



ASSISTANT ADMINISTRATOR FOR AIR AND RADIATION

WASHINGTON, D.C. 20460

October 20, 2026

Thomas Redlinger
JP3 Measurement LLC
5775 North Sam Houston Parkway West
Houston, TX 77086

Dear Mr. Redlinger,

This letter is in response to JP3 Measurement LLC's ("JP3") letter dated February 11, 2026. In that letter, JP3 requests U.S. Environmental Protection Agency ("EPA") approval of an alternative test method for demonstrating compliance with 40 CFR Part 63, Subpart CC, National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries ("Subpart CC").

JP3 seeks to use the VeraCal optical system to measure individual component composition and determine net heating value ("NHV"), as required by 40 CFR 63.670(j)(1) and 63.670(j)(3), consistent with the provisions of 63.7(f). The EPA's Office of Air and Radiation is the delegated authority for approval determinations on any major alternatives to test methods and other compliance determination procedures required under 40 CFR parts 59, 60, 61, 63, and 65.

Based on the information provided in JP3's letter, the EPA approves the request to use the VeraCal optical system as an alternative to the allowance of Gas Chromatography for compositional and NHV determination as specified in Table 13 of 40 CFR 63.670, with the caveat that JP3 determine hydrogen concentration by analyzer. A copy of this letter and the enclosures must be included in any certification test report or test plan for which this alternative test method is used for compliance with Subpart CC requirements.

If there are additional questions regarding this approval, please contact the EPA's Office of Air and Radiation Measurement Technology Branch at emc@epa.gov.

Sincerely,

Abigale D. Tardif
Acting Assistant Administrator

Enclosure

1. EPA MACT CC Alternative Test Method Request

JP3 Measurement, LLC

EPA MACT CC Alternative Test Method Request

February 11, 2026

Produced by:

Roger Nounou
Emissions Data Services Leader
1.713.927.5642
rnounou@flotekind.com

5775 North Sam Houston Parkway
Suite # 400
Houston, Texas 77086

JP3 VeraCal

MACT CC Alternative Test Method Request

February 11, 2026

JP3 Measurement
5775 North Sam Houston Parkway West
Houston, TX 77086

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Measurement Technology Group (MTG)
109 T.W. Alexander Drive
Research Triangle Park, NC 27711

Attn: Subpart CC Alternative Monitoring Method Review

Subject:

Request for Approval of an Alternative Test Method for Flare Vent Gas Composition Monitoring
Using the JP3 VeraCal® System Pursuant to 40 CFR §63.7(f) and §63.670(j)

Dear Sir or Madam:

I am writing on behalf of JP3 Measurement LLC, a provider of analytical measurement technologies that support the oil and gas industry in meeting federal air quality requirements, including those established under 40 CFR Part 63, Subpart CC (MACT CC). We recognize the critical role of MACT CC in reducing emissions and promoting efficient combustion practices, and we are committed to supporting regulated facilities in achieving and demonstrating compliance with these standards.

We appreciate EPA's prior approval of our VeraCal calorimeter as Alternative Test Method 157 (ALT-157) for determining net heating value (NHV), expressed in Btu/scf, for gas routed to enclosed combustion devices or flares subject to 40 CFR Part 60, Subpart OOOOb. Building on this approval, we respectfully seek EPA approval to extend the use of the VeraCal instrument as an alternative test method for demonstrating compliance with the requirements of 40 CFR Part 63, Subpart CC §§63.670(j)(1) and 63.670(j)(3), consistent with the provisions of §63.7(f).

The VeraCal system integrates advanced optical calorimetry techniques to deliver precise, real-time measurements of the individual component concentrations and net heating value (NHV) of process gas streams. Unlike conventional gas chromatographs (GCs), VeraCal requires no carrier

gas or chromatographic separation. Instead, it employs proprietary multivariate calibration algorithms to quantify hydrocarbon components and NHV_{VG} . The VeraCal system continuously measures, calculates, and records the individual component concentrations present in the flare vent gas, which is consistent with the regulatory requirement of §63.670(j)(1). Additionally, the system uses its real-time measurement of compositional data to determine NHV_{VG} , which is consistent with the regulatory requirement of §63.670(j)(3).

MACT CC, specifically the §63.670(j) requirement is cited by Part 98, Subpart W that requires compositional and NHV monitoring of combustion waste streams. The industry has already expressed concerns about the limited lab equipment and service personnel available to fully comply with the regulations that cite to the root regulatory requirement of §63.670(j). Process calorimeters and composition analyzers, including optical-based analyzers, such as ours, measure continuously without the need for onsite personnel, making this solution not only the most comprehensive with real-time high-frequency data, but also the safest solution. By keeping technicians away from hazardous zones and off roads, our solution contributes to reducing driving-based emissions and further enhancing safety measures in the industry. Given the backlog of field GC availability and the limited lab capacity for sample analysis, JP3 VeraCal analyzer provides a readily available solution that does not require lab sample analysis, thus allowing flare owners to comply with the regulations sooner and more efficiently.

Looking at the specific requirements of the regulation, JP3's VeraCal system meets the continuous monitoring, accuracy, calibration, data recording, reporting, recordkeeping, and QA/QC requirements of 40 CFR Part 63 Subpart CC. We have provided details in the attached document.

MACT CC §63.644(a) requires the following for continuous individual component composition monitoring (§63.670(j)(1)) or NHV monitoring (§63.670(j)(3)):

- *“All monitoring equipment shall be installed, calibrated, maintained, and operated according to manufacturer's specifications or other written procedures that provide adequate assurance that the equipment will monitor accurately and, except for CPMS installed for pilot flame monitoring, must meet the applicable minimum accuracy, calibration and quality control requirements specified in **table 13 of this subpart**.”*

MACT CC Table 13 requires the following for continuous individual component composition monitoring (§63.670(j)(1)):

- *“Minimum accuracy requirements: As specified in Performance Specification 9 of 40 CFR part 60, appendix B”*
- *“Calibration requirements: Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that a single daily mid-level calibration check can be used (rather than triplicate analysis), the multi-point calibration can be conducted quarterly (rather than monthly), and the sampling line temperature must be maintained at a minimum temperature of 60 °C (rather than 120 °C).”*

MACT CC Table 13 requires the following for continuous NHV monitoring using a calorimeter (§63.670(j)(3)):

JP3 Measurement EPA MACT CC Alternative Test Method Request

- *“Minimum accuracy requirements: ± 2 percent of span”*
- *“Calibration requirements: ...Calibration requirements should follow manufacturer's recommendations at a minimum.”*

EPA previous approval of JP3's VeraCal system under NSPS OOOOb pointed to its ability to meet the Minimum accuracy requirements: ± 2 percent of span along with meeting and exceed the calibration requirements of 40 CFR Part 60 Appendix B, Performance Specification 9. A full description of the methods and standards used are included in the attached.

The industry has limited practical instrumentation to address the measurement of individual component concentration and net heat value, especially in remote and uncontrolled environmental conditions. Designed to meet the practical demands of the industry, our calorimeter features robust design, low maintenance, and seamless integration into existing systems. Unlike other analyzers, JP3's system can be installed in field operations and does not require a controlled environment or shelter. Its adaptability and dependability render it a valuable asset for operators striving to comply with EPA standards. JP3 has been providing calorimetry measurements to the industry for several years, typically in the harsh midstream and upstream environments. While our technology is not adapted to detect trace levels of contaminant products that are required for some of the downstream flare operations, we provide a comprehensive solution for individual component concentrations and net heating value assessments across the upstream and midstream industries. To validate the accuracy of JP3's results, we have worked with third party auditors to verify our data and methodology.

Enclosed is comprehensive data affirming the JP3 system's adherence to EPA standards and requirements found in the MACT CC regulation. The documentation includes our technological overview, applied methods and standards, and pertinent validation data. Furthermore, we have included an adaptation of Method 320, tailored to align with our advanced technology.

Our commitment to assisting our clients with regulatory compliance is unwavering. Many are either already employing our systems or looking to utilize these systems for flare-monitoring purposes. We seek confirmation from the EPA that data generated by our systems will be recognized and accepted by the EPA for purposes of MACT CC compliance and any other rules that cite to the MACT CC requirements. To this end, we have proactively presented validation data aligned with Method 301 in our recent discussions and in this correspondence. While we do not deem it a necessity, we trust that the enclosed materials fulfill the requirements of the Method 301 waiver process.

Should the EPA require additional time to deliberate on the regulations, methodologies, and endorsed practices, we respectfully request provisional approval for the utilization of data from our instruments during this period of evaluation.

We welcome the opportunity to continue discussing how JP3 Measurement can support MACT CC compliance. If you have any questions in the meantime, please contact Roger Nounou, 713.927.5642 rnounou@flotekind.com

**JP3 Measurement
EPA MACT CC Alternative Test Method Request**

Thank you for considering our commitment to environmental compliance and innovation. We look forward to the opportunity to support the industry's goals to surpass regulatory standard.

Sincerely,

A handwritten signature in blue ink, appearing to read 'TMR', with a stylized flourish at the end.

Thomas M. Redlinger, P.E.
Vice President Data Analytics

Table of Contents

JP3 VeraCal MACT CC ATM Request Letter	2
Method of Emission Limitation for Determination of Individual Component Concentration and Net Heating Value Compliance with 40 CFR 63 Subpart CC	7
Background	7
Operational Flow Charts	10
Optical/ Spectroscopic Calorimetry	10
Model Development.....	15
Summary of Practice	17
Method Discussion.....	18
Method of Analysis	20
Quality Assurance and Control	21
Model Testing	22
Analyzer Reproducibility and Repeatability	22
Calibration of local results against global and local models.....	25
Model Performance Quality Metrics	28
Accuracy	29
Limitations	32
Compliance with CFR Regulations for JP3's Calorimeters	32
Record Keeping and Documentation	33
Summary	35
Appendix A: Example Installations	37
Appendix B: JP3 NIR Spectroscopy Work Process/ Method of Use adapted from Method 320 FTIR Alternative to Gas Chromatograph.....	40
Appendix C: Process Flow Charts	41
Appendix D: Validation Data Sets	49

Method of Emission Limitation for Determination of Individual Component Concentration and Net Heating Value Compliance with 40 CFR 63 Subpart CC

February 11, 2026

JP3 Measurement, LLC ("JP3") is providing additional background information on the measurement technology used to conduct monitoring of control devices used to demonstrate compliance with MACT CC requirements.

As detailed below, the JP3 equipment complies with the method requirements of the calorimeter and gas chromatograph to continuously determine the individual component concentration and NHV of the flare vent gas. This document is intended to clarify and remove any questions about the use of the JP3 VeraCal system applicability as an alternative monitoring method within the regulation.

Background

The determination of the individual component concentration and net heating value (NHV) of the inlet gas to a flare has been traditionally managed by calorimeters and gas chromatography as part of regulatory compliance. These systems are typically supported by the analytical staff available at the facility and are part of the larger structure of analytical instrumentation. Gas chromatography plays a large role in determining the constituent level components within the gas stream, and it is one of the few technologies adapted for this analysis. Traditional calorimeters are available in a number of configurations to find the heating values where the industry or regulation does not require speciation. The VeraCal system works by providing both heating values and individual component concentrations.

JP3 Calorimeter Summary

For nearly a decade, JP3 systems have been deployed to analyze streams of natural gas, natural gas liquids, and condensates across a wide range of operating environments. During this time, JP3 developed the VeraCAL optical calorimeter system, which integrates JP3's optical spectrometers (Verax or CAL-X analyzers) with a dedicated sample processing system and reference cell. The VeraCAL system uses optical components, flow cells, and a probe-based sample conditioning assembly, potentially including a pump and pressure regulator, to directly measure the near-infrared (NIR) absorption spectrum of low-pressure gas streams routed to control devices.

The system incorporates a heater and heated sample lines to maintain consistent sample temperature and prevent condensation. All components are housed in a Class I, Division 2–rated enclosure, making the system suitable for field deployment, resistant to dust and debris, and operable across ambient temperatures ranging from -4°F to 122°F . Maintenance requirements are minimal, with historical annual downtime of less than 1 percent. In addition, the system continuously monitors its operational status and reports system health indicators through cloud-based monitoring software.

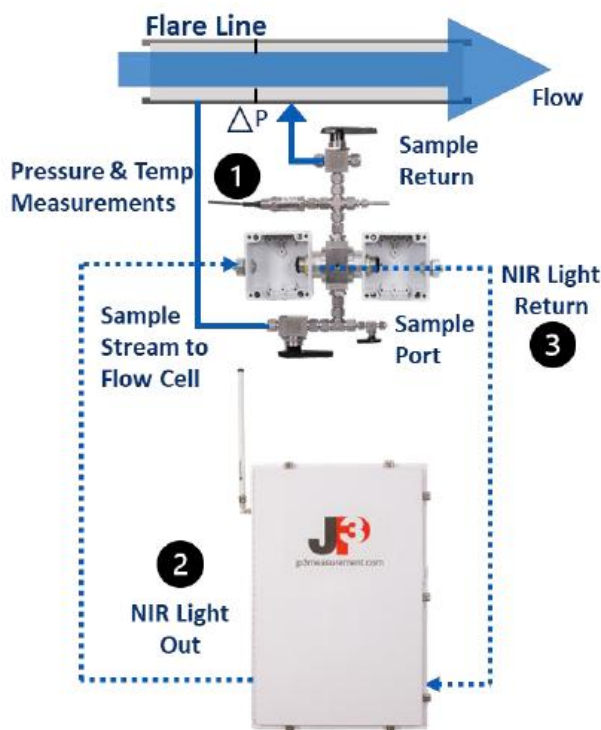


Figure 1: JP3 Analyzer Schematic

The NIR spectra is used to conduct the determination of individual component concentrations and heating value either by applying a numerical model based on the NIR spectra of known hydrocarbon blends is used to speciate and quantify hydrocarbons and carbon dioxide in the stream. The heating value is then calculated based on the hydrocarbon concentrations using ASTM D3588-98 (2017) or GPA 2172-19.

The system's ability to analyze gas streams at pipeline conditions, without the need to withdraw or vent samples, combined with a rapid response time of typically 15 to 30 seconds between analyses offers significant advantages over gas chromatography for natural gas applications. In

addition, the instrument is well suited for operation under the complex and demanding conditions commonly encountered at upstream and midstream facilities.

The Verax analyzer has been used successfully in processing plants and other non-pipeline applications, and JP3 has found that its measurement repeatability and reproducibility can be better than that of gas chromatographs (GCs).

The Verax spectrometer is unique in its use of an NIR spectrum library to directly quantify individual hydrocarbons through C6+, liquid “cuts” through C15+, and carbon dioxide. A proprietary algorithm compares each measured absorption spectrum to known natural gas compositions to quantify individual components of the stream being analyzed. Nitrogen, which cannot be quantified by this approach, is reported as the balance component of each analysis. Heating values and relative densities are also determined by comparisons to the spectrum library. Natural gas samples collected from field sites were used to build the algorithm using ASTM D8321 and ASTM D6122, and after spectroscopic analysis, each sample was analyzed by an independent laboratory via gas chromatograph (GC) method ASTM D1945 for its composition and physical properties. The lab results, including compositions through C9+, heating values, and relative densities, formed the database from which the correlations in the algorithm were built. The JP3 sample library includes coverage of the entire multivariate liquid hydrocarbon spectrum, over 50,000 validated samples, more than 350,000 property validation results.

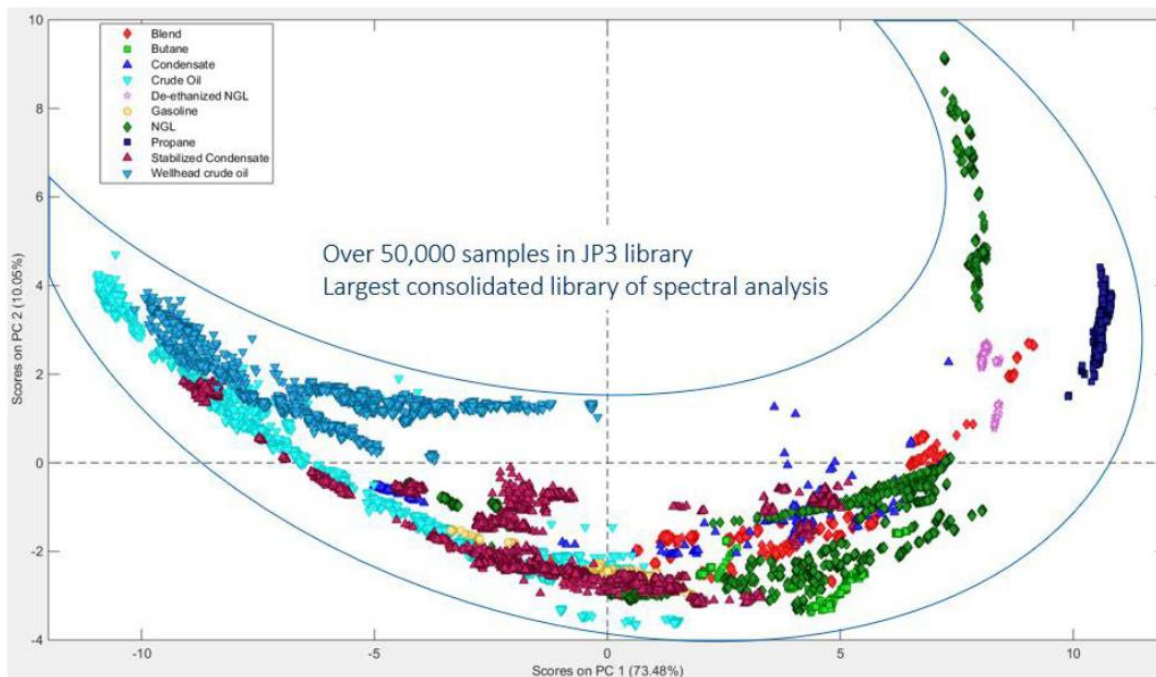


Figure 2: Hydrocarbon Data Library

Operational Flow Charts

Appendix C contains flow charts which show the VeraCAL operation, calibration, validation and installation procedures. Figure C1 describes the overall process of MACT CC monitoring. Prior to installation, the site is reviewed, the model has been developed, and the analyzer has been built and calibrated in the factory. During installation, the installation validation and model validation samples are taken (see Figures C3& C4). Figure C2 describes normal operation. A daily validation, Figure C7, occurs daily, and the data is reviewed and a report prepared. Figures C5 & C6 show factory and quarterly calibration procedures which are discussed later in the Method and Performance Specification. The installation and daily validation procedures are likewise discussed in the Method and Performance Specifications, both of which can be found in the Appendix of this document.

Optical/ Spectroscopic Calorimetry

Optical spectroscopy is a scientific technique used for analyzing the composition of different substances based on their interaction with light. It involves measuring the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules to identify chemical compositions, quantify different compounds, and determine physical properties of substances. This method leverages the principle that each element or compound has a unique spectral signature when exposed to light, allowing for precise identification and quantification.

In the context of environmental monitoring and regulation compliance, optical spectroscopy serves as a powerful tool for detecting and measuring the concentration of various pollutants and greenhouse gases in the atmosphere. Technology's sensitivity and specificity make it an ideal choice for applications requiring continuous monitoring and reporting in line with EPA standards, including regulations MACT CC, which focus on controlling emissions from petroleum refineries.

Figure 3 presents the near-infrared (NIR) spectral data for common hydrocarbon gases, labeled C1 through C6, typically found in flaring processes. It displays how the intensity of light absorption varies across different wavelengths, ranging approximately from 1550 to 1800 nanometers. The peaks and troughs in the graph represent the unique spectral signatures of each hydrocarbon component, with the y-axis indicating the absorbance and the x-axis representing the wavelength. The pronounced peak, especially visible for one of the components, signifies a strong absorption feature, likely corresponding to a specific vibrational transition of the molecule. Each line, representing a different hydrocarbon (from methane (C1) to hexane (C6)), shows how the NIR spectrum can be used to distinguish between these compounds based on their spectral features.

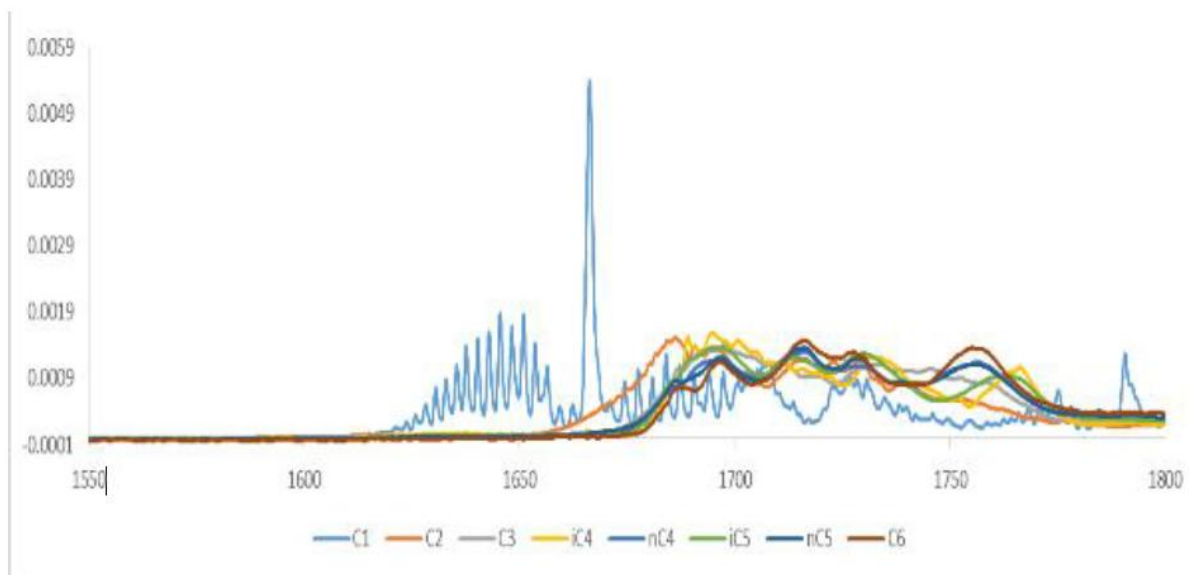


Figure 3: Hydrocarbon species spectra

GPA Standard 2119 “Test Method for Determination of Trace Contaminants in Hydrocarbon Gases by Optical Spectroscopy” and ASTM D6122 “Standard Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer Based Analyzer Systems” provide guidelines for using optical spectroscopy to quantify hydrocarbon gases. These standards outline the procedures for sample preparation, measurement, and data analysis, ensuring that the results are accurate, reliable, and consistent with industry standards. By adhering to GPA 2119 and ASTM D6122, we can demonstrate that our technology not only meets the EPA's requirements for environmental monitoring and emissions reporting but also aligns with recognized industry practices for analytical testing.

Spectral model development is essential for establishing a mathematical predictive relationship between physical samples and their spectral data, which is later used for process predictions.

The initial step involves verifying the correct operation of the sampling system and the instrument. Subsequently, a collection of physical samples alongside their spectral data takes place to build a mathematical model that measures future process conditions. These samples should cover a range of compositions, temperatures, and pressures that the normal process might encounter. The number of samples needed for an accurate model depends on the variability in composition, operation, and environmental conditions. Insufficient calibration sample coverage can lead to uncertainty in process analysis. If the process chemistry is well-understood and environmental conditions are consistent, lab-generated calibration samples may suffice. Otherwise, direct sampling of the process over time is required to obtain a representative set of samples.

JP3 Measurement EPA MACT CC Alternative Test Method Request

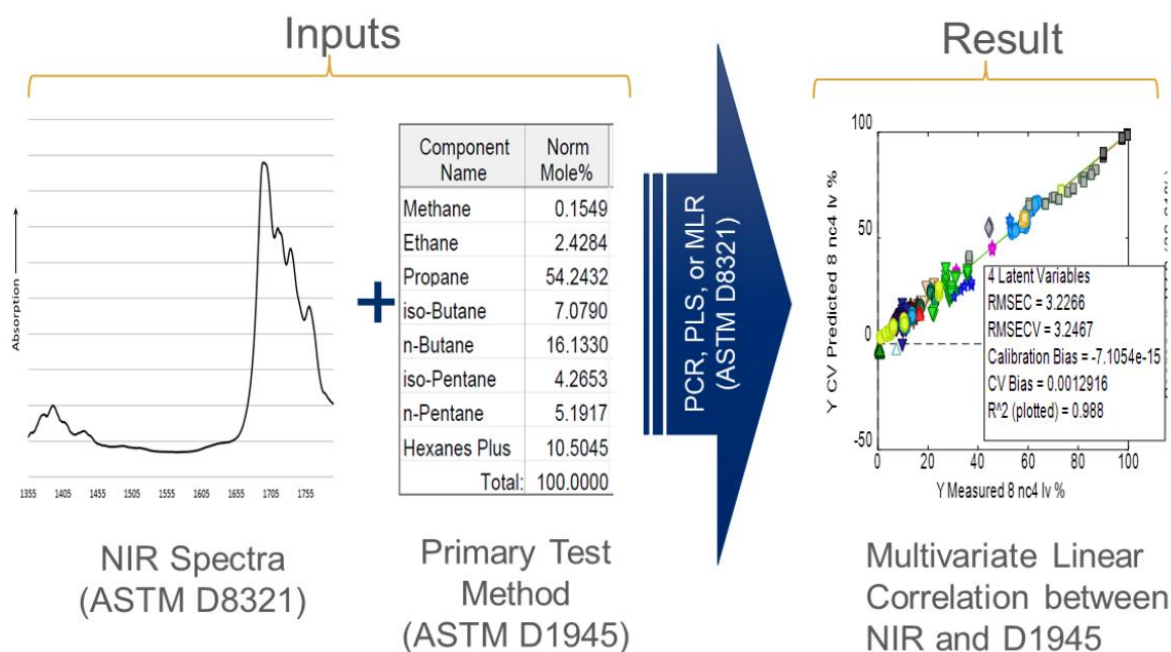


Figure 4: JP3 Process

The success of a spectral model relies heavily on the accuracy of the reference data. Assessing the repeatability of the analytical reference techniques is necessary to understand the magnitude and sources of errors, whether they arise from the reference data or the spectroscopy. This evaluation must consider variations in the physical sampling process, not just in the reference data. Reference data accuracy guidelines can be derived from GPA Midstream standards for specific analytical techniques. Human factors, such as operator variation, especially in physical sample collection, are significant potential error sources. To ensure proper sample collection, adherence to Method 18, Method 320, GPA 2174, and GPA 2166 is recommended but not mandatory for quality model development. The analytical reference data is considered the benchmark for spectral modeling, requiring high-quality and stable long-term performance. Any significant change in the reference technique can compromise the spectral model's integrity.

In the flowchart from ASTM D6122-15, Figure 5, a process analyzer validation starts with the analyzer in normal operation. It requires acceptable spectral data sets (excluding outliers and non-inliers) for initial evaluation. If this criterion is not met, the process circles back to normal operation to gather more data. Once enough data is collected, the process continues to assess whether there is sufficient variation to conduct a D6708 assessment. If the variation is adequate, the analyzer undergoes level-specific validation. The validation outcome depends on two conditions: if the results are statistically in control and if the bias is within user specifications. If both conditions are met, the analyzer passes level-specific validation. Conversely, if results are

not in control or the bias exceeds the user specification, the analyzer fails and requires problem correction before restarting the process.

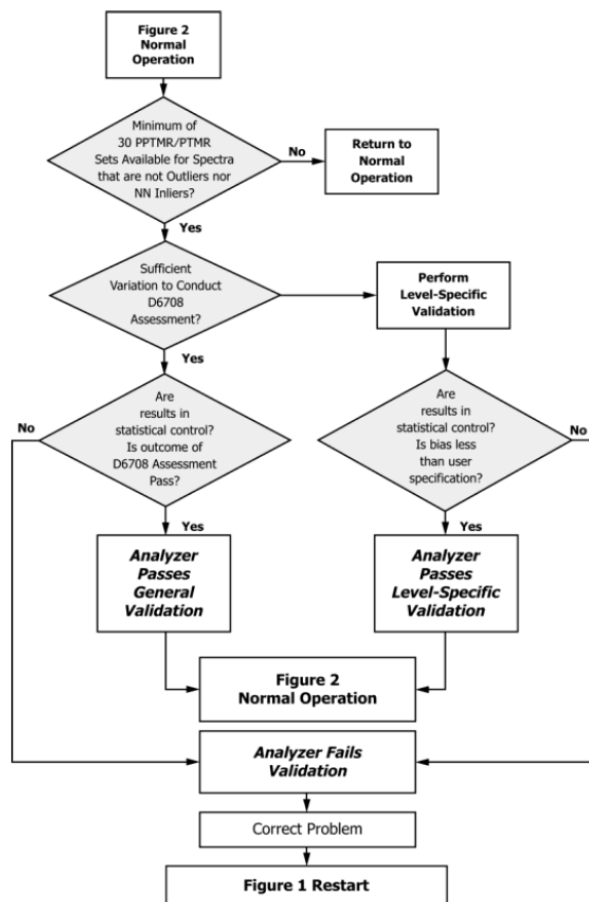


Figure 5: ASTM D6122 Process flow chart

The JP3 process, Figure 13, adheres to the ASTM D6122-15 and GPA 2119 standards by incorporating a structured workflow for developing and validating analytical models:

1. **Spectra Collection:** The process begins with the collection of spectral data for calibration samples. This includes gathering reference data and spectra from both library samples and on-site local samples, ensuring a broad representation of conditions.
2. **Data Preprocessing:** The collected data is then preprocessed, which may involve normalization, outlier detection, and correction of any spectral interferences. This step is crucial to prepare the data for accurate model building.
3. **Principal Component Analysis Development:** Following preprocessing, principal component analysis (PCA) or similar multivariate techniques are used for analysis development. This helps in reducing the dimensionality of the data and identifying the significant variables for model building.

4. **Model Test & QA:** The developed model is then rigorously tested and subjected to quality assurance protocols. This ensures that the model is robust, reliable, and valid for predicting the properties of interest in new samples.
5. **Model Deployment:** Once the model passes the testing and QA phase, the production model is uploaded via cellular modem to the JP3 calorimeter units, signifying the deployment phase where the model is used in actual process monitoring and analysis.

The JP3 process ensures that calibration samples cover the necessary range of compositions and conditions as stipulated in the general validation practice in ASTM D6122. The model development is data-driven, grounded on empirical analysis, which aligns with the guidelines for building spectral models and process analyzer validation. Furthermore, by using a cellular modem for model deployment, the JP3 process incorporates a secure and efficient method for updating and maintaining the analytical system in the field. This systematic approach underscores compliance with the standards for process analyzer validation and model development.

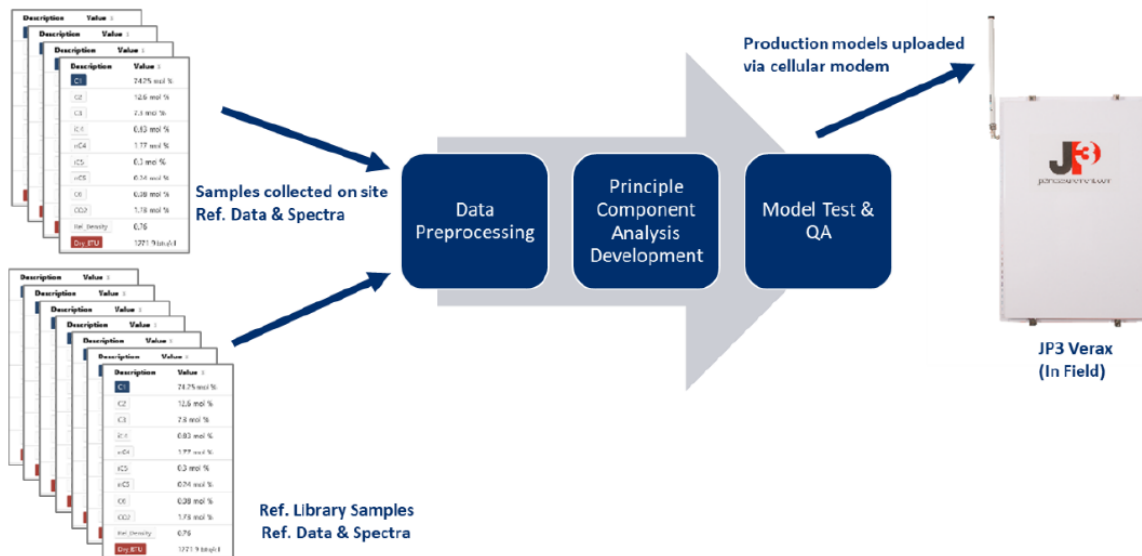


Figure 6: JP3 Modeling process flow chart

GPA 2119 4.3.1.2 states “The analytical reference data is taken to be the ‘truth’ in spectral modeling, so its long-term quality/stability are of utmost concern and importance. The reference technique can never ‘go away’ or change in any significant regard.”

The JP3 analyzer systems produce measurements that are correlated with primary ASTM or GPA test methods using chemometric models, such as classical least squares (CLS) or partial least squares (PLS). Any read point can measure any combination of the properties including Net Heating Value and molar composition. Each analytical standard contains individual precision

specifications. The combination of application and analytical method used determines the final performance of the resulting models, which commonly equals published ASTM/GPA performance/precision data where available.

The JP3 analyzer systems do not measure diatomic gases, such as N₂ and H₂. Such gases do not have NIR absorption features and do not interfere with hydrocarbon measurements. The concentration of all non-hydrocarbon components can be calculated by difference (100% - hydrocarbon concentrations) as supported by GPA 2119. N₂ does not have any contribution to the NHV calculation, but H₂ does. The calculated or modeled NHV result will be lower than the actual NHV if H₂ is present in the flare gas. Therefore, net heating value reported by the JP3 system will be conservative.

Model Development

The JP3 Verax analyzer measures the composition and physical properties of a gas or liquid hydrocarbon product based on near infrared (NIR) spectroscopy. The measurement principle as well as development and validation of multivariate analyses is referenced to ASTM D8321-22 standard.

The NIR spectrometer used in the JP3 Verax analyzer covers 1355-1795 nm wavelength range, which measures the absorption of the NIR light by hydrocarbon molecules in first vibrational overtones and combination bands. Inside the laser module, a microelectromechanical system (MEMS) filter is tuned to scan the laser output wavelength continuously with 0.1nm to 0.5nm step resolution. Only a narrow band of wavelengths (less than 1nm bandwidth) is transmitted to a sample flow cell and then to a single detector at any given time. The total scanning time for the entire wavelength range is approximately 100 milliseconds (ms). Typically, the JP3 Verax analyzer averages 8 scans in less than 1 second for a single beam spectrum collection before the mathematical and model analyses. The NIR spectrometer has an internal module to measure the wavelength reference and amplitude reference signals. The wavelength and power of the laser output are monitored and corrected for every spectrometer scan to ensure the spectral repeatability and reproducibility. This is critical for successful multivariate spectroscopic analyses.

Since the light incident on the sample cannot be directly measured, an NIR spectrum involves the collection of two separate single-beam spectra, a background b and a sample spectrum s . The background is measured when there is no sample present (e.g., nitrogen gas filled in the flow cell) in the NIR beam. The single beam spectrum of the sample is divided by the single-beam background to produce a transmission spectrum t . The transmission spectrum is converted to an absorbance spectrum a , using a negative logarithm base 10. An example is illustrated in Figure 7 and the raw data are included in the attached “Absorbance Spectrum Calculation.xlsx” file.

$$t = s/b \quad (1)$$

$$a = -\log_{10} t \quad (2)$$

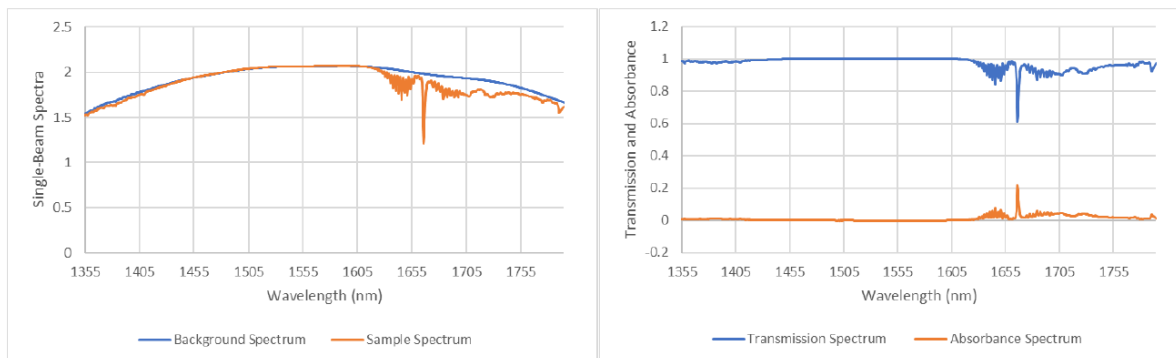


Figure 7: Example of transmission and absorbance spectra calculation

The NIR spectroscopy is based on the Beer-Lambert Law. For a single component sample, the absorbance at a wavelength is proportional to the concentration, the pathlength, and the absorptivity of the component. For multiple mixture samples, Beer-Lambert Law can be expressed in a multivariate form.

$$X = BCA \quad (3)$$

X is an n by f matrix of the sample spectra (mixture spectra), A is a c by f matrix of the spectra of the s components in the samples (pure component spectra), C is an n by c matrix of the concentrations of the c components in the n samples, and B is an n by n diagonal matrix of the pathlengths. The following figure shows pure gas component spectra of C1 (Methane) to nC4 (normal Butane) as an example. The raw spectra are included in the attached “Pure Gas Component Spectra.xlsx” file.

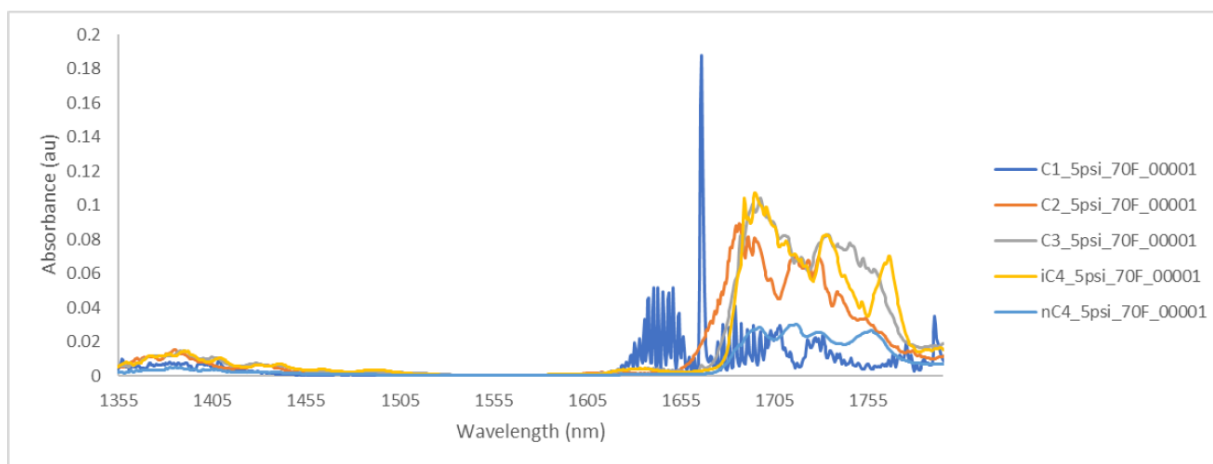


Figure 8: Pure gas component spectra of C1 to nC4

To maintain the above linear relationship between absorbance and concentration, an appropriate flow cell pathlength is chosen to avoid any absorption saturation while achieving a good signal to noise ratio (SNR). Based on the application information, the ideal absorbance spectrum should be as strong as possible but less than 1 au (absorbance unit). For liquid samples, the pathlength is typically 2mm. For gas samples, the pathlength is dependent on the gas pressure. JP3 analyzers use 50mm flow cell for the flare gas measurement that is close to atmospheric pressure.

Summary of Practice

Multivariate mathematics is applied to correlate the spectra measured for a set of calibrations samples to component concentrations or property values for the set of samples. The resultant multivariate model is applied to the analysis of spectra of unknown samples to predict the component concentration or property values for the unknown sample. The component concentrations and property values which are used in establishing and validating the multivariate model are measured by a Primary Test Method (PTM), typically an ASTM standard test method (e.g., ASTM D1945). The values are herein referred to as Primary Test Method Results (PTMR). The predicted results produced by application of the model for the analysis of a spectrum are referred to as Predicted Primary Test Method Results (PPTMR). The calibration and validation samples can be prepared in the lab or pulled from the process directly for the online analyzer.

Classical least squares (CLS), partial least squares (PLS) and locally weighted regression (LWR) are examples of multivariate mathematical techniques that are commonly used for the development of the multivariate model. Statistical tests are applied to detect outliers during the development of the multivariate model. Outliers include high leverage samples (samples whose spectra contribute a statistically significant fraction of one or more of the spectral variables used in the model), samples with high spectral residuals (suggestive of unmodeled components) and samples whose PTMR values are inconsistent with the model. For the purpose of simplicity, a CLS example is used in this document.

Validation of the multivariate model is performed by using the model to analyze a set of model validation samples and statistically comparing the PPTMR values for the model validation samples to PTMR values measured for these samples, to test for bias in the model and for the degree of agreement of the model with the PTM.

Statistical tests are applied to detect when PPTMR produced by application of the model represent extrapolation of the calibration. A spectrum is labeled an outlier if its leverage exceeds that of the calibration samples, or if the spectrum produces high spectral residuals suggesting the presence of components which were not in the calibration samples.

Method Discussion

JP3 analyzers determine the individual component concentration and NHV by directly calculating or determining from molar composition by ASTM 3588. This method closely follows the FTIR Method 320 for the collection of waste gases. Method 320 does have some specific language relevant only to mid-range FTIR calibration. We have provided an updated work practice or Method to help clarify the differences (Appendix B).

The heating value calculations are based in sampling results from primary test methods, like ASTM D1945. The testing results from ASTM D1945 or equivalent are used to build a linear model (CLS) to determine the heating values or composition. This process is similar to the conversion of residual oxygen results or thermocouple calibration response ranges developed for other calorimeters that convert instrument response to heating value readings. We further validate our models with samples analyzed by gas chromatography via ASTM D1945 and Method 18. JP3 NIR Analyzer follows ASTM D8321-22 standard in developing and validating multivariate analyses to determine the physical, chemical, and performance properties of natural gas, natural gas liquids, refined fuels, condensates, and crude oils. The properties against which a multivariate model is calibrated and validated are measured by a Primary Test Method (PTMs), which is ASTM D1945 and/or GPA 2261 method for Natural Gas (flare) applications. The calibration and validation samples are pulled at site after analyzer installation or prepared in the lab with gas mixtures. The samples are typically sent to a lab for PTM analysis. A full description of the methods and standards used are included in the attached.

Looking at the specific requirements of the regulation, JP3's VeraCal system meets the continuous monitoring, accuracy, calibration, data recording, reporting, recordkeeping, and QA/QC requirements of 40 CFR Part 63 Subpart CC. We have provided details in the attached document.

MACT CC §63.644(a) requires the system to meet the applicable minimum accuracy, calibration and quality control requirements specified in table 13 of this subpart.

MACT CC Table 13 requires the following for continuous individual component composition monitoring (§63.670(j)(1)):

- “Minimum accuracy requirements: As specified in Performance Specification 9 of 40 CFR part 60, appendix B”
- “Calibration requirements: Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that a single daily mid-level calibration check can be used (rather than triplicate analysis), the multi-point calibration can be conducted quarterly (rather than monthly), and the sampling line temperature must be maintained at a minimum temperature of 60 °C (rather than 120 °C).”

JP3 Measurement EPA MACT CC Alternative Test Method Request

MACT CC Table 13 requires the following for continuous NHV monitoring using a calorimeter (§63.670(j)(3)):

- “Minimum accuracy requirements: ± 2 percent of span”
- “Calibration requirements: ...Calibration requirements should follow manufacturer's recommendations at a minimum.”

A summary of the methods and standards used can be seen in Tables 1 and 2 below:

Table 1 Calculation and Process Methods

Test Method / Standard	JP3 Application
Calculation Methods	
ASTM D3588/GPA 2172	JP3 Follows this method for determining net heating value (equations and tables)
ASTM D8321	JP3 Follows this method for developing and validating the multivariate analyses to determine the properties of gas
Process Collection Methods	
Method 320	JP3 closely follows Method 320, JP3 has adopted this method for NIR analyzers
ASTM D1945/GPA 2261	This primary test method is used by the lab to measure hydrocarbon concentrations for validation samples which are used to validate JP3 performance

Table 2 Validation Methods

Test Method / Standard	JP3 Application
Method 320	JP3 closely follows Method 320, JP3 has adapted this method for NIR analyzers
Method 301	JP3 uses the requirements in Method 301 for validation
Method 18	JP3 follows the sample collection process within Method 18 to obtain validation samples
ASTM D1945/GPA 2261	This primary test method is used by the lab to measure hydrocarbon concentrations for validation samples which are used to validate JP3 performance
ASTM D6122	JP3 uses this method to validate multivariate models

JP3 calorimeter systems calculate the heating values based on the method described in ASTM D3588, Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density in Gaseous Fuels. This method is consistent with other industry standards like GPA 2166, 2261, 2145 and 2172, which are also used by JP3 when appropriate. All of these standards determine the ideal gas heating value at base conditions (14.696 psia and 60°F (15.6°C)) by calculating from the molar composition and the respective ideal gas values for the components.

JP3 calorimeters can also directly determine heating values using ASTM D8321, based on ASTM D1945 and then validated locally with ASTM D1945, and ensure consistency with the practices included within the MACT CC standards. 40 CFR Part 63 Table 13 requires the calorimeter to maintain a minimum accuracy of ± 2 percent of span. The JP3 calorimeter has been measuring heating value for the industry for over ten years and has over 800 samples validated by ASTM 1945. The JP3 calorimeters have been exposed to internal and external audits, as well as hundreds of validation samples, as shown in Figure 5, confirming adherence to this requirement.

To increase the JP3 system's adherence to other approved EPA Methods for monitoring stationary sources (e.g., Method 18 and Method 320), small adjustments could be made to JP3's processes. These adjustments may include moving the reference standard for measurement from GPA 2145 or 2261 to ASTM D3588 and adjusting quarterly calibrations with reference gases to replace sampling corrections using ASTM 1945.

Method of Analysis

The ASTM D3588 standard requires determining the molar composition of the gas in accordance with any ASTM or GPA method that yields the complete composition, exclusive of water, but including all other components present in amounts of 0.1% or more, in terms of components or groups of components listed in ASTM D3588, Table 1, up to 98% of the total sample.

JP3 follows ASTM D8321-22 standard in developing and validating multivariate analyses to determine the physical, chemical, and performance properties of natural gas, natural gas liquids, refined fuels, condensates, and crude oils. The properties against which a multivariate model is calibrated and validated are measured by Primary Test Methods (PTMs), which are analyzed by gas chromatography via ASTM D1945 and/or GPA 2261 method for Natural Gas (flare) applications. The calibration and validation samples are pulled at the site after the analyzer installation or prepared in the lab with gas mixtures, consistent with Method 18.

This JP3 compositional analysis process is similar to EPA TEST METHOD 320—Measurement of Vapor Phase Organic and Inorganic Emissions By Extractive Fourier Transform Infrared (FTIR) Spectroscopy. The Method 320 procedure is based on EPA Method 301 (40 CFR part 63, appendix (A)), which may be used to validate the method for the analytes in a gas matrix. As indicated by Method 301, validation at one source may also apply to another type of source if it can be shown that the exhaust gas characteristics are similar at both sources. Method 320 uses the same optical spectroscopy techniques, calibration, sampling, batch sampling, and quality assurance as the JP3 calorimeter for the determination of molar composition.

As with the FTIR Method 320, the JP3 Calorimeters include a “method validation” procedure. This “method validation” procedure can be done with a known NIST gas(es) spiking process or

batch sampling. In the “spiking method,” the known gases are dynamically measured at the same time as the calorimeter measures the gas from the sample probe. The validation measurements are statistically independent of the unknown source gas but are designed to include similar gas characteristics of the fuel gas. The bias and correction factors can be applied using section 6.3.2.2 of Method 301, which is consistent with Method 320. The calibration and validation exceed the requirements in 40 CFR Part 63 Subpart MACT CC that incorporate Method 18 and Appendix B, Performance Specification 9. These require only a daily calibration, while the JP3 systems can conduct the calibration/ validation at each measurement.

Method 320 includes an Addendum, which is the Protocol For The Use Of Extractive Fourier Transform Infrared (FTIR) Spectrometry for The Analyses Of Gaseous Emissions From Stationary Sources. Method 320 and the method used by JP3 calorimeters are very similar, with the exception that Method 320 indicates the procedure is applicable to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band.” The JP3 spectrometers, the core technology within the calorimeters, use the near-infrared spectrum band instead of the mid-infrared band; the rest of Method 320 can be applied. This difference will not impact the system's ability to speciate organic compounds, C1-C6+. Both mid-infrared and near-infrared bands have hydrocarbon absorption features. The light absorption at the mid-infrared band is much stronger than the near-infrared band. But with appropriate path length of the flow cell, the near-infrared absorption spectroscopy can achieve the same Limit of Detection as FTIR.

The JP3 calorimeters additionally incorporate the applicable portions of Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. This method is designed to measure gaseous organics emitted from an industrial source is designed for use by Gas Chromatography (GC) at ppm level sources. In terms of understanding heating values regulated by the 40 CFR 63 CC, the ppm levels are not impactful in the assessment of heating value. In Method 18, major organic compounds are separated by the GC by its detection principles. The separated components are compared to known compounds under identical conditions. The JP3 calorimeter performs the same analysis, the detection technology separates the components, and comparisons are made to known compounds that have either been speciated by other GCs using ASTM 1945 or directly referenced against known reference gases.

Method 18 Section 8.0 Sampling procedure can be followed. A detailed work process is included in Appendix B and C.

Quality Assurance and Control

JP3 uses several methods to ensure the calorimeter systems remain within the industry calibration norms. Pursuant to our internal manufacturing controls, 40 CFR 63 subpart CC Table

13, and the requirements of Appendix B, Performance Specification 9, the calorimeters are typically calibrated on a quarterly basis. Calibration timing is dependent on operator preference and other variables.

Model Testing

In accordance with ASTM D6122, JP3 conducts regular, periodic, continual validation and calibration by plotting control charts of the differences between methods. The control chart in the image is indicative of the model testing process adhering to ASTM D6122 standards. ASTM D6122 sets the guidelines for validating the performance of an analytical process, including continual calibration by comparing it to a reference method. Model testing involves regular, systematic checks by plotting control charts, such as the one depicted, to track the differences between the results obtained by the JP3 system and the reference or laboratory method over time. This allows for monitoring of the system's consistency and precision.

The chart shows the Independent Component Analysis (ICA) levels over a sequence of timestamps, with error bars indicating the variability or confidence intervals of the measurements. A specific lab result is highlighted, providing a value with its standard deviation and associated barcode and timestamp, serving as a reference point for calibration. Trained in-house chemometricians conduct these model tests to ensure that the analytical models used by the JP3 system remain accurate and reliable. The role of the chemometrician is to apply statistical methods to chemical data to maintain the validity of the analytical models, ensuring compliance with the established ASTM standard.



Figure 9: Example of iC4 validation samples collected over 18 months on a fractionation NGL stream tested via ASTM D6122

Analyzer Reproducibility and Repeatability.

Analyzer repeatability can be determined from the analyzer results during periods when the process sample is relatively constant.

The provided table, Table 3, showcases the results of an audit assessing the accuracy of the spectrometers, focusing on their repeatability and reproducibility in measuring natural gas components, and compares them to the GPA 2261-13 limits. Repeatability refers to the precision under the same operating conditions over a short interval of time, while reproducibility relates to the precision between different operators, methods, and equipment over longer periods. The reproducibility varies by component concentration but typically improves with an increase in the component's presence in the gas stream. The audit found that the worst-case scenario for heating value reproducibility was 0.10% variance between detectors on the same spectrometer and 0.29% between different spectrometers.

The chart reveals that the Verax system exhibits repeatability and reproducibility within the limits set by the Gas Processors Association (GPA) standard 2261-13. Moreover, according to an audit performed by Southwest Research Institute (SwRI) in 2015, Verax's repeatability surpasses the American Petroleum Institute's (API) requirements for Gas Chromatographs (GCs) significantly, by approximately an order of magnitude.

In the context of ASTM and CFR standards, which set the broader framework for analytical procedures and quality assurance in the industry, the Verax system's performance can be considered in compliance. Specifically, ASTM standards for testing methods would mandate that equipment demonstrates a certain degree of precision and accuracy—criteria that Verax appears to meet as per the results shown. Moreover, under CFR regulations, which may require demonstration of equipment reliability and measurement precision for regulatory compliance, the high repeatability and acceptable reproducibility of the Verax system could provide assurance of its suitability for regulatory applications.

The audit's findings by Dr. Darin L. George in December 2018, underscore the reliability of the Verax 75M spectrometers for precise and consistent natural gas measurements, aligning with industry standards and regulations for measurement technologies.

Audit of Verax™ Accuracy Assessment Procedures Conclusions, December 2018

“This study has quantified the repeatability and reproducibility of natural gas measurements by several Verax 75M spectrometers. **The repeatability of the units is better than API’s repeatability requirements for GCs by approximately an order of magnitude.** The reproducibility of analyses between multiple detectors on a given spectrometer, and between multiple spectrometers, varies with the components being reported. As with GCs, reproducibility improves as the amount of the component in the gas stream increases. The worstcase reproducibility of heating values for the same gas was found to be 0.10% between different detectors on the same Verax unit and 0.29% between different units.” - Darin L. George, Ph.D.

JP3 Measurement EPA MACT CC Alternative Test Method Request

Table 1: Reproducibility of JP3 Verax Output Quantities across all Spectrometers, Detectors and Test Cells

Sample #1		GPA 2261-13 Limits		Verax Results	
Component	Mol %	Repeatability Limit	Reproducibility	Verax Avg U95 Repeatability (2 Xs StdDev)	Verax U95 Reproducibility (2Xs StdDev)
Nitrogen	.0299	0.029	0.086	0.0001	0.002
Methane	72.199	0.033	0.761	0.0068	0.076
CO2	1.682	0.005	0.144	0.0016	0.024
Ethane	14.260	0.030	0.162	0.0017	0.015
Propane	7.134	0.011	0.100	0.0020	0.021
I-Butane	0.910	0.010	0.019	0.0005	0.006
n-Butane	2.042	0.016	0.051	0.0016	0.019
I-Pentane	0.449	0.007	0.021	0.0006	0.008
n-Pentane	0.478	0.009	0.021	0.0007	0.009
Hexanes +	0.481	0.011	0.036	0.0018	0.022
Rel Den	0.79	-	-	0.0002	0.001
BTU/scf	1324.892	-	-	0.159	1.996

JP3 used Section 11.0 of Method 301 to validate the bias and precision of a flare application. The following table lists the results.

Table 2: Flare Method 301 Bias and Precision Validation

Site 1 Flare Example (12 Samples or 6 Quadruplicate Samples)					
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy
Allowed Limit		4.28	2.571	10%	
NHV	N/A	0.30	1.78	N/A	< ±2% of span
C1	0.1 mol%	0.25	0.21	N/A	< ±6% of span
C2	0.3 mol%	0.57	0.08	N/A	< ±5% of span
C3	0.3 mol%	1.57	2.43	N/A	< ±2% of span
iC4	0.3 mol%	1.70	2.52	N/A	< ±2% of span
nC4	0.3 mol%	0.83	0.45	N/A	< ±2% of span
iC5	0.3 mol%	0.03	1.41	N/A	< ±2% of span
nC5	0.3 mol%	0.05	1.46	N/A	< ±2% of span
C6+	0.3 mol%	0.29	1.99	N/A	< ±2% of span

A ruggedness testing was studied on 10 different gas streams with 59 validation samples. The table below shows the results. Additionally, Figure 17 below shows the accuracy to be within +/- 1% of span.

Table 3: Ruggedness Data for Fuel Gas Application

Fuel Gas Example (10 Gas Streams -59 Samples)					
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy
NHV	N/A	0.1902	2.761	0.34%	< ±2% of span
C1	0.1 mol%	0.5564	4.422	0.69%	< ±2.0% of span

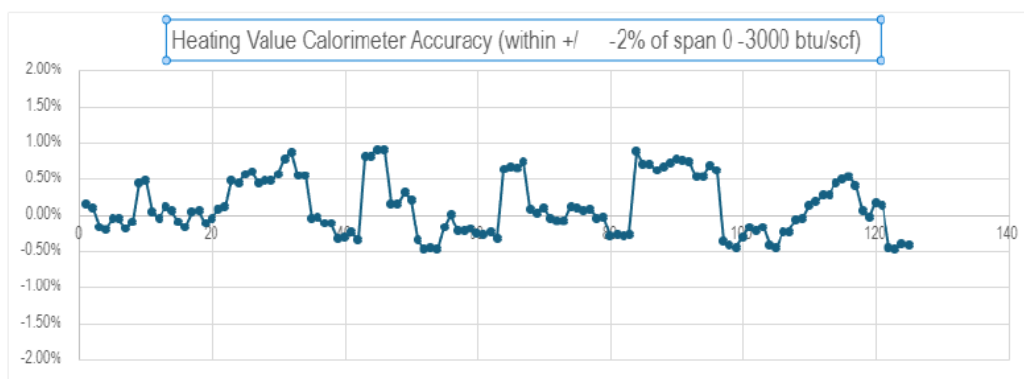


Figure 10: Heating Values for Fuel Gas Application

Calibration of local results against global and local models

Figure 11, presents a methodical validation of calorific value predictions for various gaseous substances, facilitating compliance with the rigorous regulatory standards delineated in 40 CFR Part 63 Subpart CC Table 13. The graph juxtaposes predicted calorific values against actual measurements, delineated as 'Calibration' and 'Test' data points, with calorific values expressed in British Thermal Units (BTUs) per cubic foot (cf).

The adherence of data points to the green reference line, indicating a 1:1 correlation, exemplifies the predictive model's robust alignment with the true calorific values. The metrics encapsulated within the chart – RMSEC, RMSECV, RMSEP, Calibration Bias, CV Bias, Prediction Bias, and coefficients of determination (R^2) for both calibration, cross-validation, and prediction – serve as critical indicators of the model's precision and accuracy. Notably, R^2 values proximate to unity and minimal biases are indicative of the model's exceptional performance.

This calibration and validation protocol appears to rigorously fulfill the calibration gas specifications mandated by Appendix B Performance Specification 9 and 40 CFR Part 63

Subpart CC Table 13, affirming the reliability and accuracy of the predictive model within established regulatory confines. The precise alignment with these standards ensures the suitability of the predictive model for its intended analytical applications in the oil and gas sector, thereby cementing its role in regulatory and quality assurance contexts.

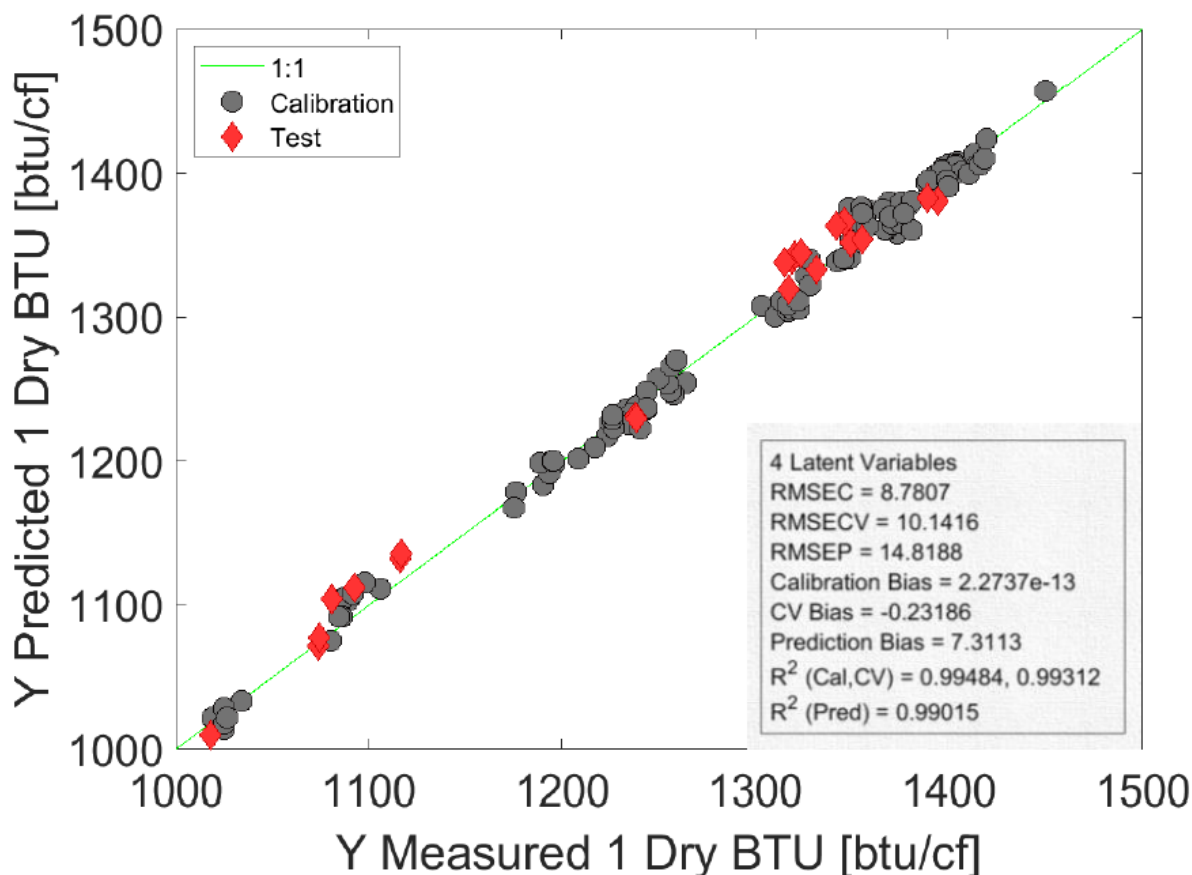


Figure 11: Accuracy Data

The image below outlines the calibration process of the JP3 system in adherence to MACT CC, designed to ensure precise and consistent measurement of various gas attributes. Here's a breakdown of the depicted procedure:

1. Deployment of Mobile JP3 System:
 - a. A mobile JP3 system is deployed to continuously sample a customer's flare gas. This system allows for collecting real-time data representative of operational conditions.
2. Local Validation Sample Collection:
 - a. Concurrently, local validation samples are taken for laboratory analysis via Method 18 and DASTM 1945. This dual approach of on-site and laboratory

analysis ensures that the mobile system's measurements can be verified against controlled lab conditions.

3. Laboratory Analysis and Validation:

- a. The collected samples undergo laboratory analysis according to standards set by CFR (Code of Federal Regulations), ASTM (American Society for Testing and Materials), and GPA (Gas Processors Association) Regulatory requirements. This step validates the local results and ensures compliance with the specified regulations.

4. Continuous Monitoring and Data Transfer:

- a. The system continuously monitors the flare gas and sends data to the cloud every 2 minutes.

5. Spectrum Calibration/validation and Wavelength Tuning:

- a. Spectrum calibration/validation is performed daily or as needed, using NIST (National Institute of Standards and Technology) traceable gases. Additionally, wavelength adjustment occurs with every scan to maintain accuracy.

6. Audit and Final Validation:

- a. The process includes an audit report detailing hydrocarbons from C1 to C6+, Net Heating Value, pressure, and temperature measurements. Final validation samples are then taken for lab analysis to complete the calibration cycle.

The process shown below is meticulously designed to satisfy the accuracy and calibration requirements of the MACT CC regulation, which demand reliable data for environmental reporting and operational control. The regulations often require operators to follow stringent procedures for equipment calibration and data validation to ensure that the reported figures truly represent the emissions and composition of gases being measured. The combination of real-time monitoring with rigorous laboratory validation in this process reflects a commitment to maintaining high standards of measurement integrity.

JP3 Measurement EPA MACT CC Alternative Test Method Request

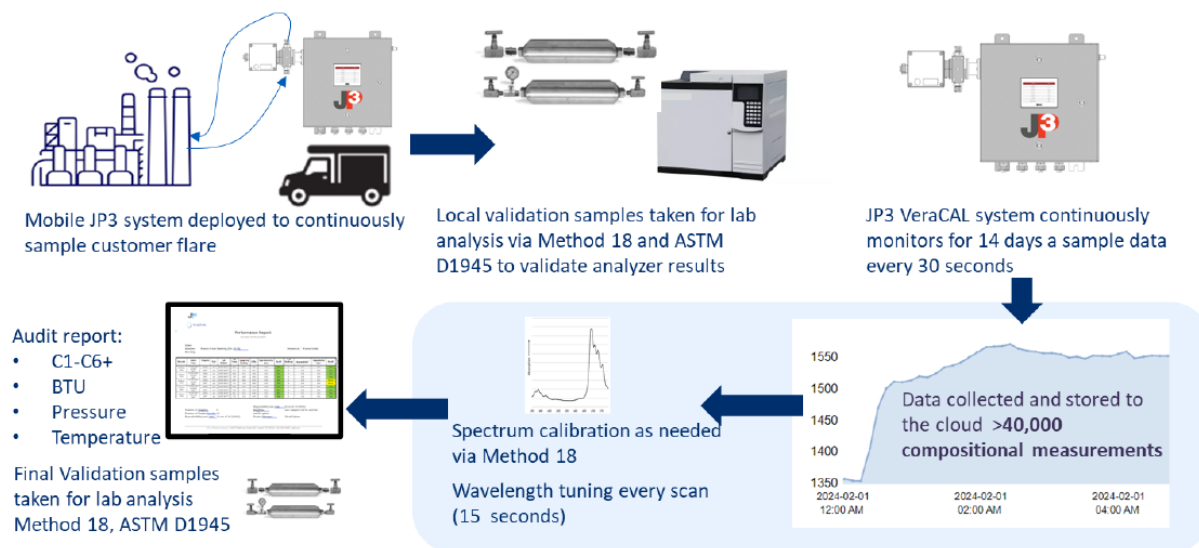


Figure 12: JP3 Flare monitoring process

Model Performance Quality Metrics

The example image (not real data) below depicts a three-dimensional Principal Component Analysis (PCA) scatter plot, commonly used in multivariate statistical analysis to monitor the performance of a system like a calorimeter. PCA reduces the dimensionality of data while preserving most of the variance, helping to identify patterns and outliers.

In the context of calorimeter analytics, T^2 (Hotelling's T-squared) and Q statistics (also known as Q residuals) are used to detect unusual variations within the dataset. T^2 captures variations within the model's boundaries it identifies samples that exhibit unusual behavior in the space defined by the principal components (PCs). A sample with a large T^2 value is highlighted on the graph, indicating a significant variation within the established model structure.

On the other hand, the Q statistic measures variations outside the model's boundaries essentially capturing discrepancies that the model fails to explain. A sample with a large Q value, as shown on the plot, indicates a variation that lies outside the scope of the model, which can be indicative of errors or external factors not accounted for in the current model.

In compliance with regulatory requirements, such as those specified by environmental or quality control standards, the calorimeter system reviews each measurement against these statistical thresholds to ensure accuracy. If readings fall outside acceptable limits of T^2 or Q, they may be flagged for potential issues.

The VeraCAL system is further equipped with a reference cell that contains calibration gases. This cell is critical for maintaining the integrity of the system, as it is used as a benchmark to validate each reading. By continuously comparing actual readings against the known values in the reference cell, the system can self-check and correct for any drifts or malfunctions, ensuring it operates within the parameters set by regulatory standards and maintains accurate readings throughout its service.

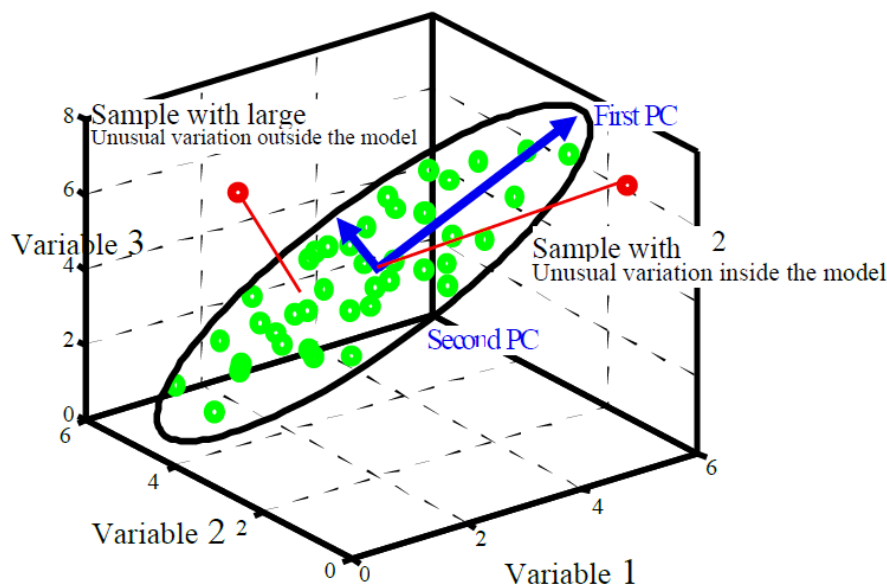


Figure 13: Statistical Analysis Example

Accuracy

The graph below, Figure 14, depicts the calibration test results for a calorimeter measuring the percentage of methane (CH₄), as mandated by the accuracy standards set forth in 40 CFR Part 63 Subpart CC Table 13. This is an example of system accuracy testing demonstrating that the system meets the regulations stipulating the precision requirements for such measurements.

In Figure 14, the x-axis represents the calorimeter's percentage readout of methane's calorific value, spanning from 97.0% to 103.0%. The y-axis enumerates the frequency of these readings, taken every half minute over a 14-day period. The calibration standard requires the calorimeter's readings to be confined within $\pm 2\%$ of methane's true calorific value and the 10% requirement of Appendix C Performance Specification. A normal distribution is evident from the graph, with a peak around the 100% mark, which denotes the nominal value of methane's calorific value according to the calorimeter's scale.

JP3 Measurement EPA MACT CC Alternative Test Method Request

This distribution suggests that the readings are clustered near the expected true value, indicating that the calorimeter is performing within the acceptable tolerance range as per the cited regulatory standard. Such a concentration of data points within the 98% to 102% range would typically signify compliance with the calibration accuracy required by 40 CFR Part 63 Subpart CC Table 13. The detailed statistical evaluation, including an analysis of variance and other relevant statistical assessments, formally confirms that the distribution of readings meets the stringent criteria set by the regulation. This formal analysis validates the calibration accuracy of the calorimeter, ensuring its suitability for regulatory and operational purposes.

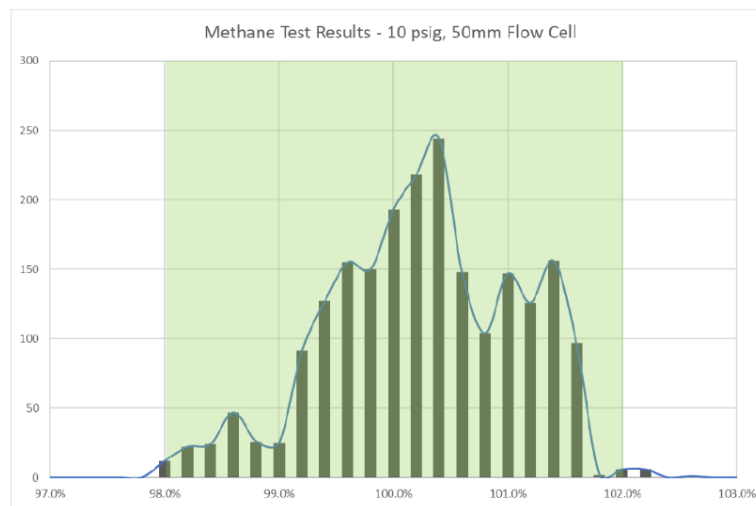


Figure 14: Methane Testing 14 day, 30-second interval validation

Figure 15, below, shows the results of a broader series of tests, which were conducted across the United States over a three-year period. These tests also aimed to meet the $\pm 2\%$ accuracy requirement for the calorimeter's measurement of the calorific value. The histogram displays the difference between the measured values and the reference values, divided by the reproducibility pass limit, and then multiplied by 100% to express this as a percentage.

In this chart, the x-axis indicates the percentage difference from the reference value, ranging from -5% to +5%. The y-axis indicates the frequency of these occurrences. The central peak, which aligns closely with the 0% mark, suggests that most samples fall within a narrow range around the reference value. This indicates a high level of accuracy and precision in the measurements.

To be compliant with the regulatory standard for calorimeters that requires an accuracy within $\pm 2\%$, the majority of the data points would need to be within the -2% to +2% range on this graph. The density of the data points within this interval suggests the equipment used for these real-world tests is operating within the required performance criteria.

This test data pertains to a variety of gas types encountered in the oil and gas industry, such as associated gas, flare gas products, fuel gases, and other upstream and midstream products. These gases often have a more complex composition than pure methane (CH₄), which may impact the calibration and measurement process.

The data in Figure 15 represents over a four-year period and multiple analyzers, 567 out of 665 samples, representing approximately 97% of the total, conform to the $\pm 2\%$ of span accuracy requirement. This level of compliance indicates a high degree of precision for the majority of the measurements across diverse gas compositions and suggests that the testing apparatus is capable of maintaining the standard under varied conditions.

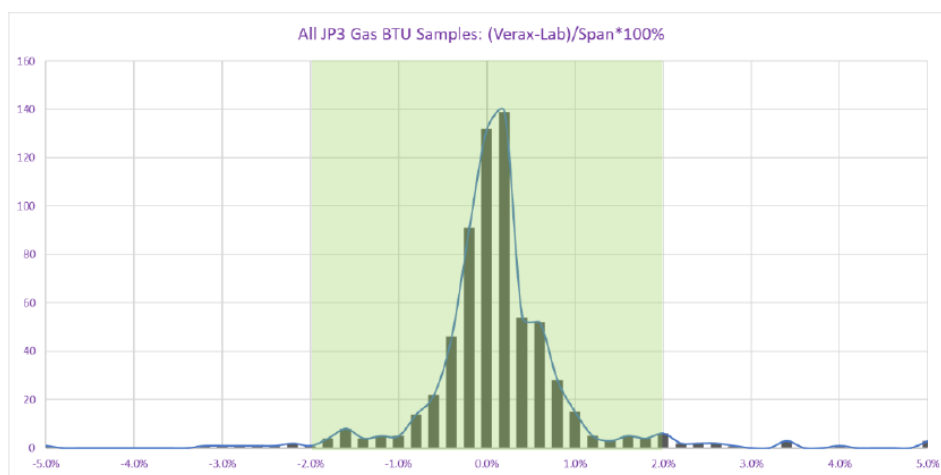


Figure 15: All gas samples NHV

The existence of outliers, as mentioned, can be attributed to factors such as sampling errors, the initial phases of model validation and creation, or changes in the processes that may necessitate All JP3 Gas BTU Samples: (Verax-Lab)/Span*100% recalibration as part of quality control procedures. These factors are common in real-world industrial settings, where conditions may vary significantly, and they underscore the importance of ongoing calibration and quality assurance to ensure that measurement equipment remains accurate and reliable over time.

Considering the nature of the gases tested and the complexities involved, a 97% compliance rate within the strict $\pm 2\%$ margin is indicative of robust performance, particularly when factors leading to outliers are identified and addressed through recalibration and quality processes. Continued refinement of these processes, along with regular equipment maintenance and calibration, would likely improve accuracy and reproducibility, further aligning with the regulatory standards as detailed in 40 CFR Part 63 Subpart CC Table 13, as well as the calibration gas specifications required by Appendix B Performance Specification 9.

To formally ascertain compliance, it would be necessary to calculate the percentage of measurements that fall within the $\pm 2\%$ range, which would indicate the reproducibility and

accuracy of the calorimeter in various conditions over the extended period. Should this percentage meet or exceed the required standard, the testing apparatus would be deemed to adhere to the calibration accuracy specifications as detailed in 40 CFR §60.5417c(d)(8)(ii)(A) and considering the calibration gas requirements stipulated in 40 CFR Part 63 Subpart CC Table 13 and Part 60 Appendix B Performance Specification 9.

Limitations

GPA 2119 outlines the use of optical spectroscopy to identify the chemical composition of single-phase hydrocarbon fluids, either gas or liquid. According to the specifications, the components listed in Table 6 can be adjusted according to manufacturer guidelines but generally align with JP3 performance limitations. Composite mixes within the ranges in the table are suitable for any qualifying optical/ spectroscopy calorimetry method. GPA 2119 notes limitations in detecting certain weak or inactive spectral components like Nitrogen in gases, which may require supplementary methods or technologies for quantification. These components may be quantified by difference or alternate technologies may also be utilized in conjunction with optical spectroscopy to obtain empirical analyses for the spectrally weak or spectrally inactive components. Fortunately, those weak or inactive spectral components usually do not have heat value contributions and will not contribute to the net heating value of the gas being tested.

Table 4: Recommended Gas Phase Components Limits of Detection in GPA 2119

Table 1: Recommended Gas Phase Components and Compositional Ranges

Components	Concentration Range (Mole %)
Nitrogen	0.10 – 30
Carbon Dioxide	0.10 – 30
Methane	40 – 100
Ethane	0.10 – 25
Propane	0.10 – 15
iso-Butane	0.10 – 4.0
n-Butane	0.10 – 4.0
iso-Pentane	0.10 – 2.0
n-Pentane	0.10 – 2.0
Hexanes	0.10 – 2.0
Heptanes	0.10 – 2.0
Octanes	0.10 – 1.0
Nonanes Plus	0.10 – 1.0

Compliance with CFR Regulations for JP3's Calorimeters

JP3's calorimeters not only fulfill but surpass the requirements set forth in the Code of Federal Regulations (CFR) for calorimetric analysis, as well as the performance specifications for gas chromatography systems under Appendix B, Performance Specification 9.

Calorimeter Compliance: As shown above, JP3's calorimeters excel in accurately determining the heating value of gases. Their performance goes beyond the accuracies required by the CFR, delivering precise and consistent measurements crucial for environmental compliance. This advanced capability is vital for monitoring fuel quality and ensuring efficient combustion processes as mandated by regulatory standards.

Gas Chromatography Equivalence: While JP3's calorimeters utilize optical spectroscopy for analysis, they meet and exceed the stringent criteria designated for gas chromatography in terms of precision, calibration, and accuracy. Despite the difference in the underlying technology, JP3's calorimeters provide analytical results that align with the performance specifications for gas chromatographs. This ensures that the composition of flare gases is quantified with exceptional accuracy, facilitating accurate emissions calculations and adherence to regulatory requirements.

The outstanding repeatability and reproducibility of JP3's calorimeters affirm their reliability for consistent measurements of gas composition and heating value. Such dependable performance is critical for continuous emissions monitoring systems (CEMS), which are rigorously regulated by the CFR. JP3's calorimeters are instrumental for the industry to meet federal environmental guidelines, particularly in flare management and other applications that require rigorous measurement of heating values and compositional analysis.

JP3's calorimeters are not only compliant with the demanding requirements of the CFR for calorimeters and gas chromatographs but also provide a comprehensive and superior analytical solution for the precise monitoring of hydrocarbon gas streams.

Record Keeping and Documentation

JP3 maintains rigorous record-keeping practices, ensuring adherence to the reporting requirements of 40 CFR 60 and 63, as well as state-specific regulations and permit conditions. Our system leverages the Edge Web Interface and JP3 Cloud Infrastructure to document the number and type of equipment, with real-time data and analytics available to provide accurate emission estimates. For facilities under our management, fugitive emission calculations are derived using established methodologies from state and federal guidelines, taking into account continuous monitoring and control efficiencies.

In accordance with regulations, records of sensor calibration, bump tests, sensor data, and meteorological data are electronically maintained and readily exportable for regulatory review by the EPA or equivalent state agencies. Furthermore, our cloud-based platform archives sensor placement records, ensuring all components are accounted for and properly monitored. JP3 also ensures a comprehensive Fugitive Emission Management Plan (Test and Installation Planning or IKO) is in place, with clear documentation of compliance strategies available in various formats

for verification and audit purposes. Records are preserved for a minimum of five years, with at least two years of data easily accessible in electronic or other suitable formats, fulfilling both federal and state record-keeping requirements.

The JP3 system exemplifies meticulous record keeping and documentation through its integrated process, which employs state-of-the-art technology to ensure comprehensive monitoring and data management. At the core of the system is the calorimeter's computer, which captures detailed measurements at the customer facility. These measurements are then processed locally via the JP3 Edge Software Stack, which employs logical processing, model processing, and analytic engines, all of which are crucial for real-time data assessment and quality control.

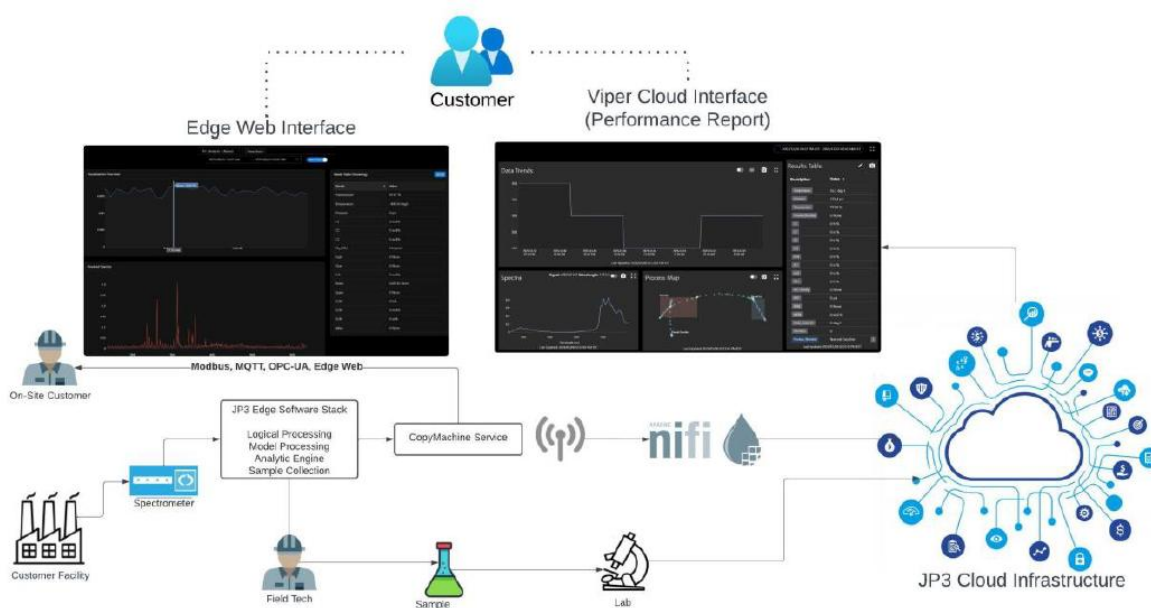


Figure 16: JP3 Realtime Monitoring Software and Data Storage

For on-site customers, the Edge Web Interface provides immediate access to data trends, spectra, and operational insights, enabling swift decision-making. This interface supports a variety of communication protocols such as Modbus, MQTT, and OPC-UA, ensuring versatile connectivity options.

Quality assurance and quality control (QA/QC) are integral to the process, with local data storage ensuring that all information is securely archived. Field technicians contribute to the QA/QC process by collecting samples for laboratory verification via Method ASTM-D1945, thus providing a reliable cross-check of the online measurements. System health checks are monitored through Viper as well and notices will alert users to operational issues.

Data flows seamlessly to the cloud with updates at least every two minutes, where the Viper Cloud Interface presents performance reports in a user-friendly format. The JP3 Cloud

Infrastructure, powered by technologies like Apache NiFi, orchestrates the data flow, maintaining integrity and security while facilitating complex data transformations and routing.

JP3 leverages cellular data transmission to ensure real-time, secure transfer of analytical results from the calorimeter to cloud storage. This approach guarantees the swift availability of data while maintaining high standards of data integrity and confidentiality. Our robust cloud infrastructure offers unparalleled data management and archival solutions, ensuring long-term accessibility and compliance with regulatory standards. The customer data portal, Figure 15, accessible through the Edge Web Interface, provides an interactive, user-friendly environment for customers to view performance reports, trend analyses, and actionable insights. This comprehensive data ecosystem allows for efficient monitoring, expedited decision-making, and seamless compliance reporting as shown in Figure 17 below.

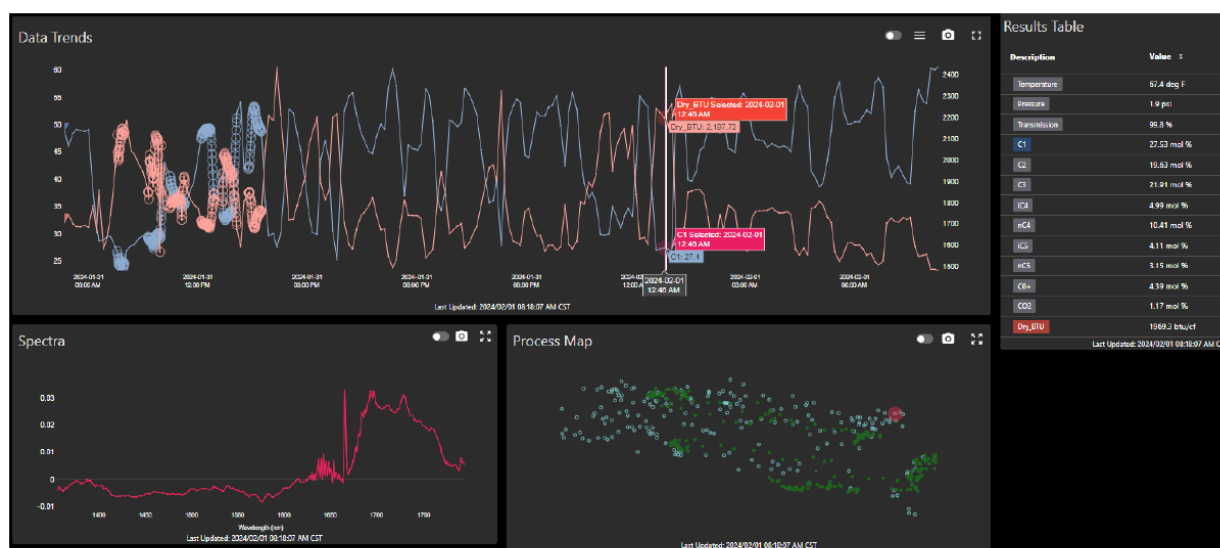


Figure 17 Customer Portal

Collectively, this sophisticated infrastructure not only supports but also enhances record-keeping and documentation practices. The real-time data coupled with fault detection and performance analytics provide an unparalleled level of transparency and traceability, meeting and exceeding industry requirements for accurate and accessible reporting.

Summary

The JP3 VeraCAL system is a calorimeter for determining the heating value of combustible gases in compliance with EPA regulations. The instrument's capability to provide precise compositional analysis through optical spectroscopy directly contributes to the accurate calculation of heating values. This is in line with the calorimetric requirement to measure the

energy content of fuels, fulfilling a pivotal role in environmental monitoring and regulatory adherence.

The instruments' audits, calibration data, and multi-year field implementations all exemplify the repeatability and reproducibility standards required by industry-leading measurement equipment and underscore their reliability and accuracy in calorimetric measurements. Such precision is critical to ensuring that the heating values derived from the compositional data are trustworthy and consistent.

Employing spectroscopic techniques, the JP3 measures the heating value by interpreting the interaction of light with gas molecules. This method is not only highly precise but also well-suited for the variable conditions of field operations where conventional calorimetric methods may not be practical. The robustness of the JP3's calorimeter instruments in various environments aligns with the EPA's MACT CC regulatory intent to provide precise measurements of individual component composition and net heating value.

Furthermore, the ability of the systems to perform in remote locations provides a better solution to the industry than other commonly available calorimeters or complex GC systems. The JP3 Calorimeter, VeraCAL, meets the industry's need for accurate, real-time calorimetry outside the confines of a laboratory setting. This adaptability ensures that it is a vital tool for meeting the regulatory requirements intended to mitigate emissions of VOCs and other pollutants from flare operations.

The JP3 calorimeters provide accurate heating values essential for environmental compliance. Its technological sophistication enhances the industry's capabilities to measure and control the quality of hydrocarbon fuel sources in adherence to EPA regulations.

Appendix A: Example Installations

The accompanying images depict the versatility of JP3's calorimeters, installed at a variety of sites, throughout various basins as listed in Table 7 to perform continuous monitoring of heating values in flare gas applications. These installations showcase the adaptability of the equipment, ranging from long-term, fixed installations to mobile setups designed for short-term testing. Over a two-week sampling period across these diverse locations, the JP3 calorimeters accurately monitored a wide range of NHV values, from 1,191 up to 1,835, and methane concentrations varying between 33% to 80%. The examples provided reflect a selection of applications across different geographies in the U.S., demonstrating JP3's calorimeters' robustness and reliability in a myriad of operational contexts.





Figure A1: JP3 Analyzer Installation Examples



Figure A2: Gas Plant Example Installation



Figure A3: Flare Application Example



Figure 43: Well Site Example Installation

**Appendix B: JP3 NIR Spectroscopy Work Process/
Method of Use adapted from Method 320 FTIR
Alternative to Gas Chromatograph**

Appendix B: JP3 NIR Spectroscopy Work Process/ Method of Use adapted from Method 320 FTIR alternative to Gas Chromatograph

METHOD 3XX – Measurement of Vapor Phase Organic and Inorganic Emissions by NIR Spectroscopy

Method 3XX is an approved alternative method to Gas Chromatograph for continuously determining the NHV of the inlet gas to the enclosed combustion device or flare at standard conditions in upstream and midstream applications.

1.0 Scope and Application. Persons unfamiliar with basic elements of NIR spectroscopy should not attempt to use this method. This method describes sampling and analytical procedures for extractive emission measurements using near-infrared (NIR) spectroscopy. Procedures for collecting and treating data for developing NIR calibrations are outlined. Definitions, terms, and calibration techniques are described. The calibration establishes a multivariate correlation between the spectral features and the properties to be predicted. This correlation is herein referred to as the multivariate model. Criteria for validating the performance of the multivariate model are described. The properties against which a multivariate model is calibrated and validated are measured by Primary Test Methods (PTMs) and the results of the PTM measurement are herein referred to as Primary Test Method Results (PTMR). The analysis of the spectra using the multivariate model produces a Predicted Primary Test Method Result (PPTMR). The sampling procedure described here is extractive. Flue gas is extracted through a heated gas transport and handling system.

For some sources, sample conditioning systems may be applicable. This method describes sampling and analytical procedures for extractive emission measurements using NIR spectroscopy. The method covers the determination of the chemical composition and physical properties of single-phase gas fluids using NIR spectroscopy.

1.1.1 Analytes. Analytes include hazardous air pollutants (HAPs) for which reference spectra have been developed. Other compounds can also be measured with this method if reference spectra are prepared according to ASTM D8321.

1.1.2 Applicability. This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the NIR spectral region, about 4000 to 12,500 cm^{-1} (0.8 to 2.5 μm). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path gas cell. Spectra of samples are collected using double beam NIR absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations.

1.1.3 Analytical Principle. In the NIR band, most molecules that are present in the flue gases of midstream and upstream enclosed combustion and flares exhibit characteristic gas phase absorption spectra that may be recorded by NIR systems. Such systems consist of a source of NIR radiation, an enclosed sample cell of known absorption pathlength, an NIR detector, optical elements for the

transfer of NIR radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both the quantitative analyses of spectral data. The absorption spectra of pure gases and mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern NIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. ASTM D8321 describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

1.2 Method Range and Sensitivity. Analytical range and sensitivity depend on the frequency-dependent analyte absorptivity, instrument configuration, data collection parameters, and gas stream composition. Instrument factors include: (a) spectral resolution, (b) detector sensitivity and response, and (c) absorption path length. Typical Component Ranges are found in Table 1: Recommended Gas Phase Components and Compositional Ranges.

Table 1: Recommended Gas Phase Components and Compositional Ranges

Components	Concentration Range (Mole %)
Nitrogen (by difference)	0.10 – 50
Carbon Dioxide	0.10 – 30
Methane	0.30 – 100
Ethane	0.10 – 100
Propane	0.10 – 100
iso-Butane	0.10 – 50
n-Butane	0.10 – 50
iso-Pentane	0.10 – 30
n-Pentane	0.10 – 30
Hexanes Plus	0.10 – 20

1.2.1 For any optical configuration the analytical range is between the absorbance values of about 0.01 (NIR transmittance relative to the background = 0.98) and 1.0 ($T = 0.1$). (For absorbance >1.0 the relation between absorbance and concentration may not be linear.)

1.2.2 The concentrations associated with this absorbance range depend primarily on the cell path length and the sample temperature. An analyte absorbance greater than 1.0, can be lowered by decreasing the optical path length. Analyte absorbance increases with a longer path length. Analyte detection also depends on the presence of other species exhibiting absorbance in the same analytical region. Additionally, the estimated lower absorbance (A) limit ($A = 0.01$) depends on the root mean square deviation (RMSD) noise in the analytical region.

1.2.3 The concentration range of this method is determined by the choice of optical configuration.

1.2.3.1 The absorbance for a given concentration can be decreased by decreasing the path length or by diluting the sample. There is no practical upper limit to the measurement range.

1.3 *Sensitivity*. The limit of sensitivity is based on the optical configuration. Wavelength (frequency) stability of spectrometers and spectrophotometers is often a critical factor in the performance of a multivariate calibration. The estimation of the sensitivity of a multivariate model to changes in the wavelength (frequency) scale provides a useful parameter against which instrument performance can be judged. The wavelength sensitivity of a multivariate model will depend on a variety of factors, including the optical and digital resolution of the instrument relative to the bandwidths of the sample being measured. Calculation of a wavelength sensitivity is done to provide a useful diagnostic for analyses conducted on the same type of analyzer.

1.4 *Data Quality*. Data quality shall be determined by executing the procedures in ASTM D8321. A multivariate model is developed using one or more of the mathematical techniques described in ASTM D8321 Section 14, Section 17, and Appendix X1. The multivariate model is preferably tested using cross-validation methods to produce statistics such as SECV or PRESS (see 17.3.9 of ASTM D8321). Other statistics can also be used to judge the overall quality of the calibration.

1.4.1 Measurement objectives shall be established by the choice of detection limit (DL_i) and analytical uncertainty (AU_i) for each analyte.

1.4.2 An instrumental configuration shall be selected. An estimate of gas composition shall be made based on previous test data, data from a similar source or information gathered in a pre-test site survey. Spectral interferants shall be identified using the selected DL_i and AU_i and band areas from reference spectra and interferant spectra. The baseline noise of the system shall be measured in each analytical region to determine the minimum analyte uncertainty (MAU) of the instrument configuration for each analyte and interferant (MIU_i).

1.4.3 Data quality for the application shall be determined, in part, by measuring the RMS (root mean square) noise level in each analytical spectral region. The RMS noise is defined as the RMSD of the absorbance values in an analytical region from the mean absorbance value in the region.

1.4.4 The MAU is the minimum analyte concentration for which the AU_i can be maintained; if the measured analyte concentration is less than MAU_i then data quality are unacceptable.

2.0 *Summary of Method*

2.1 Principle.

2.1.1 NIR absorption spectroscopy is performed by directing an NIR beam through a sample to a detector. The frequency-dependent NIR absorbance of the sample is measured by comparing this detector signal (single beam spectrum) to a signal obtained without a sample in the beam path (background).

2.1.2 Most molecules absorb NIR radiation and the absorbance occurs in a characteristic and reproducible pattern. The NIR spectrum measures fundamental molecular properties and a compound can be identified from its NIR spectrum alone.

2.1.3 Within constraints, there is a linear relationship between NIR absorption and compound concentration. If this frequency dependent relationship (absorptivity) is known (measured), it can be

used to determine compound concentration in a sample mixture.

2.1.4 Absorptivity is measured by preparing, either in the laboratory or in the field, standard samples of compounds at known concentrations and measuring the NIR “reference spectra” of these standard samples. Field samples can also be from the source directly and the concentrations are provided from a Primary Test Method (PTM), typically a lab gas chromatograph based on ASTM D1945. These “reference spectra” are then used in sample analysis: (1) Compounds are detected by matching sample absorbance bands with bands in reference spectra, and (2) concentrations are measured by comparing sample band intensities with reference band intensities.

2.2 *Sampling and Analysis.* In extractive sampling a probe assembly and pump are used to extract gas from the exhaust of the affected source and transport the sample to the gas cell. Typically, the sampling apparatus is similar to that used for single-component continuous emission monitor (CEM) measurements.

2.2.1 The digitized NIR spectrum of the sample in the NIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law.

$$A_i = a_i b c_i \quad (1)$$

Where:

A_i = absorbance at a given frequency of the i th sample component.

a_i = absorption coefficient (absorptivity) of the i th sample component.

b = path length of the cell.

c_i = concentration of the i th sample component.

2.2.2 Comparison to a Primary Test Method (PTM) and Analyte spiking are used for quality assurance (QA). NIR spectroscopies require calibration to determine the proportionality relationship between the signals measured and the component concentrations or properties that are to be predicted. During the calibration, spectra are measured for samples for which these PTMRs are known, and the multivariate relationship between the sample spectral signals and the PTMRs is determined. The relationship, the multivariate model, is then applied to the spectrum of an unknown sample to predict the PPTMR for that sample. Using Analyte spiking (section 8.6.2 of this method) an analyte is spiked into the gas stream before the NIR Analyzer sample filtering systems. Analyte concentrations in the spiked samples are compared to analyte concentrations in unspiked samples. Since the concentration of the spike is known, this procedure can be used to determine if the sampling system is removing the spiked analyte(s) from the sample stream.

2.3 *Reference Spectra Availability.*

2.4 *Operator Requirements.* The *NIR Spectroscopy* analyst shall be trained in setting up the instrumentation, verifying the instrument is functioning properly, and performing routine maintenance. The analyst must evaluate the initial sample spectra to determine if the sample matrix is consistent with pre-test assumptions and if the instrument configuration is suitable. The analyst must be able to modify the instrument configuration, if necessary.

2.4.1 The spectral analysis shall be supervised by someone familiar with NIR procedures.

2.4.2 A technician trained in instrumental test methods is qualified to install and operate the sampling system. This includes installing the probe and heated line assembly, operating the analyte spike system, and performing moisture and flow measurements.

3.0 Definitions

3.1 *Analyte*. A compound that this method is used to measure. The term “target analyte” is also used. This method is a multi-component method; therefore, several analytes may be targeted for a given test.

3.2 *Reference Spectrum*. NIR spectrum of an analyte or a mixture of multiple analytes prepared under controlled, documented, and reproducible conditions according to written procedures. A library of reference spectra is used to measure analytes in gas samples.

3.3 *Standard Spectrum*. A spectrum that has been prepared from a reference spectrum through a (documented) mathematical operation. A common example is de-resolving of reference spectra to lower-resolution standard spectra (Protocol, appendix K to the addendum of this method). Standard spectra, prepared by approved, and documented, procedures can be used as reference spectra for analysis.

3.4 *Concentration*. In this method concentration is expressed as a molar concentration, mol%, in ppm-meters, or in (ppm-meters)/K, where K is the absolute temperature (Kelvin). The latter units allow the direct comparison of concentrations from systems using different optical configurations or sampling temperatures.

3.5 *Interferant*. A compound in the sample matrix whose NIR spectrum overlaps with part of an analyte spectrum. The most accurate analyte measurements are achieved when reference spectra of interferants are used in the quantitative analysis with the analyte reference spectra. The presence of an interferant can increase the analytical uncertainty in the measured analyte concentration.

3.6 *Gas Cell*. A gas containment cell that can be evacuated. It is equipped with the optical components to pass the NIR beam through the sample to the detector. Important cell features include: path length (or range if variable), temperature range, materials of construction, and total gas volume.

3.7 *Sampling System*. Equipment used to extract the sample from the test location and transport the sample gas to the NIR analyzer. This includes sample conditioning systems.

3.8 *Sample Analysis*. The process of interpreting the NIR spectra to obtain sample analyte concentrations. This process is usually automated using a software routine employing a classical least squares (cls), partial least squares (pls), or K- or P-matrix method.

3.9 *One hundred percent line*. A double beam transmittance spectrum obtained by combining two background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero absorbance line is used to measure the baseline noise in the spectrum.

3.10 *Background Deviation*. *Background deviation* means a deviation from 100% transmittance in any region of the 100% line.

3.11 *Batch Sampling*. A procedure where spectra of discrete, static samples are collected. The gas cell is filled with sample and the cell is isolated. The spectrum is collected. Finally, the cell is evacuated to prepare for the next sample.

3.12 *Continuous Sampling*. A procedure where spectra are collected while sample gas is flowing through the cell at a measured rate.

3.13 *Sampling resolution*. The spectral resolution used to collect sample spectra.

3.16 *Reference CTS*. Calibration Transfer Standard spectra that were collected with reference spectra.

3.17 *CTS Standard*. *Calibration transfer standard (CTS)* means a certified gas calibration standard used to verify instrument stability. For the purposes of this method, the CTS must be methane, ethane, carbon dioxide or other hydrocarbons present in common flare or waste gas applications.

3.18 *Test CTS*. CTS spectra collected at the sampling resolution using the same optical configuration as for sample spectra. Test spectra help verify the resolution, temperature and path length of the NIR system.

3.19 *RMSD*. Root Mean Square Difference, defined in EPA FTIR Protocol, appendix A.

3.20 *Sensitivity*. The noise-limited compound-dependent detection limit for the NIR system configuration. This is estimated by the MAU. It depends on the RMSD in an analytical region of a zero absorbance line.

3.21 *Quantitation Limit*. The lower limit of detection for the NIR system configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum. Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.

3.21 *Quantitation Limit*. The lower limit of detection for the NIR system configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum. Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.

3.22 *Independent Sample*. A unique volume of sample gas; there is no mixing of gas between two consecutive independent samples. In continuous sampling two independent samples are separated by

at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell).

3.23 Measurement. A single spectrum of flue gas contained in the NIR cell.

3.24 Run. A run consists of a series of measurements. At a minimum a run includes 8 independent measurements spaced over 1 hour. *Run* means a series of samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.25 Validation. Validation of NIR measurements is described in sections 13.0 through 13.4 of this method. Validation is used to verify the test procedures for measuring specific analytes at a source. Validation provides proof that the method works under certain test conditions.

3.26 Validation Run. A validation run consists of at least 24 measurements of independent samples. The samples measured are completed with a NIR cell containing a “Known gas concentration”. The known samples are compared to the compositional data. Alternatively, 6 “process stream” quadruplicate samples are compared to the PTM (ASTM D1945 or equivalent compositional analysis). The length of the run is determined by the interval between independent samples.

3.27 Screening. Screening is used when there is little or no available information about a source. The purpose of screening is to determine what analytes are emitted and to obtain information about important sample characteristics such as moisture, temperature, and interferences. Screening results are semi-quantitative (estimated concentrations) or qualitative (identification only). Various optical and sampling configurations may be used. Sample conditioning systems may be evaluated for their effectiveness in removing interferences. It is unnecessary to perform a complete run under any set of sampling conditions. Spiking is not necessary, but spiking can be a useful screening tool for evaluating the sampling system, especially if a reactive or soluble analyte is used for the spike.

3.29 Surrogate. A surrogate is a compound that is used in a QA spike procedure (section 8.6.2 of this method) to represent other compounds. The chemical and physical properties of a surrogate shall be similar to the compounds it is chosen to represent. Under given sampling conditions, usually a single sampling factor is of primary concern for measuring the target analytes: for example, the surrogate spike results can be representative for analytes that are more reactive, more soluble, have a lower absorptivity, or have a lower vapor pressure than the surrogate itself.

3.30 Absorbance. The negative logarithm of transmission represented by the relationship $A = -\log(I/I_0)$, where I is the transmitted intensity of light, and I_0 is the incident intensity of light upon a molecule.

3.31 Absorptivity. The amount of NIR radiation absorbed by each molecule.

3.32 Analyte Spiking. The process of quantitatively adding calibration standards to source effluent. Analyte spiking is used to evaluate the ability of the sample transport and NIR measurement systems to quantify the target analyte(s).

3.33 Analytical Algorithm. The method used to quantify the concentration of both target analyte(s) and additional compounds in a sample matrix that may introduce analytical interferences in each NIR

spectrum.

3.34 Analytical Interference. A spectral feature that complicates, and may even prevent, the analysis of an analyte. Analytical interferences can be background or spectral interferences. Background interferences result from a change in light throughput relative to the single beam background. This can be due to factors such as deposits on reflective surfaces and windows, temperature changes, a change in detector sensitivity, a change in NIR source output, or instrument electronics failure. Spectral interferences arise due to the presence of interfering compounds that have overlapping absorption features with the analytes of interest.

3.35 Apodization. A mathematical transformation that is used to adjust the instrument line shape for measured peaks. There are various types of apodization functions; the most common are boxcar, triangular, Happ-Genzel, and Beer-Norton functions.

3.36 Background Spectrum. A spectrum taken in the absence of absorbing species or sample gas matrix, typically conducted using nitrogen, vacuum, or air.

3.37 Bandwidth. The width of a spectral feature. This width is commonly listed as the full width at half the maximum of the spectral feature.

3.38 Beam Splitter. A device located in the interferometer that divides the incoming NIR radiation into two separate beams that travel two separate paths before recombination.

3.39 Classical Least Squares. A method of analyzing multicomponent spectra by scaling reference absorbance spectra to unknown measured spectra.

3.40 Double Beam Spectrum. A transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

3.41 Fundamental CTS. An NIST-traceable CTS reference spectrum with known temperature and pressure that has been obtained using an absorption cell with an accurately known optical pathlength.

3.42 Partial Least Squares. A method for analyzing multicomponent spectra by combining features from principal component and multiple regression analysis. It has been found to be most useful when predicting a set of dependent variables from a large set of independent variables.

3.43 Resolution. The minimum separation that two spectral features must have to distinguish one feature from the another.

3.44 Test. The series of runs required by the applicable regulation.

3.45 Transmittance. The amount of NIR radiation that is not absorbed by the sample. Percent transmittance is represented by the following equation: $\%T = (I/I_0) \times 100\%$.

4.0 Interferences.

4.1 Analytical Interferences. An analytical interference is a spectral feature that complicates (in extreme cases may prevent) the analysis of an analyte. Analytical interferences are classified as background or spectral interference.

4.1.1 Background Interference. This results from a change in throughput relative to the single beam background. It is corrected by collecting a new background and proceeding with the test. In severe instances the cause must be identified and corrected. Potential causes include: (1) Deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, (3) a change in the NIR source output, or (4) failure in the instrument electronics. In routine sampling throughput may degrade over several hours. Periodically a new background must be collected, but no other corrective action will be required.

4.1.2 Spectral Interference. This results from the presence of interfering compound(s) (interferant) in the sample. Interferant spectral features overlap analyte spectral features. Any compound with an NIR spectrum, including analytes, can potentially be an interferant. The ASTM D8321 procedures adjust for absorbance band overlaps in each analytical region to determine if potential interferants shall be classified as known interferant. Water vapor is common spectral interferants. Water Vapor has a strong NIR spectra and is present in many sample matrices at high concentrations relative to analytes. The extent of interference depends on the (1) interferant concentration, (2) analyte concentration, and (3) the degree of band overlap. Choosing an alternate analytical region can minimize or avoid the spectral interference.

4.2 Sampling System Interferences. These prevent analytes from reaching the instrument. The analyte spike procedure is designed to measure sampling system interference, if any.

4.2.1 Temperature. A temperature that is too low causes condensation of analytes or water vapor. The materials of the sampling system and the NIR gas cell usually set the upper limit of temperature.

4.2.2 Reactive Species. Anything that reacts with analytes. Some analytes, like formaldehyde, polymerize at lower temperatures.

4.2.3 Materials. Poor choice of material for probe, or sampling line may remove some analytes. For example, HF reacts with glass components.

4.2.4 Moisture. In addition to being a spectral interferant, condensed moisture removes soluble compounds.

5.0 Safety

The hazards of performing this method are those associated with any stack sampling method and the same precautions shall be followed. Many HAPs are suspected carcinogens or present other serious health risks. Exposure to these compounds should be avoided in all circumstances. For instructions on the safe handling of any particular compound, refer to its material safety data sheet. When using analyte standards, always ensure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the system under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to section 8.2 of this method for leak check procedures. This method does not address all of the potential safety risks associated with its use. Anyone performing this method must follow safety and health practices consistent with applicable

legal requirements and with prudent practice for each application.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

The equipment and supplies are based on the schematic of the sampling system. Either the batch or continuous sampling procedures may be used with this sampling system. Alternative sampling configurations may also be used, provided that the data quality objectives are met as determined in the post-analysis evaluation. Other equipment or supplies may be necessary, depending on the design of the sampling system or the specific target analytes.

6.1 Sampling Probe. Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to transport analytes to the infrared gas cell. Special materials or configurations may be required in some applications.

6.2 Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter (required) rated for 99 percent removal efficiency at 1-micron (e.g., Balston™) connected at the outlet of the heated probe. These filters are optional but may be desirable in some applications.

6.3 Sampling Line/Heating System. Heated (sufficient to prevent condensation) stainless steel, polytetrafluoroethane, or other material inert to the analytes.

6.4 Gas Distribution Manifold. A heated manifold allowing the operator to control flows of gas standards and samples directly to the NIR system or through sample conditioning systems. Usually includes flow meter, valve for selecting and sending sample to the analyzer, and a by-pass vent. This is typically constructed of stainless steel tubing and fittings, and high-temperature valves. Depending on the sampling and validation procedures, a manifold may not be required.

6.5 Stainless Steel Tubing. Type 316, appropriate diameter (e.g., 3/8 in.) and length for heated connections. Higher grade stainless may be desirable in some applications.

6.6 Calibration/Analyte Spike Assembly. A three way valve assembly (or equivalent) to introduce analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack particulate filter and the NIR analytical instrument.

6.7 Mass Flow Meter (MFM). These are used for measuring analyte spike flow. The MFM shall be calibrated in the range of 0 to 5 L/min and be accurate to ±2 percent (or better) of the flow meter span.

6.8 Gas Regulators. Appropriate for individual gas standards.

6.9 Polytetrafluoroethane Tubing. Diameter (e.g., 3/8 in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10 Sample Pump. A leak-free pump (e.g., KNF™), with by-pass valve, capable of producing a

sample flow rate of at least 5 L/min through 50 ft of sample line. If the pump is positioned upstream of the distribution manifold and NIR system, use a heated pump that is constructed from materials non-reactive to the analytes. If the pump is located downstream of the NIR system, the gas cell sample pressure will be lower than ambient pressure and it must be recorded at regular intervals.

6.13 *NIR Analytical System*. Spectrometer and detector, capable of measuring the analytes to the chosen detection limit. The system shall include a personal computer with compatible software allowing automated collection of spectra.

6.15 *Pressure Gauge*. Capable of measuring pressure from 0 to 1,500 psig to within ± 5 psi.

6.16 *Temperature Gauge*. Capable of measuring the cell temperature to within ± 2 °C.

6.17 *Sample Conditioning*. One option is a condenser system, which is used for moisture removal. This can be helpful in the measurement of some analytes. Other sample conditioning procedures may be devised for the removal of moisture or other interfering species.

7.0 *Reagents and Standards*

7.1 *Analyte(s) Gas*. Obtain a certified gas cylinder mixture containing all of the analyte(s) at concentrations within ± 10 percent of the emission source levels (expressed in mol%).

7.2 *Calibration Transfer Standard(s)*. Select the calibration transfer standards (CTS) according to ASTM D8321. Obtain a National Institute of Standards and Technology (NIST) traceable gravimetric standard of the CTS (± 2 percent).

7.3 *Reference Spectra*. *Reference spectrum* means a spectra of a sample gas obtained at a known concentration or known gas mixture under controlled conditions of pressure, temperature, and pathlength.

8.0 *Sampling and Analysis Procedure*

Three types of testing can be performed: (1) Screening, (2) emissions test, and (3) validation. Each is defined in section 3 of this method.

8.1 *Pretest Preparations and Evaluations*. Using the procedures in sections 5, 6, 7, and 8 of ASTM D8321, determine the optimum sampling system configuration for measuring the target analytes. Use available information to make reasonable assumptions about moisture content and other interferences.

8.1.1 *Analytes*. Select the required detection limit (DL_i) and the maximum permissible analytical uncertainty (AU_i) for each analyte (labeled from 1 to i). Estimate, if possible, the maximum expected concentration for each analyte, C_{MAX_i} . The expected measurement range is fixed by DL_i and C_{MAX_i} for each analyte (i).

8.1.2 *Potential Interferants*. List the potential interferants. This usually includes water vapor, but may also include some analytes and other compounds.

8.1.3. *Optical Configuration.* Choose an optical configuration that can measure all of the analytes within the absorbance range of 0.01 to 1.0.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (section 1.3 of this method discusses MAU and protocol appendix D gives the MAU procedure). The MAU for each analyte, i , and each analytical region, m , depends on the RMS noise.

8.1.7 Analytical Program. Prepare computer program based on the chosen analytical technique. Use as input reference spectra of all target analytes and expected interferants. Reference spectra of additional compounds shall also be included in the program if their presence (even if transient) in the samples is considered possible. The program output shall be in mol% and shall be corrected for differences between the reference path length, L_R , temperature, T_R , and pressure, P_R , and the conditions used for collecting the sample spectra. If sampling is performed at ambient pressure, then any pressure correction is usually small relative to corrections for path length and temperature, and may be neglected.

8.2 Leak-Check. The sample system should be leak-free.

8.3 Detector Linearity. Once an optical configuration is chosen, use one of the procedures of sections 8.3.1 through 8.3.3 to verify that the detector response is linear. If the detector response is not linear, decrease the aperture, or attenuate the NIR beam. After a change in the instrument configuration perform a linearity check until it is demonstrated that the detector response is linear.

8.4 Data Storage Requirements. All field test spectra shall be stored on a computer disk. The stored information includes sample processed absorbance spectra, background, and CTS absorbance spectral model. Additionally, documentation of all sample conditions, instrument settings, and test records must be recorded on hard copy or on computer medium.

8.6 Pre-Test Calibrations

8.6.1 *Calibration Transfer Standard.* Fill the NIR cell to atmospheric pressure with the CTS gas. Alternatively, purge the cell with 10 cell volumes of CTS gas. (If purge is used, verify that the CTS concentration in the cell is stable by collecting two spectra 2 minutes apart as the CTS gas continues to flow. If the absorbance in the second spectrum is no greater than in the first, within the uncertainty of the gas standard, then this can be used as the CTS spectrum.) Record the spectrum.

8.6.2 *QA Spike.* This procedure assumes that the method has been validated for at least some of the target analytes at the source. For emissions testing perform a QA spike. Use a certified standard, if possible, of an analyte, which has been validated at the source. One analyte standard can serve as a QA surrogate for other analytes which are less reactive or less soluble than the standard. Perform the spike procedure of section 9.2 of this method. Record spectra of at least three independent (section 3.22 of this method) spiked samples. Calculate the spiked component of the analyte concentration. If the average spiked concentration is within 0.7 to 1.3 times the expected concentration, then proceed with the testing. If applicable, apply the correction factor from the Method 301 of this appendix validation test (not the result from the QA spike).

8.7 *Sampling.* If analyte concentrations vary rapidly with time, continuous sampling is preferable

using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible. Continuous sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, Continuous sampling is preferred. Batch sampling and continuous static sampling are used for screening and performing test runs of finite duration. Either technique is preferred for sampling several locations in a matter of days. Batch sampling gives reasonably good time resolution and ensures that each spectrum measures a discrete (and unique) sample volume. Continuous static (and continuous) sampling provides a very stable background over long periods. Like batch sampling, continuous static sampling also ensures that each spectrum measures a unique sample volume. It is essential that the leak check procedure under vacuum (section 8.2 of this method) is passed if the batch sampling procedure is used. It is essential that the leak check procedure under positive pressure is passed if the continuous static or continuous sampling procedures are used. The sampling techniques are described in sections 8.7.1 through 8.7.2 of this method.

8.7.1 Batch Sampling. Evacuate the absorbance cell to ≤ 5 mmHg absolute pressure. Fill the cell with exhaust gas to ambient pressure, isolate the cell, and record the spectrum. Before taking the next sample, evacuate the cell until no spectral evidence of sample absorption remains. Repeat this procedure to collect eight spectra of separate samples in 1 hour.

8.7.2 Continuous Static Sampling. Purge the NIR cell with 10 cell volumes of sample gas. Isolate the cell, collect the spectrum of the static sample and record the pressure. Before measuring the next sample, purge the cell with 10 more cell volumes of sample gas.

8.7.3 Collection of Line Samples:

8.7.3.1 Withdraw line samples in accordance with accepted sampling methods as given by Practices ASTM D1265, D4057, D4177, or D7453, whichever is applicable. Flush the entire sample loop with the process stream sample prior to withdrawal of the line sample.

8.7.3.2 The intent of this practice is to collect samples that correspond directly to the spectra being collected by the analyzer. Collect the sample at a port close to the optical probe and at a time correlated with the collection of the sample spectrum. This practice requires that parameters that can impact the result also be recorded at the time of sample collection and the effect of these parameters is properly accounted for when comparing the results with the primary test method result. For a more detailed discussion of the various lag times that can influence the correspondence between the analyzer measurement and collection of line samples, see Practice D3764 and Guide D7278.

8.8 Sampling QA and Reporting

8.8.1 Sample integration times shall be sufficient to achieve the required signal-to-noise ratio. Obtain an absorbance spectrum by filling the cell with N₂, pulling a vacuum, or leaving the cell filled with ambient air. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans used is sufficient to achieve the target MAU.

8.8.2 Assign a unique file name to each spectrum.

8.8.3 Store copies of processed spectra on computer disks.

8.8.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, signal integration time), and the spectral file name.

8.9 Signal Transmittance. While sampling, monitor the signal transmittance. If signal transmittance (relative to the background) changes by 50 percent or more, obtain a new background spectrum. Optical cell cleaning or optical re-alignment may be performed before obtaining the new background spectrum.

8.10 *Post-test CTS*. After the sampling run, record another CTS spectrum.

8.11 Post-test QA

8.11.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.11.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it may be necessary to use a shorter path length or dilute the sample.

8.11.3 Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ± 5 percent of the mean value.

9.0 *Quality Control*

9.1 *Initial Spectral Model Validation* A spectral model can only be truly tested with the use of fully independent validation samples (i.e., sample NOT included in the generation of the spectral model). After spectral modeling is nominally complete, the spectral model is tested using the validation sample set. The deviations in the validation set predictions are documented and describe the accuracy and precision of the spectral model (e.g., figures of merit) relative to the analytical reference technique. This validation exercise needs to occur periodically for the spectral model to ensure performance consistency and detect performance issues (e.g., bias, precision change). The frequency of validation depends on the complexity and rate of change of the process and environmental conditions and perhaps upon the stringency of accuracy/precision requirements of the applications. Initial spectral model validation should occur after the spectral model has been completed and under typical operating conditions.

9.1.1 Gas Phase Products A reference standard prepared in accordance with GPA 2198 or samples analyzed at a laboratory shall be used to validate the accuracy and repeatability of the instrumentation and spectral model. The comparable analytical results shall meet ASTM D1945 or GPA 2261 repeatability and reproducibility for gas phase products.

9.2 *Continuing Spectral Model Verifications*. Performance of the system should be monitored. This should be done by both taking periodic eight (8) representative process samples for comparison to laboratory analyses and diagnostic trending and/or system alarms associated with each analysis. The schedule of the validation samples can vary according to the application.

9.3 With a single NIR instrument, introduce flow and begin collecting spectra of two unspiked samples. Collect spectra of two known samples, with the representative product contained in the flue gas (i.e., methane.) If the spiked sample is collected in the same NIR cell as the unspiked sample, allow for 10 cell volumes of unspiked sample to purge the NIR cell. Repeat this procedure until 12 or more samples are collected. Review the expected concentrations of the spiked samples. The concentration results are analyzed statistically to determine if there is a systematic bias in the method for measuring a particular analyte. If there is a systematic bias, within the limits allowed by Method 301 of this appendix, then a correction factor shall be applied to the analytical results. If the systematic bias is greater than the allowed limits specified in Method 301, this method is not valid and cannot be used.

9.3.1 Spike Materials. Use a certified standard (accurate to ± 2 percent) of the target analyte, if one can be obtained. If a certified standard cannot be obtained, gases verified by ASTM D1945 may be substituted.

10.0 Calibration and Standardization When a spectroscopic, multivariate analysis is used to estimate component concentrations or properties, or both, it is desirable to periodically test the analysis (instrument and model) to ensure that the performance of the analysis is in control and produces results consistent with expectations based on the multivariate model statistics. The user is referred to ASTM D6122 which discusses validation of spectroscopic analyzers for petroleum products and liquid fuels.

10.1 *Signal-to-Noise Ratio (S/N)*. The RMSD in the noise must be less than one tenth of the minimum analyte peak absorbance in each analytical region. For example if the minimum peak absorbance is 0.01 at the required DL, then RMSD measured over the entire analytical region must be ≤ 0.001 .

10.2 *Absorbance Path length*. Verify the absorbance path length by comparing reference CTS spectra to test CTS spectra.

10.3 *Instrument Resolution*. Measure the line width of appropriate test CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.

10.4 *Bias & Slope*: The use of bias and slope adjustments to improve calibration or prediction statistics for NIR multivariate models is appropriate provided that the calibration is fully revalidated whenever bias and slope is adjusted. Prediction errors requiring continued bias and slope corrections may indicate drift in PTMR, changes in the character of the samples, sample handling, sample presentation, instrument response function, or wavelength/frequency stability. If a multivariate model fails during the continual validation, the performance of the instrument should be evaluated using the appropriate instrument performance tests, and any instrument problem that is identified should be corrected. If control samples are used, checks should be performed on the PTM to ensure that PTMRs are correct. If instrument maintenance is performed, calibration transfer or instrument standardization procedures, or both, should be followed to reestablish the calibration.

[This document closely follows Method 320, in the recent instructions by EPA on Alternate

Technology Requests, Section 11 is listed as “Procedures”, a Procedures Section has been added to the end of this document.]

11.0 Data Analysis and Calculations

11.1 During routine operation of the analyzer, validation tests are conducted on a regular, periodic basis to demonstrate that the analyzer results remain in statistical agreement with results for the primary test method. Prediction deviations (Δ) are monitored using statistical quality control charts at a frequency that is commensurate with the criticality of the application. Between validation tests, performance tests are conducted to verify that the instrument is performing in a consistent fashion.

12.0 Method Performance

12.1 Spectral Quality. Refer to ASTM D8321 for analytical requirements, evaluation of data quality, and analysis of uncertainty.

12.2 Sampling QA/QC. The analyte spike procedure of section 9 of this method, the QA spike of section 8.6.2 of this method, and the validation procedure of section 13 of this method are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations. This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 9.0 and 8.6.2 of this method and results from a previous method validation study support the use of this method in the application. Several factors can contribute to uncertainty in the measurement of spiked samples. Factors which can be controlled to provide better accuracy in the spiking procedure are listed in sections 12.2.1 through 12.2.4 of this method.

12.2.1 Calibration gas. Usually the calibration standard is certified to within ± 2 percent. With reactive analytes, such as HCl, the certified accuracy in a commercially available standard may be no better than ± 5 percent.

12.2.2 Temperature. Temperature measurements of the cell shall be quite accurate. If practical, it is preferable to measure sample temperature directly, by inserting a thermocouple into the cell chamber instead of monitoring the cell outer wall temperature.

12.2.3 Pressure. Accuracy depends on the accuracy of the barometer, but fluctuations in pressure throughout a day may be as much as 2.5 percent due to weather variations.

13.0 Method Validation Procedure

This validation procedure, which is based on EPA Method 301 (40 CFR part 63, appendix (A)), may be used to validate this method for the analytes in a gas matrix. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.

13.1 Section 6.0 of Method 301 (40 CFR part 63, appendix A), the Analyte Spike procedure, is used with these modifications. The statistical analysis of the results follows section 12.0 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

13.1.1 The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.

13.1.1.1 Sample stability is not calculated as the NIR system does not retain samples and analysis is conducted in near real time.

13.1.2 The spike gas is introduced before the NIR Analyzer sample filtering systems.

13.1.3 Spiked effluent may be separated from the unspiked sample and measured simultaneously.

13.1.4 A single NIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).

13.1.5 All of the validation measurements are performed sequentially in a single “run” (section 3.26 of this method).

13.1.6 The measurements analyzed statistically are each independent (section 3.22 of this method).

13.1.7 A validation data set can consist of more than 12 spiked and 12 unspiked measurements, or 6 quadruplicate samples when comparing the candidate test method against a validated method.

13.2 *Batch Sampling.* The procedure in sections 13.2.1 through 13.2.2 may be used for stable processes. If process emissions are highly variable, the procedure in section 13.2.3 shall be used.

13.2.1 With a single NIR instrument and sampling system, begin by collecting spectra of two unspiked samples. Introduce the spike flow into the sampling system and allow 10 cell volumes to purge the sampling system and NIR cell. Collect spectra of two spiked samples. Turn off the spike and allow 10 cell volumes of unspiked sample to purge the NIR cell. Repeat this procedure until the 24 (or more) samples are collected.

13.2.2 In batch sampling, collect spectra of 24 distinct samples. (Each distinct sample consists of filling the cell to ambient pressure after the cell has been evacuated.)

13.2.3 Alternatively, a separate probe assembly, line, and sample pump can be used for spiked sample. Verify and document that sampling conditions are the same in both the spiked and the unspiked sampling systems. This can be done by wrapping both sample lines in the same heated bundle. Keep the same flow rate in both sample lines. Measure samples in sequence in pairs. After two spiked samples are measured, evacuate the NIR cell, and turn the manifold valve so that spiked sample flows to the NIR cell. Allow the connecting line from the manifold to the NIR cell to purge thoroughly (the time depends on the line length and flow rate). Collect a pair of spiked samples. Repeat the procedure until at least 24 measurements are completed.

13.3 Simultaneous Measurements With Two NIR Systems. If unspiked effluent concentrations of the target analyte(s) vary significantly with time, it may be desirable to perform synchronized measurements of spiked and unspiked sample. Use two NIR systems, each with its own cell and sampling system to perform simultaneous spiked and unspiked measurements. The optical

configurations shall be similar, if possible. The sampling configurations shall be the same. One sampling system and NIR analyzer shall be used to measure spiked effluent. The other sampling system and NIR analyzer shall be used to measure unspiked flue gas. Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.3.1 If batch sampling is used, synchronize the cell evacuation, cell filling, and collection of spectra. Fill both cells at the same rate (in cell volumes per unit time).

13.3.2 If continuous sampling is used, adjust the sample flow through each gas cell so that the same number of cell volumes pass through each cell in a given time (i.e. $TC_1 = TC_2$).

13.4 *Statistical Treatment*. The statistical procedure of EPA Method 301 of this appendix, section 12.0 is used to evaluate the bias and precision. For NIR testing a validation “run” is defined as spectra of 24 independent samples, 12 of which are spiked with the analyte(s) and 12 of which are not spiked. Section 11.0 of EPA Method 301 is used to evaluate the bias and precision when comparing the candidate test method against a validated method.

13.4.1 *Bias*. Determine the bias using equation 7:

$$B = S_m - CS \quad \text{Eq. 7}$$

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

CS = Expected concentration of the spiked samples

13.4.2 *Correction Factor*. Evaluate the statistical significance of the bias. If it is determined that the bias is significant, then calculate a correction factor (CF). Analytical results of the test method are multiplied by the correction factor, if $0.7 \leq CF \leq 1.3$. If it is determined that the bias is significant and $CF > \pm 30$ percent, then the test method is considered to “not valid.”

13.4.3 If measurements do not pass validation, evaluate the sampling system, instrument configuration, and analytical system to determine if improper set-up or a malfunction was the cause. If so, repair the system and repeat the validation.

13.5 Alternatively, comparing the candidate test method against a validated method can be used to determine the bias and precision of the NIR system. The statistical analysis of the results follows section 11.0 of EPA Method 301.

14.0 *Pollution Prevention*

The extracted sample gas is vented outside the enclosure containing the NIR system and gas manifold after the analysis. In typical method applications the vented sample volume is a small fraction of the source volumetric flow and its composition is identical to that emitted from the source. When analyte spiking is used, spiked pollutants are vented with the extracted sample gas. Approximately 1.6×10^{-4} to 3.2×10^{-4} lbs of a single HAP may be vented to the atmosphere in a typical validation run of 3 hours. (This assumes a molar mass of 50 to 100 g, spike rate of 1.0 L/min,

and a standard concentration of 100 ppm). Minimize emissions by keeping the spike flow off when not in use.

15.0 Waste Management

Small volumes of laboratory gas standards can be vented through a laboratory hood. Neat samples must be packed and disposed according to applicable regulations. Surplus materials may be returned to supplier for disposal.

Gas Phase Product Limitations - Most optical spectroscopic technologies are unable to quantify some or all inert components, such as Nitrogen, in the gas phase. These components may be quantified by difference or alternate technologies may also be utilized in conjunction with optical spectroscopy to obtain empirical analyses for the inert components.

16.0 References

1. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, EPA Contract No. 68D20163, Work Assignment I-32, September 1994.
2. "FTIR Method Validation at a Coal-Fired Boiler". Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No.: EPA-454/R95-004, NTIS No.: PB95-193199. July, 1993.
3. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.
4. "Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.
5. "Fourier Transform Infrared Spectrometry," Peter R. Griffiths and James de Haseth, Chemical Analysis, 83, 16-25,(1986), P.J. Elving, J.;D. Winefordner and I.M. Kolthoff (ed.), John Wiley and Sons.
6. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.
 1. 7. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," Applied Spectroscopy, 39(10), 73-84, 1985.

ASTM D6122 - Standard Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer Based Analyzer Systems

ASTM D6708 - Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

ASTM D8321 - Standard Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements

GPA 2166 - Obtaining Natural Gas Samples for Analysis by Gas Chromatography

GPA 2174 - Obtaining Liquid Hydrocarbons Samples for Analysis by Gas Chromatography

GPA 2177 - Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

GPA 2198 - Selection, Preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends

GPA 2261 - Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography

GPA 2186 - Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography

GPA 2286 - Method for the Extended Analysis of Natural Gas and Similar Gaseous Mixtures by Temperature Programmed Gas Chromatography

17.0 Tables, Diagrams, Flowcharts and Validation Data

11.0 Procedures

Spectroscopic Multivariate Quantitative Analysis Procedure

1. *Selecting the Calibration Set* – The calibration set is intended to represent all the chemical and physical variation which would normally be encountered during routine analysis for the desired application. For the CLS example, we would like to get the individual pure component spectra for the hydrocarbons in the lab.
2. *Determination of Concentrations or Properties, or Both, for Calibration Samples* – The chemical, physical or performance properties, or both, of samples in the calibration set must be accurately and precisely measured by the PTM in order to accurately calibrate the multivariate model for prediction of the unknown samples. For simple mixtures containing only a few chemical components, it is generally possible to prepare mixtures that can serve as standards for the multivariate calibration. For complex mixtures, preparation of calibration standards is generally impractical, and the multivariate calibration of a spectroscopic analysis must typically be performed on actual process samples. The process samples are sent to an analytical lab for analysis based on one or more ASTM standards as PTMs (ASTM D1945 or GPA 2261 for flare gas samples). For the CLS example, the pure

component samples can be purchased from a specialty gas manufacturer that provides certified values of concentrations or properties, or both, of the samples. Some properties can also be calculated from the concentrations, for example, net heating value (NHV) calculation based on ASTM D3588.

3. *The Collection of Spectra* – The collection of spectral data must be performed with care to present calibration samples, validation samples, and prediction (unknown) samples for analysis in an alike manner. Variation in sample presentation technique among calibration, validation, and prediction samples will introduce variation and error which has not been modeled within the calibration. For the CLS example, the spectra of calibration samples (individual pure components) are collected in the lab (Figure 2). The spectra of validation samples and prediction samples can be collected in the lab or during the process measurement.
4. *Calculating the Multivariate Model* – The calculation of multivariate (calibration) models may involve a variety of data treatments and algorithms. A variety of statistical techniques are used to evaluate and optimize the model.
 - a. The common spectra preprocessing algorithms used are spectral range selection, numerical derivatives, smoothing filters, standard normal variate, mean centering, etc. Hydrocarbon absorption features are mainly located at higher wavelength region. Typically, select 1600-1795nm range for building the multivariate model. Numerical derivatives can remove varying baselines. Digital filters may be employed to smooth data, improving signal to noise ratio. Standard normal variate normalizes the spectra, but it is not used in CLS models. Mean-centering refers to a procedure in which the average of the calibration spectra (average spectral intensity over the calibration spectra as a function of spectral position) is calculated and subtracted from the spectra of the individual calibration samples prior to the development of the model.
 - b. Multivariate mathematical techniques are used to relate the spectra measured for a set of calibration samples to the PTMRs obtained by applying the PTM to the same set of samples. The object is to establish a multivariate model that can be applied to the spectra of future, unknown, samples to predict property or concentration values (PPTMRs). For the CLS model, equation (3) can be solved for the spectra of the components:

$$\underline{A} = (\underline{C}'\underline{C})^{-1}\underline{C}'\underline{B}^{-1}\underline{X} \quad (4)$$

JP3 uses MatLab (MathWorks) and PLS_Toolbox (Eigenvector Research, Inc.) to build multivariate models. An example of CLS model is attached as “CLS_1psi_70deg.mat” file.

The predicted concentrations of the components of an unknown sample with spectrum $\underline{x}$ measured with pathlength b is then given by

$$\underline{c} = b^{-1}\underline{x}\underline{A}'(\underline{A}\underline{A}')^{-1} \quad (5)$$

- c. Inverse Least Squares (ILS) techniques are also utilized as described in Chapter 14 of ASTM D8321. Briefly, ILS techniques attempt to solve the problem described by:

$$\underline{y} = \underline{X}\underline{p} + \underline{e} \quad (6)$$

Where $\underline{y}$ is a vector of primary test method results, $\underline{X}$ is a matrix of spectra responses, $\underline{p}$ is a

prediction vector and e is the residual error vector. The prediction vector is estimated in a way that minimizes the sum of squares of the errors. In the case of multilinear regression (MLR) a selective portion of the spectral response matrix is chosen which correlates most directly with the primary test method. In principal component regression (PCR) and partial least squares (PLS) the spectral responses are first projected into a reduced principal component or latent variable space before the regression vector is estimated. This projection simplifies the spectral response matrix and focuses on spectral features with the greatest correlation to the primary test method. Once determined, the prediction vector is multiplied by a new, unknown spectral response to calculate the predicted primary test method result.

- d. Various procedures and statistics are used to evaluate and optimize the performance of multivariate models. The standard error of calibration (SEC), standard error of cross-validation (SECV), and outlier statistics (Hotelling's T-Squared and Q-Residual) are used in JP3's model building process to optimize the number of variables and the performance of multivariate models. The CLS model is much simpler that doesn't have SEC or SECV statistics.
5. *Establishing Criteria for Identifying Outliers During Analysis* – Based on the outlier statistics for the calibration spectra, limits are set for each statistic. If, during analysis of an unknown, the value for an outlier statistic exceeds the limit, the spectrum is considered an outlier and the PPTMR is considered invalid. JP3 Verax analyzer has two sets of model alarm limits for Hotelling's T-Squared and Q-Residual, one set for warning and the other set for fault. When warning happens, the models are still working and the analyzer still outputs the prediction results. The data will be reviewed to evaluate the cause of the alarm. When fault happens, the analyzer will block the model prediction results.
6. *Validation of the Multivariate Model* – Validation of the efficacy of a specific multivariate model requires that the model be applied for the analysis of a separate set of model validation samples, and that the PPTMR values for these samples be statistically compared to PTMR values obtained by application of the PMT to these same samples. Both lab prepared samples and process samples can be used for model validation purpose.
7. *Application of the Model for the Analysis of Unknowns* – The multivariate model is applied to the spectra of unknown samples to produce the PPTMR. Outlier statistics are used to detect when the analysis involves extrapolation of the model. For the CLS example, equation (5) is used to predict the concentrations of unknown samples.
8. *Routine Analysis and Monitoring* – Once the efficacy of one or more multivariate model is established, the equations must be monitored for continued accuracy and precision. For online measurement, process samples are usually used to monitor the model performance. Alternatively, a known standard sample can be injected to the flow cell for performance check. Simultaneously, the instrument performance must be monitored to trace any deterioration in performance to either the multivariate model itself or to a failure in the instrument. A few instrument parameters are monitored automatically for JP3 Verax analyzer, such as transmission, spectral noise level, spectrometer wavelength drift correction, internal temperatures.
9. *Calibration Transfer and Instrument Standardization* – A model built using calibration spectra from one analyzer may be used to analyze unknown samples on additional analyzers, or on the first

analyzer after major maintenance has been performed. It may be necessary to adjust the model or the analyzers in order to achieve acceptable PPTMR and outlier statistics. In this practice, the term calibration transfer is used to refer to procedures that are used to adapt the model from the first analyzer to perform correctly on the other analyzers. Instrument standardization is used to refer to procedures that are used to adapt the other analyzers to adequately match the first analyzer such that no change to the model is required to achieve correct performance. For JP3 Verax analyzer, the spectrometer-to-spectrometer repeatability is excellent due to the internal wavelength reference and amplitude reference module. Every spectrometer scan is monitored and corrected based on the wavelength reference and amplitude reference signals. We typically use the same wavelength step resolution and wavelength range for all our installations. The spectra format is consistent. The calibration transfer is straightforward.

Appendix C: Process Flow Charts

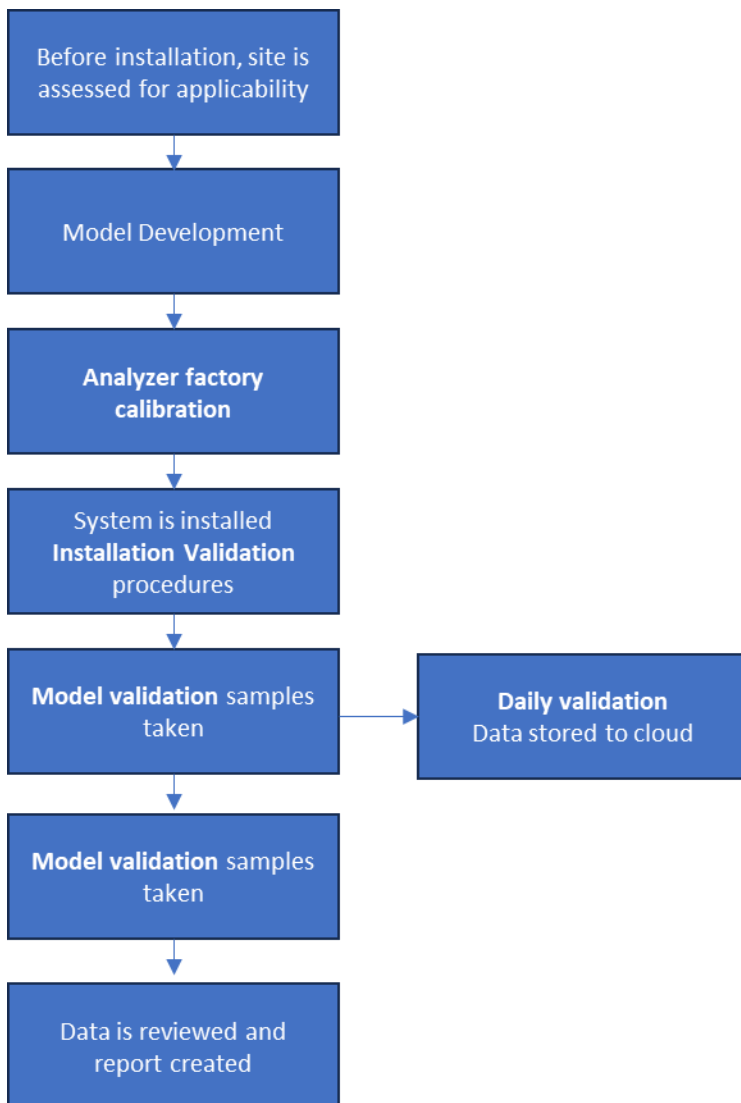


Figure C1: VeraCal Process Monitoring

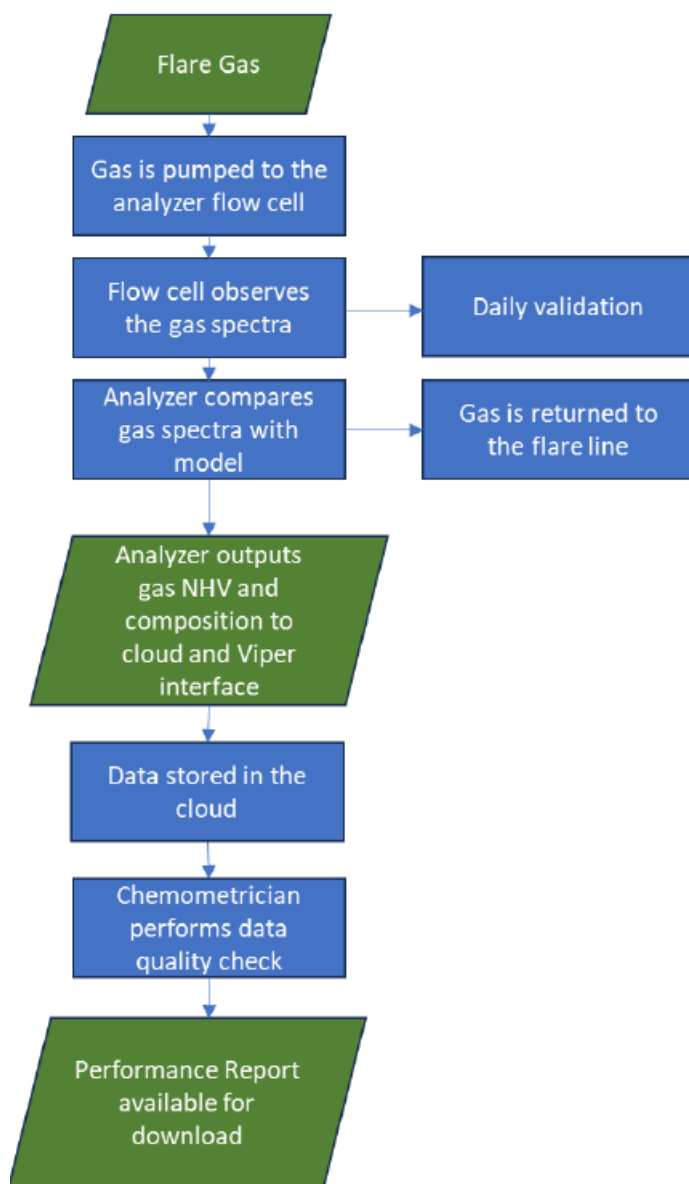


Figure C2: Normal Operation Flow Chart

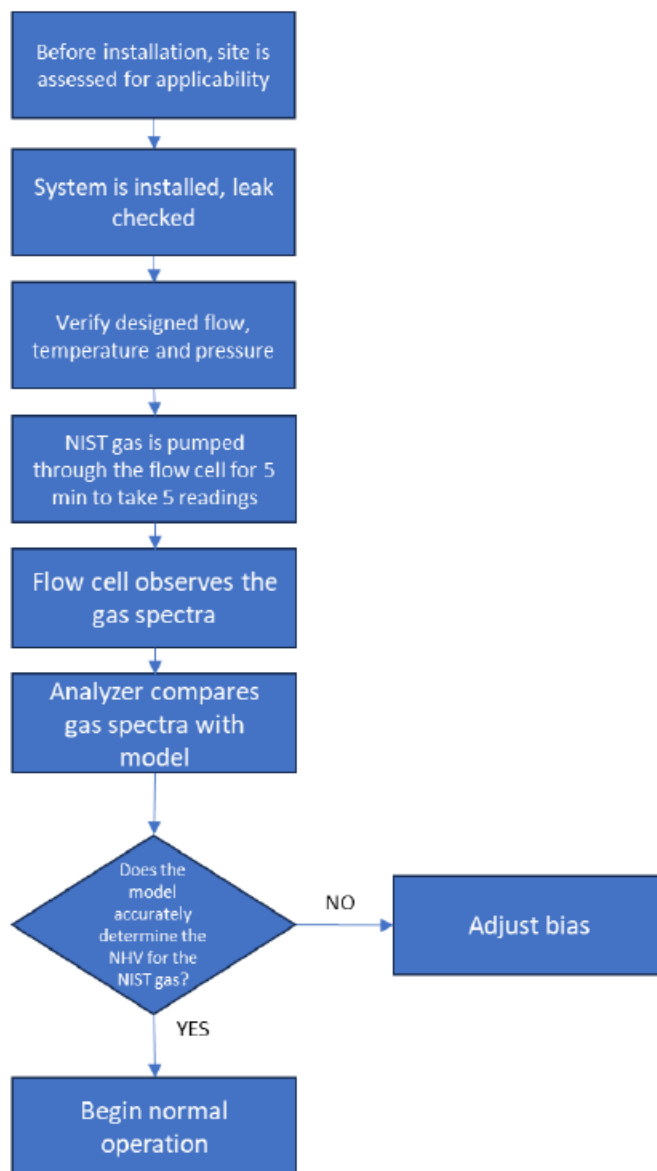


Figure C3: Installation Procedures

**JP3 Measurement
EPA MACT CC Alternative Test Method Request**

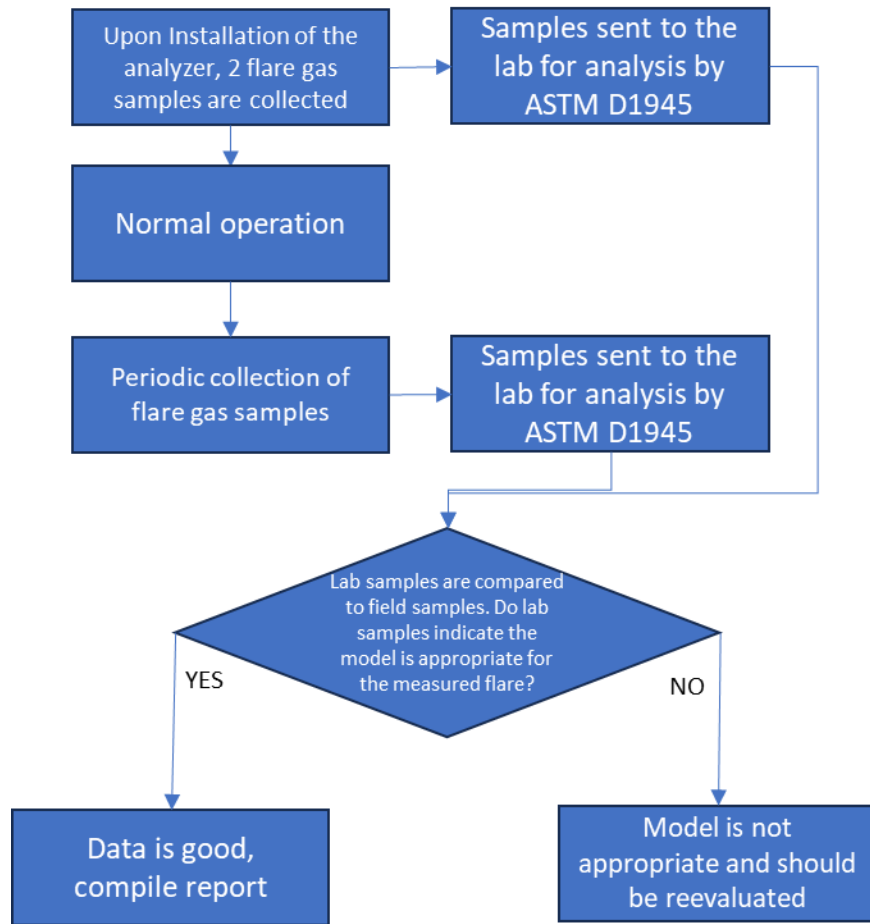


Figure C4: Model Development

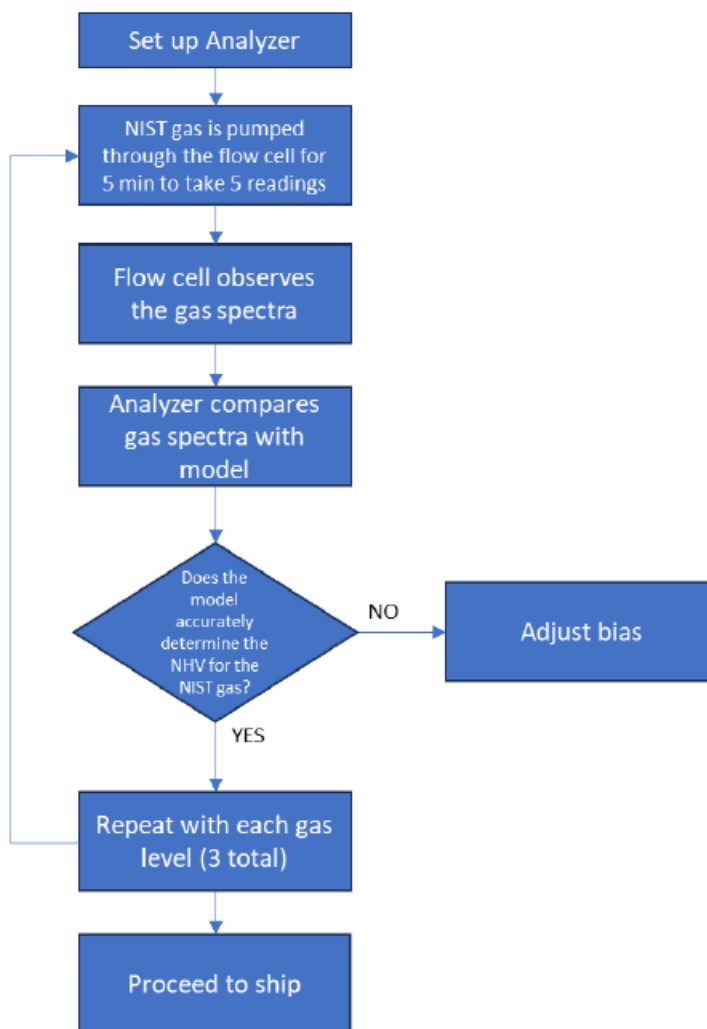


Figure C5: Model Development

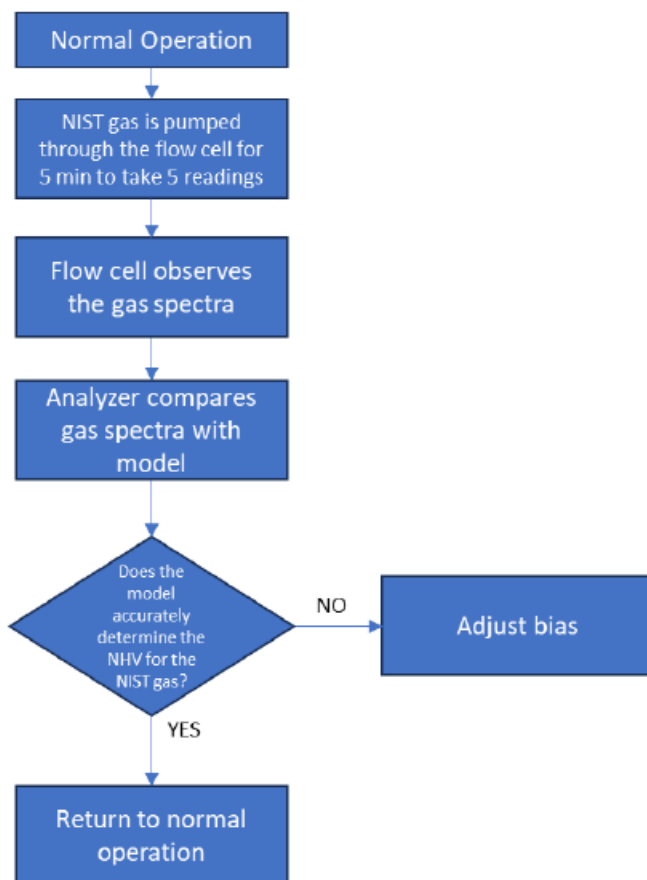


Figure C6: Quarterly Calibration

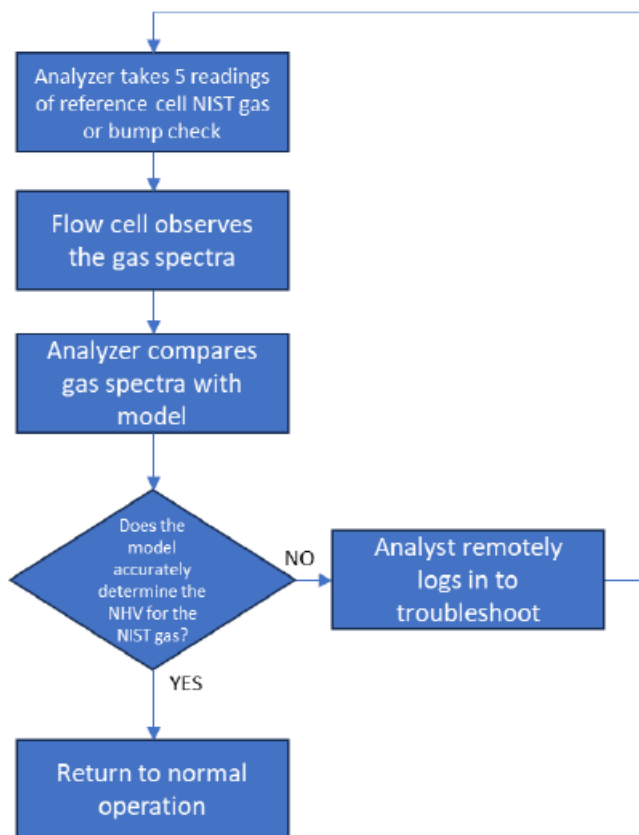


Figure C7: Daily Validation

Appendix D: Validation Data Sets

The following datasets represent validation data for the JP3 analyzers. These sites represent several different basins including Eagle Ford, Marcellus, Bakken and Permian. They also cover multiple applications including flare, fuel gas, and vaporization. The range of NHV covered by these data is 400-2000BTU. Site 4, a vapor recovery application includes low BTU Net Heating Values. Site 6 consists of a 3-month validation run where the JP3 analyzer was inline with a process GC.

For the data sets for Sites there are 12 field samples taken for analysis by GC, paired with 12 readings from the JP3 analyzer. Each quadruplicate sample has two measurements by GC and two measurements by the JP3 analyzer.

Site 1 Flare Example (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.571	10%			
NHV	N/A	0.30	1.78	N/A	< ±2% of span	1241.93	1275.53
C1	0.1 mol%	0.25	0.21	N/A	< ±6% of span	77.96	77.67
C2	0.3 mol%	0.57	0.08	N/A	< ±5% of span	9.70	9.58
C3	0.3 mol%	1.57	2.43	N/A	< ±2% of span	6.08	5.24
iC4	0.3 mol%	1.70	2.52	N/A	< ±2% of span	1.35	1.73
nC4	0.3 mol%	0.83	0.45	N/A	< ±2% of span	1.71	1.64
iC5	0.3 mol%	0.03	1.41	N/A	< ±2% of span	0.59	0.76
nC5	0.3 mol%	0.05	1.46	N/A	< ±2% of span	0.49	0.63
C6+	0.3 mol%	0.29	1.99	N/A	< ±2% of span	0.14	0.34

Site 2 Fuel Gas Example (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.57	10%			
NHV	N/A	2.19	0.12	N/A	< ±2% of span	1187.84	1188.33
C1	0.1 mol%	2.57	2.66	1.30%	< ±2.5% of span	81.45	80.40
C2	0.3 mol%	1.99	2.59	8.7%	< ±2.5% of span	9.99	10.94
C3	0.3 mol%	2.36	0.78	N/A	< ±2% of span	4.28	4.44
iC4	0.3 mol%	0.96	0.53	N/A	< ±2% of span	0.47	0.45
nC4	0.3 mol%	0.69	1.31	N/A	< ±2% of span	1.08	0.96
iC5	0.3 mol%	0.57	2.41	N/A	< ±2% of span	0.22	0.18
nC5	0.3 mol%	1.00	2.50	N/A	< ±2% of span	0.24	0.20
C6+	0.3 mol%	4.00	2.18	N/A	< ±2% of span	0.27	0.21

Site 3 Depropanizer Gas Example (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.571	10%			
NHV	N/A	1.44	0.69	N/A	< ±2% of span	1864.23	1859.31
C1	0.1 mol%	1.09	1.55	N/A	< ±2% of span	29.22	29.55
C2	0.3 mol%	0.65	0.24	N/A	< ±2.1% of span	27.71	27.80
C3	0.3 mol%	0.79	2.17	N/A	< ±2% of span	36.10	35.41
iC4	0.3 mol%	1.06	1.06	N/A	< ±2% of span	2.17	2.26
nC4	0.3 mol%	0.70	0.91	N/A	< ±2% of span	3.00	3.13
iC5	0.3 mol%	0.29	2.35	N/A	< ±2% of span	0.03	0.04
nC5	0.3 mol%	0.00	1.49	N/A	< ±2% of span	0.01	0.01
C6+	0.3 mol%	2.98	1.67	N/A	< ±2% of span	0.03	0.01

JP3 Measurement EPA MACT CC Alternative Test Method Request

Site 4 Vapor Recovery (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.571	10%			
NHV	N/A	1.97	1.34	N/A	< ±2% of span	283.61	292.70
C1	0.1 mol%	0.53	2.45	N/A	< ±2% of span	0.06	0.04
C2	0.3 mol%	1.19	0.22	N/A	< ±2% of span	0.03	0.03
C3	0.3 mol%	0.41	2.48	N/A	< ±2% of span	0.00	0.01
iC4	0.3 mol%	0.37	0.68	N/A	< ±2% of span	0.04	0.04
nC4	0.3 mol%	1.24	2.48	N/A	< ±2% of span	1.61	1.47
iC5	0.3 mol%	1.20	0.50	N/A	< ±2% of span	2.10	2.12
nC5	0.3 mol%	3.38	2.11	N/A	< ±2% of span	2.55	2.73
C6+	0.3 mol%	2.11	2.97	7%	< ±2% of span	1.40	1.51

Site 5 Field Gas Example (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.571	10%			
NHV	N/A	0.20	1.46	N/A	< ±2% of span	1047.87	1039.27
C1	0.1 mol%	0.69	1.00	N/A	< ±2% of span	93.54	93.23
C2	0.3 mol%	1.68	0.33	N/A	< ±2% of span	3.61	3.53
C3	0.3 mol%	1.93	1.74	N/A	< ±2% of span	0.91	0.64
iC4	0.3 mol%	0.49	0.99	N/A	< ±2% of span	0.13	0.20
nC4	0.3 mol%	0.67	2.09	N/A	< ±2% of span	0.14	0.23
iC5	0.3 mol%	0.46	0.29	N/A	< ±2% of span	0.09	0.07
nC5	0.3 mol%	1.45	0.71	N/A	< ±2% of span	0.04	0.03
C6+	0.3 mol%	0.09	0.32	N/A	< ±2% of span	0.13	0.10

Site 6 Sales Gas Example (12 Samples or 6 Quadruplicate Samples)							
Property	Limit of Detection	Precision F-Statistics	Bias T-Statistics	Relative Bias	Accuracy	Average VERAX determined value	Average GC determined value
Allowed Limit		4.28	2.571	10%			
NHV	N/A	3.15	1.18	N/A	< ±2% of span	1029.93	1030.27
C1	0.1 mol%	1.48	0.18	N/A	< ±2% of span	93.11	93.11
C2	0.3 mol%	1.84	0.98	N/A	< ±2% of span	4.20	4.23
C3	0.3 mol%	3.09	0.87	N/A	< ±2% of span	0.32	0.31