AUDITING GAS ANALYSIS LABS

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Introduction to Lab Auditing:

Natural gas can be analyzed at petroleum laboratories using a number of methods including ones written for compositional analysis and identification of various contaminants. The results from these analyses can affect how much a product trades for and can also be used to identify deadly contaminants like H2S. Small inaccuracies in results from a lab can be exacerbated when applied to vast quantities of natural gas that one analysis could represent. A lab audit can be costly but usually this pales in comparison to the amount of money that can be lost due to inaccurate measurement or safety incidents from inaccurate contaminant quantification. The means of measuring the performance of a laboratory is done through a process called auditing.

One of the most common types of natural gas analysis is called a compositional analysis which breaks out the major hydrocarbon constituents of the gas into the individual mol% and wt.% values. Once the percentage of each component is quantified, heat or energy values like wet and dry gas BTU's can be calculated. Compositional analysis methods are most commonly written for use on gas chromatographs (GCs). In recent years, IR (infrared) and Raman technologies have also been employed to give a gas compositional analysis, but they are usually reserved for field use, and I will focus on GC's for this discussion. The data generated on a compositional analysis report (Ex GPA 2261 & 2286) can be used for measurement, custody transfer, air & environmental compliance reporting, product specification, accounting, and safety. It is for these reasons that it is typically worth the resources and effort for a company to either conduct an audit themselves or use an industry specific third-party auditor to perform an audit on the lab.

There are many other components of natural gas that can be analyzed at the lab such as sulfur containing compounds, oxygenates, trace metals, olefins, and many more (ASTM D5504, D7423, D6350, D1946, etc.). Typically, a lab analysis report will specify which method was followed to produce the results and each of these methods will have performance criteria written within that can be measured and graded as passing or failing.

When is an Audit Necessary?

From an internal laboratory operations perspective, an audit should be performed at least as often as the method or lab accreditation specifies. Checking instrument calibration, which is often a piece of an audit, should be performed regularly and at least according to method requirements. Typically, this means running a calibration check daily or weekly. When routine or unforeseen maintenance is required on instrumentation and parts are changed or upgraded, an audit should be performed on the equipment. Personnel changes could also warrant an audit that includes verifying proper training and processes are being followed.

As a customer of a lab, auditing can ensure you are receiving defensible data when discrepancies inevitably arise. For instance, at pipeline custody transfer points, there is usually a meter registering volume upon which royalties are based and paid from. Usually, one or both companies will also select spot or compositional samples to be routinely collected so product quality considerations can be factored into the monetary equation. When two different labs give differing results on the same sample, an audit is necessary to determine true accuracy. Ideally, auditing one or both labs will bring their results within method reproducibility requirements and thus relieve any discrepancy.

Lab Accreditation Audits

Audits can be mandated and governed by accreditation sanctioning bodies like ANAB and NELAP to provide accreditation to a laboratory. For example, ANAB will conduct annual audits and issue certifications like ISO 17025 to a laboratory which can be displayed by the lab ensuring prospective or current customers that they have met the qualifications put forth by ANAB. These sanctioning body audits are usually robust and broad in nature and require a fully executed quality control department that has at a bare minimum the following: a thoroughly vetted quality manual, standard operating procedures (SOP's), quality processes for various aspects of the lab like technician training records, corrective action reports, and revised report formats to be both written and performed. Often, these sanctioning bodies can provide accreditations to many different industries and as such will require more processes to be implemented than what is necessary for the lab to function. A lab in the petroleum industry maintaining an ANAB or NELAP accreditation is going above and beyond what is required by the petroleum industry. A certification from ANAB or NELAP will usually list the specific methods the lab is

accredited for and so these types of audits usually also have a method performance aspect that is evaluated as written into the method procedures.

Method Performance Audits

Customers of laboratories may perform an audit on a laboratory to ensure the data they are receiving is accurate and defensible. In the barest form, an audit may take the outline of simply bringing a certified standard (performance evaluation sample) to the lab and verifying the lab can hit reproducibility and repeatability requirements. When the lab knows they are being audited with a PE, this is called a blind sample because the lab does not know the true composition of the sample. If a PE is given to the lab unknowingly and ran as a typical customer sample, this is known as a double-blind evaluation. A double-blind is perhaps less common because care must be taken in preparing the PE to mimic a typical sample and this is usually costly and difficult to achieve. A double-blind audit evaluation would be the best means of auditing a lab as there would be no special consideration given to the PE by the lab.

Customer audits are typically more specific and will focus on the analysis method being currently run on the customer's samples. Usually, the audit will focus on meeting the method written performance criteria and less on the thoroughness of the quality system of the lab company in general, but it could be as thorough as the customer wishes. Interviewing lab personnel for knowledge and compliance of SOP's can be documented and presented in the audit report. Further, process evaluation like following method procedures can also be evaluated and findings presented in the audit report. Paying a premium to have a third party conduct the audit can ensure all aspects of the lab personnel, processes, and performance are being fully vetted but is not necessary. Simply purchasing a PE sample and following performance criteria as outlined in the method can be a cost conscious and effective means for any company to verify their labs' results.

Method Performance Criteria

ASTM and GPA methods will usually have precision criteria written within that is based on empirical data gathered from a variety of laboratories (statistical analysis of a round robin study) that defines how accurate data can be if following method procedures. Two of the most commonly referred to measures of precision are defined as reproducibility and repeatability. From GPA 2261-20:

- "Repeatability is the expected precision within a laboratory using the same equipment and same analyst. Repeatability is the difference in analyzed values between two sequential runs.
- Reproducibility is the expected precision when the same method is used by different laboratories using different equipment and different analysts. Reproducibility is the difference between two analyzed values."

The table for calculating repeatability and reproducibility values from GPA 2261-20 is shown below in Figure 1. Example calculations for verifying GPA 2261-20 R&R using a PE sample are shown in Figure 2. The table shown in Figure 2 explains that reproducibility is compared to the standard certificate of analysis (COA) values for both runs. Repeatability is performed between the two runs themselves. The last column indicates if the range of the value per component falls within the precision scope of the method as shown in Figure 1.

Audit Findings

Ideally, the laboratory will pass all of the precision criteria as outlined in the method and the corresponding report will show a pass for R&R on all components (example in Figure 2) but this is not always the case. It is not the responsibility of the auditor to help the lab determine what could be the cause of any failures but close review of the processes (SOP's), personnel (training), and equipment (GC maintenance) will usually help to narrow the source of the failure. The auditor report can certainly help the lab to narrow down in their efforts to correct the issue. If the auditor has organized a facility questionnaire list (example shown in Figure 3), this can be used to identify process, personnel, and equipment issues. Usually, the resulting audit failure will result in a corrective action being opened and dealt with by the lab team to document any process improvements. This correction can sometimes be done quickly and in time to rerun the PE and prove the instrument can meet precision criteria during the audit timeframe.

Additional GC Performance Criteria to Consider When Auditing

Linearity of GC Detector

Ideally, a GC detector will give a completely linear response (peak area x mol%) and thus only require a single point calibration but, this is not always true and determining if your GC creates a linear or non-linear response is important

especially if the lab's concentration range of unknown samples is wide. Some labs may implement a multi-point calibration curve or create multiple calibrations for a single instrument if their GC cannot meet linearity requirements of the range of samples they are typically given. GPA 2198-16 Section 6.3 describes a means of running a linearity check on your instrument to determine if a multi-point calibration curve is needed. Essentially, this is done by running multiple concentration blends and plotting the peak areas which will show the detector linearity. Further calculations are required, and GPA 2198-16 has further instructions I won't cover here. Figure 4 shows an example graph of a linear and non-linear detector response.

After a lab has been established, reviewing a large subsect of data from their customers and averaging the concentration of each component to determine a calibration blend that is common to the types of samples the lab receives should mitigate the inaccuracy caused by non-linear detector responses. If an auditor were to bring a PE sample that is very dissimilar to what the GC is calibrated to, this could be the cause of failure to hit precision criteria and should be considered by the auditor.

Fidelity Plot

The PE sample, usually a reference standard, being used to evaluate a GC during an audit can be used multiple times and if not handled properly can change composition. The composition of the PE can be validated using a fidelity plot as referenced in GPA 2198-16 Section 6.4. Using the reference standard mol% values and peak area measurements from the GC, the response factors can be calculated. Using log/log paper or similar computer program, plot the log response factor on the y-axis and log molecular weight of the normal hydrocarbon components on the x-axis. The resulting plot should give a straight line ($R^2 = \sim 1$) through all plotted points with a constant slope. A change in slope would indicate a change in composition. An example of calculating and plotting a fidelity plot are shown in Figure 5. An alternative means of verifying all of the components in the reference standard composition, including the isomers and non-hydrocarbon molecules, can be done using a Bernos Fidelity Plot. In this plot, there will be three lines with three different slope (r^2) values. Each one should be individually linear and changes in the R^2 values over time would indicate a change to the reference standard composition. An example of calculating and plotting a Bernos fidelity plot are shown in Figure 6.

References

Alleman, C. (2023). *Auditing Gas Analysis Labs.* https://asgmt.com/wp-content/uploads/2021/11/Auditing-Gas-Analysis-Labs.pdf

GPA Midstream Standard 2198-16: Selection, preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends

GPA Midstream Standard 2261-20: Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography

Component	Range	Repeatability	Reproducibility
Nitrogen	.02 – 15	$0.039x^{1/4}$	$0.158x^{1/2}$
Methane	50 – 100	$0.0079x^{1/3}$	$91000x^{-3}$
Carbon Dioxide	.02 – 15	$0.0042x^{1/3}$	$0.12x^{1/3}$
Ethane	.02 – 15	$0.0124x^{1/3}$	$0.0315x^{1/3}$
Propane	.02 – 15	$0.0084x^{1/8}$	$0.026x^{1/2}$
Isobutane	.02 – 8	$0.01x^{1/5}$	$0.018x^{1/2}$
n-Butane	.02 – 8	$0.0117x^{2/5}$	$0.033x^{1/2}$
Isopentane	.02 – 4	$0.009x^{1/4}$	$0.025x^{1/4}$
n-Pentane	.02 – 4	$0.01x^{1/5}$	$0.026x^{1/3}$
Hexanes Plus	.02 – 2	$0.0135x^{1/4}$	$0.051x^{1/2}$

Figure 1: Repeatability and Reproducibility equations taken from GPA 2261-20.

Instrument ID / Channel:	HGC 16 A + 16B / Front TCD #16A
Standard Name:	85% C1 STD
Standard / Sample Internal ID Number:	02-20-38-04
Standard QC / Lot / Batch Number:	061423-2
Method Reference (ASTM / GPA):	GPA-2261M
Analysis Date:	1/25/2024
Analyst Initials:	EKK

Component	Standard COA (MOL %)	Std Chk RUN 1 (MOL %)	Std Chk RUN 2 (MOL %)	GPA Repeat (MOL %)		GPA Reprod (MOL %)	Reprod Low Limit	Reprod High Limit	Run 1 Absolute Diff		Run 2 Absolute Diff		Within Range (Precision)
Nitrogen	1.01	1.016	1.012	0.04	P	0.16	0.85	1.17	0.01	P	0	P	YES
Methane	85.043	85.041	85.051	0.03	P	0.15	84.89	85.19	0	P	0.01	P	YES
Carbon Dioxide	1.499	1.497	1.499	0.01	P	0.14	1.36	1.64	0	P	0	P	YES
Ethane	4.999	5.002	5.002	0.02	P	0.05	4.95	5.05	0	P	0	P	YES
Propane	3	3.002	3.004	0.01	P	0.05	2.95	3.05	0	P	0	P	YES
Iso-Butane	1.5	1.499	1.495	0.01	P	0.02	1.48	1.52	0	P	0	P	YES
n-Butane	1.5	1.499	1.499	0.01	P	0.04	1.46	1.54	0	P	0	P	YES
Iso-Pentane	0.55	0.549	0.547	0.01	P	0.02	0.53	0.57	0	P	0	P	YES
n-Pentane	0.55	0.547	0.542	0.01	P	0.02	0.53	0.57	0	P	0.01	P	YES
Hexanes Plus	0.349	0.348	0.349	0.01	P	0.03	0.32	0.38	0	P	0	P	YES

NOTES:

1 Reproducibility is compared to the Standard COA values for both Run 1 and Run 2 for each component.
2 Repeatability is the comparison between Run 2 compared to Run 1 for each component.
3 The last column indicates if the check concentration is listed within the range indicated for the scope of the method precision criteria.
4 Per GPA 2261-20, when the calculated precision criteria is less than 0.01, 0.01 will be used as the lowest precision value.

Figure 2: Example gas audit calculations with notes identifying how reproducibility and repeatability are determined for an audit.

Figure 3: Example questionnaire given to a lab by an auditor.

Company : Location:	Date :

General Facility Conditions and Procedures

Sample Handling & Conditioning	YES	NO	N/A
Are sample cylinders heated?			
If sample cylinders are heated, to what temperature?			
Is the sample cylinder temperature monitored?			
Is the sample heated for at least 2 hours?			
Is the sample cylinder heating time monitored?			
What is the length of time used for heating sample cylinders? (# Hours)			
Are samples taken immediately from heater to analyzer, if manually transferred?			
What method is used to insulate heated sample cylinders during analysis?			
Insulated blanket			
Heated cabinet			
Other (Specify in Comments)			
Is the sample cylinder cleaned before the next use?			

Physical Facility	YES	NO	N/A
Is the analyzer room heated?			
Is the analyzer room air-conditioned?			

Carrier Gas	YES	NO	N/A
What is used for carrier gases?			
What is the purity of the carrier gas?			
Are new cylinders checked before use?			
Is the carrier gas pressure monitored?			
Is the carrier gas flow monitored?			
If yes, Carrier gas flow rate in cc/minute :			
Is a carrier gas drier used?			
If yes, type of drier material used:			
Replacement interval of carrier gas drier material:			

Quality Control program	YES	NO	N/A
Does a Quality Control program exist?			
Can a copy of the Quality Control program be obtained?			
Can a copy of the fidelity plot be obtained?			
Can a copy of the control charts be obtained?			

Company : Location:	Date :

General Facility Conditions and Procedures

Calibration Reference Blend - Gas	YES	NO	N/A
Manufacturer of Calibration Standard			
Is calibration standard age less than certification expiration date?			
If no, list the expiration date :			
Calibration Standard Pressure (New)			
Calibration Standard Pressure (Now)			
Is the gas calibration standard heated continuously?			
If no, list the amount of time heated before use :			
Calibration Standard Temperature			
List the hydrocarbon dew point of the gas standard:			
Has or could the gas calibration standard ever been exposed to a temperature below the hydrocarbon dew point?		x	
What temperature is the gas calibration standard heated to?	100F		
Is an insulation blanket or heating cabinet used for the gas calibration standard?	X		
Can the cylinder pressure of the gas calibration standard be monitored?	X		
Does the lab have calibration standards required for a test program			

Calculation	YES	NO	N/A
Are the component constants used in accordance with the latest GPA 2145?			
If no, what constants are used?			
Can the constants be verified?			
Are the calculations performed in accordance with the latest GPA 2172?			
Other methods used:			

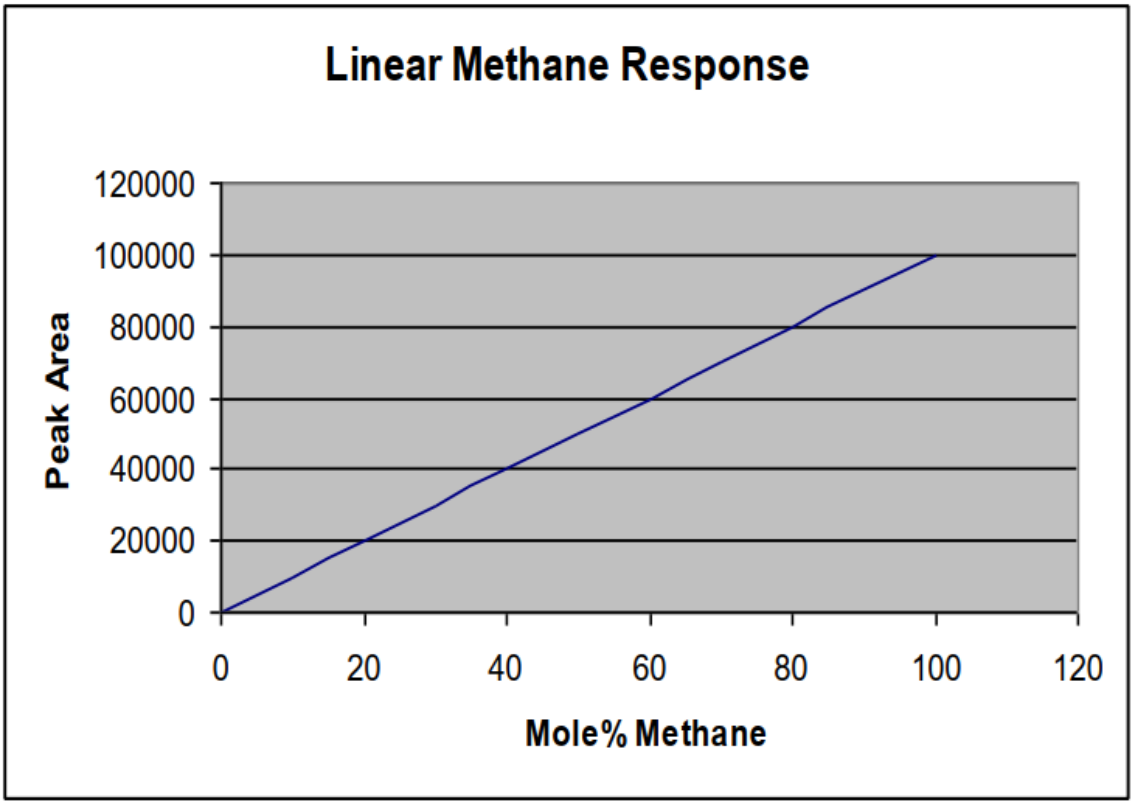
Values for C6+ or other heavy fraction						
	C6+	Mol. Wt.	Sp. Gravity	BTU	Cu.ft./ Vap-Gal	SQR b
	C7+	Mol. Wt.	Sp. Gravity	BTU	Cu.ft./ Vap-Gal	SQR b
	Other (Specify)	Mol. Wt.	Sp. Gravity	BTU	Cu.ft./ Vap-Gal	SQR b

Company : Location:	Date :

General Facility Conditions and Procedures

Sample Cylinder Cleaning Method	YES	NO	N/A
Does a Cylinder Cleaning SOP exist?			
Can a copy of the SOP be obtained?			

Type of Cleaning Performed	YES	NO	N/A
CHEMICAL RINSE			
What chemical is being used			
How is chemical removed?			
Are sample cylinders randomly checked for residue?			
STEAM			
Length of time?			
How is water removed?			
Are sample cylinders randomly checked for residue?			
PURGE			
What gas is being used?			
How are free fluids handled?			
If rinsed, what chemical?			
How is chemical removed?			
Are sample cylinders randomly checked for residue?			
HEAT			
What temperature are cylinders heated to?			
How long are cylinders heated?			
Are sample cylinders randomly checked for residue?			
AFTER CLEANING:			
Are sample cylinders stored with a vacuum?			
Are sample cylinders stored at atmosphere?			
Are sample cylinders stored with positive pressure?			
If yes at what pressure?			
If yes what gas is being used?			



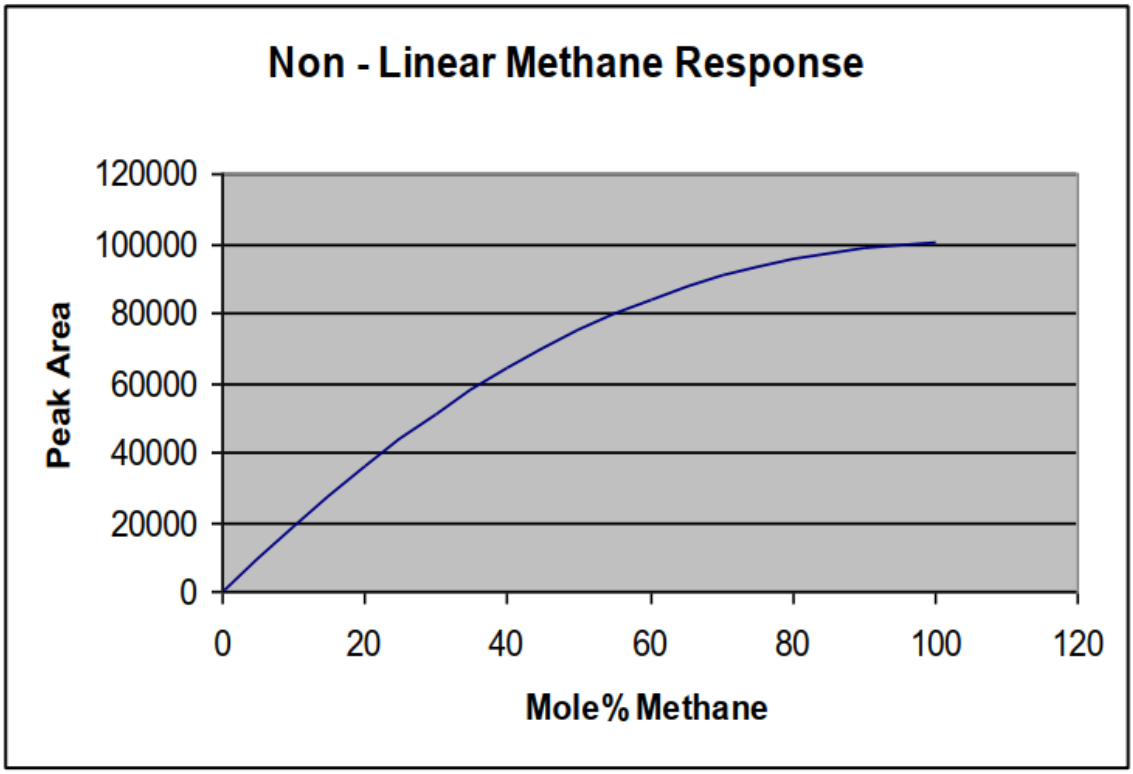


Figure 4: Examples of a linear and non-linear detector response for methane taken from GPA 2261-20.

Component	Response Factor X 10^{-4}	Mol Wt.	Log Response Factor	Log Mol Wt.
Methane	4.195	16.043	-3.37727	1.205286
Ethane	2.83	30.07	-3.54821	1.478133
Propane	2.221	44.097	-3.65345	1.644409
n-Butane	1.852	58.123	-3.73236	1.764348
n-Pentane	1.622	72.15	-3.78995	1.858236

Table 5

Example of Fidelity Plot

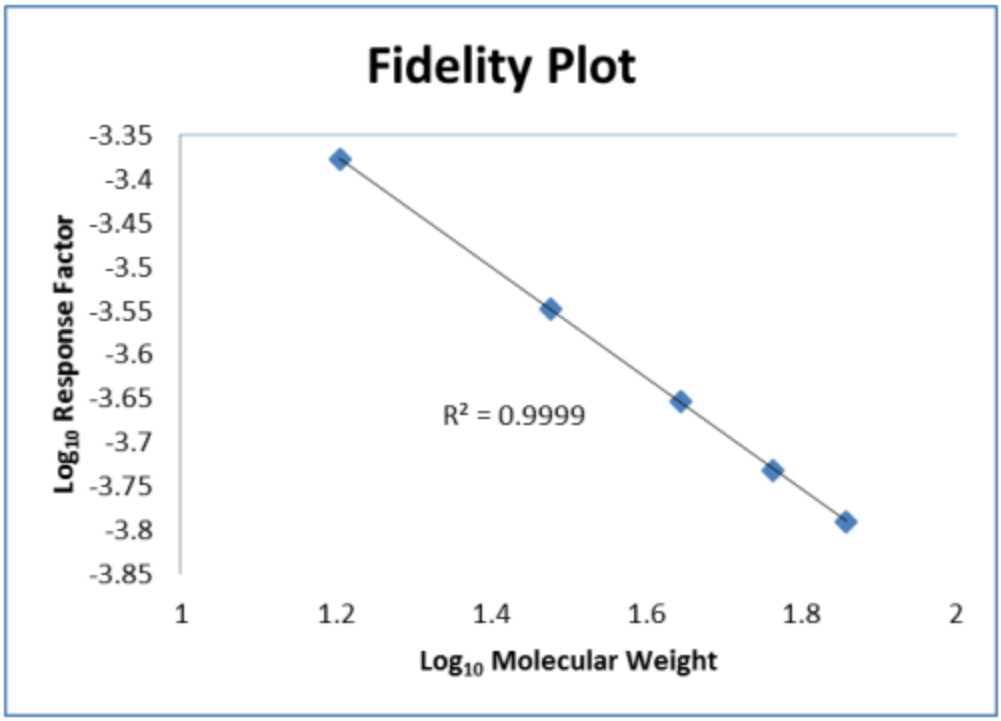


Figure 5: Example of a fidelity plot and corresponding calculations from GPA 2198-16.

Plot Data for the Bernos Fidelity Plot

Component	Response Factor X 10^{-4}	Mol Wt	Log Response Factor	Log Mol Wt.
Methane	4.195	16.043	-3.377268	1.205286
Nitrogen	3.67	28.0134	-3.435334	1.447366
Carbon Dioxide	3.28	44.0095	-3.484126	1.643546
Methane	4.195	16.043	-3.377268	1.205286
Ethane	2.83	30.07	-3.548214	1.478133
Propane	2.221	44.097	-3.653451	1.644409
n-Butane	1.852	58.123	-3.732359	1.764348
n-Pentane	1.622	72.15	-3.789949	1.858236
i-Butane	1.951	58.123	-3.709743	1.764348
i-Pentane	1.712	72.15	-3.766496	1.858236
Hexanes Plus	1.524	86.177	-3.817015	1.935391

Table 6

Example of Bernos Fidelity Plot

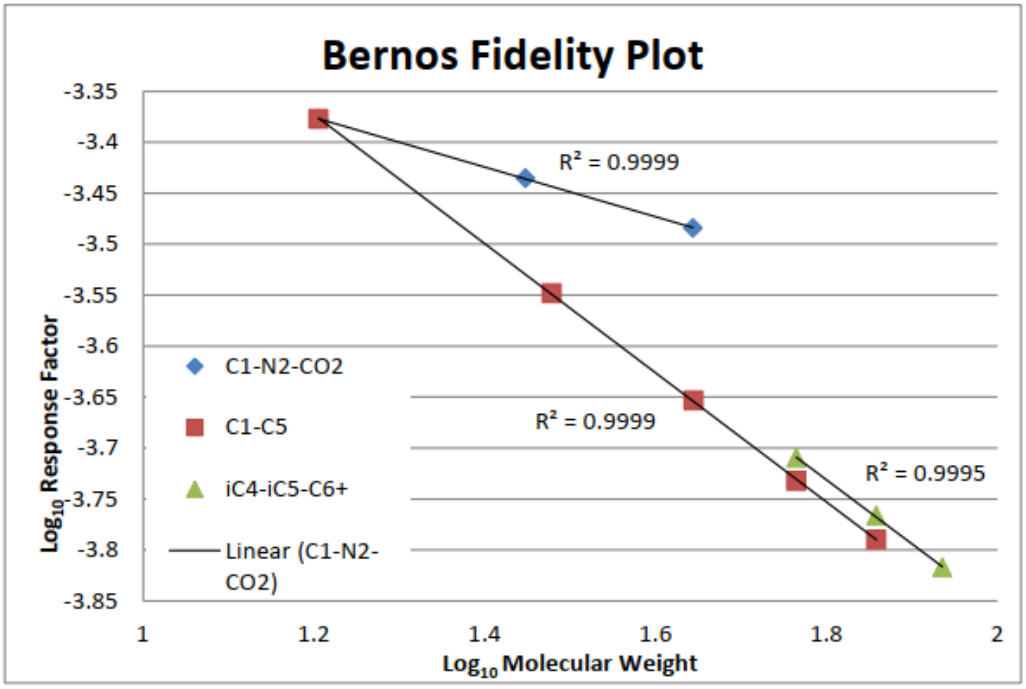


Figure 6: Example of a Bernos fidelity plot and corresponding calculations from GPA 2198-16.