bottle temp		
Cal Pressure:				150	Primary		
<i>Delivery PSI</i>				20	Delivery		
<i>Cal Blanket Temp</i>							
				80	deg F Building temp		
MV Flow Rate:				60	deg F Ambient		
Sample Flow Rate:				yes	Sunny, Clear, No Wind		
Analysis Temp:	#1	#2		450	Audit bottle sample flow [sccm]		
<i>Deg. F</i>				22.5	Audit bottle MV Flow rate [mL]		

Figure 7. Audit Record Table

Record the pressures and temperatures of the bottles and GC. This way when the audit is done the next time, the pressures and temperatures should be the same, if not make the changes so there is a consistent standard of process. The items to be recorded could be like the records as Figure 7. These are some of the numbers needed to be recorded each audit so there is a consistency in the operating parameters that might change over the course of time due to equipment or operating error. Figure 8 will show the current cal standard and the audit standard, so a comparison can be made of the components and accuracies associated with each run.

Once the numbers are recorded and analysis of the audits have been done, save all the findings and reports so they can be easily looked up and compared for the next audit. These can also be used to troubleshoot and fine tune each analyzer for optimum performance and accuracy. This will ensure that the process is accurate and profitable.

Current Cal Standard		
Cylinder #:		
Expiration Date:		
		MolPct
C6+ GPA 2261-99		0.0308
PROPANE		0.9960
i-BUTANE		0.3040
n-BUTANE		0.3040
NEOPENTANE		0.0000
i-PENTANE		0.1020
n-PENTANE		0.1020
NITROGEN		2.5000
METHANE		90.1802
CARBON DIOXIDE		0.5010
ETHANE		4.9800
TOTAL		100.0000
	BTU	1058.5
	SG	0.6177

Audit Cal Standard			
Cylinder #:			
Expiration Date:			
		MolPct	
C6+ GPA 2261-99		0.0110	
PROPANE		0.6200	
i-BUTANE		0.1020	
n-BUTANE		0.1030	
NEOPENTANE		0.0000	
i-PENTANE		0.0607	
n-PENTANE		0.0807	
NITROGEN		2.3500	
METHANE		95.0506	
CARBON DIOXIDE		0.7220	
ETHANE		0.9000	
TOTAL		100.0000	
	BTU	1008.9	
	SG	0.588	

Figure 8. Audit Standard Spec sheet

CONCLUSION

There are many different factors that can contribute to properly verifying the operation of a gas chromatograph for custody transfer locations. There are several 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, 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 to achieve the permissible errors that are satisfactory to each user's individual needs.

