CRC Report No. E-140

Low NOx and NMOG – Modeling

Final Report

September 2024

COORDINATING RESEARCH COUNCIL, INC. 5755 NORTH POINT PARKWAY ● SUITE 265 ● ALPHARETTA, GA 30022

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Low NOx and NMOG - Modeling

Project E-140

Submitted to:

Coordinating Research Council 5755 North Point Parkway, Suite 265 Alpharetta, GA 30022 Attention: Amber Leland

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POWERTRAIN ENGINEERING DIVISION

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Southwest Research Institute® Final Report September 2024

FOREWORD

This report covers modeling effort conducted by Southwest Research Institute (SwRI) for the Coordinating Research Council (CRC). The project, performed under CRC contract E-140, was conducted between August of 2022 and December of 2023. The internal SwRI project number was 03.27566. The SwRI project manager was Matt Blanks, assisted by Chris Sharp and Michael Ross. Statistical analysis and support were provided by Dr. Travis Kostan.

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1.0 EXECUTIVE SUMMARY

This report documents a project conducted by SwRI on behalf of the Coordinating Research Council (CRC). The goal of this project was to develop a model to demonstrate and identify opportunities to reduce the uncertainty of the current technology used to measure oxides of nitrogen (NOx) and non-methane organic gas (NMOG) for chassis dynamometer light-duty and medium-duty certification testing.

The United States Code of Federal Regulations (CFR) specifies the procedure and requirements for measuring exhaust emissions of NO_x and $NMOG$ from mobile sources. As a first step, the CFR requirements were reviewed and documented to identify terms that could introduce error and impact the final emission measurements. Approximately 115 terms were identified as possible sources of error. From this list, terms were removed from the list if a general cause-effect relationship could not be identified. For example, a general transfer function could not be identified that characterized the relationship between emission levels of NO_x and the load absorbed by a chassis dynamometer. Similarly, the influence of a test cell radiator cooling fan on emissions could not be determined universally. For this reason, many error terms were not included or were considered out of scope for this study. Through guidance from the CRC project committee, the initial list was reduced to 24 error terms that warranted further investigation. An individual uncertainty analysis was conducted for 22 of the 24 error terms listed in [Table 1](#page-8-0) for inclusion in the NO_x and NMOG uncertainty model. Direct model inputs, rather than an uncertainty analysis, were used for the last two error terms: THC hang-up and exhaust dilution factor. These terms are highly dependent upon equipment and procedures implemented by individual laboratories rather than the uncertainty of their value.

After individual uncertainty analyses were completed, a Monte Carlo simulation model was built to sample from each of the individual error terms and calculate the resulting overall uncertainty of NMOG + NO_x . The model is very flexible and can be tailored to vehicle, laboratory, and emission-level specifics. [Table 2](#page-9-0) gives the nominal NMOG + NO_x level without uncertainty added. It also gives the overall uncertainty using four (4) different test vehicle scenarios. For these vehicles, the estimated overall uncertainty of NMOG + NO_x was approximately 3% to 6%,

assuming THC hang-up was not present. The overall uncertainty could increase by 7% to 18% if a 100 ppb THC hang-up was not corrected. For context, the CFR limit for hang-up is five times this level (500 ppb). THC hang-up is the result of contamination in a laboratory's emission sampling system and is further discussed in the body of this report. Short-term repeatability of the NO_x and THC laboratory analyzers were also large contributors to the overall uncertainty. Dilution Factor (DF) uncertainty was also studied. An error in DF could contribute an additional 2% to 4% uncertainty to the NMOG + NO_x measurement.

*Hypothetical Tier 4 Vehicle Scenarios

[Figure 1](#page-10-0) shows the individual contribution of each error term to the overall uncertainty of NMOG + NO_x for the Tier 3 Bin 30 example vehicle given in [Table 2.](#page-9-0) Example scenarios of THC hang-up and exhaust dilution factor errors are also included in the chart, although these scenarios are highly dependent upon laboratory practices. The other example vehicles are discussed in Section 3.4.

Setting aside THC hang-up, an overall uncertainty of 3% to 6% does not prevent measurement of NMOG + NO_x , even down at the Tier 4 Bin 10 certification level. For this study, it was assumed that an engineering margin of 50% would be used by the manufacturer when calibrating the vehicle, so the modeled uncertainties would be covered by this margin. However, the 500 ppb CFR limit for THC hang-up is not sufficient and could impact the ability to demonstrate compliance at the Tier 4 levels. In this case, THC hang-up should be limited to 30 ppb. Below are recommendations to reduce the overall uncertainty of NMOG + NO_x . Additional recommendations are given in section 3.5.

- Reduce THC hang-up to below 30 ppb
- Use the average of multiple THC sample and background bag readings
- $-$ Use the average of multiple NO_x sample and background bag readings
- $-$ Use a NO_x analyzer range at or below 2 ppm
- $-$ Reduce the tolerance of propane recovery test to $+/- 1\%$

FIGURE 1. NMOG + NOX UNCERTAINTY FROM INDIVIDUAL ERROR TERMS, TIER 3 BIN 30 EXAMPLE VEHICLE

2.0 INTRODUCTION

Current emissions measurement capabilities may not be sensitive enough to measure very low Oxides of Nitrogen (NO_x) and Non-Methane Organic Gas (NMOG) emissions that will be required for future Light-Duty (LD) and Medium-Duty (MD) vehicles when certificated at Super Ultra-Low Emission Vehicle (SULEV) levels. The uncertainty and limitations of the current sampling and analytical systems technology needs to be understood to identify potential areas for improvement.

3.0 SCOPE OF WORK

The objective of this project was to develop an uncertainty model of the current methodology used to measure NMOG + NO_x for chassis dynamometer light-duty (LD) and medium-duty (MD) certification tests. Individual sources of uncertainty were identified and

analyzed to assess the error introduced by each term. The model then combined each individual error term and calculated the overall uncertainty of $NMOG + NO_x$. The model also allowed a sensitivity analysis to be conducted that identified terms that contributed substantial error. Based on the sensitivity analysis, recommendations for reducing uncertainty were made. The major tasks involved in this project are given below and details for each task are discussed in the following sections.

Major Project Tasks:

- Build a model of the typical technique used to measure NMOG and NO_x
- Compile uncertainty analysis for model inputs
- Estimate the overall uncertainty for NO_x and NMOG measurements using model
- Analyze model for sensitivity to individual inputs
- Recommend potential changes to reduce the overall uncertainty of NMOG and NOx measurements
- Provide the working model to CRC

3.1 Build a model of the current technique used to measure NMOG and NOx

The first step was to develop an uncertainty model that characterized the method and technique used to measure NMOG and NO_x . Calculations and requirements for these measurements are given in 40 CFR parts 1065 and 1066. The CFR allows the use of different measurement techniques, however, this study focused on a sampling technique that uses a Constant Volume Sampler (CVS) to dilute raw vehicle exhaust before emission measurements are taken. Appropriate CFR equations for the calculation of NMOG and NO_x are given in Appendix A and the variables for each equation are listed in [Table 3](#page-11-0) and [Table 4.](#page-12-0)

TABLE 3. CFR EQUATION VARIABLES FOR NMOG

Oxides of Nitrogen (NOx)						
Measurement	CFR Equation Variable					
H-C ratio	α					
O-C ratio	β					
$CO2$ Sample $(\%)$	XCO ₂					
CO Sample (ppm)	XCO					
CH4 Sample (ppm)	XCH ₄					
NMHC Sample (ppm)	XNMH					
NOx Sample (ppm)	X(emission)dexh					
NOx Background (ppm)	X(emission)bkgnd					
Ambient Humidity (gH2O / kg dry air)	H					
Dilute Exhaust Volume at Flow Meter (m3)	VCVSstd					
Sum of Dilute Extractions (m^3)	Vgasstd + VPMstd - Vsdastd					
Distance (mi)	D					

TABLE 4. CFR EQUATIONS VARIABLES FOR NOX

3.1.1 Model Overview

A Monte Carlo simulation was chosen rather than a traditional error formula. Traditional error propagation formulas, such as those used in the Guide to Uncertainty in Measurement (GUM), require assumptions to be made about the distributions of individual uncertainties used to calculate the overall uncertainty. Deviations of true distribution from the assumed distribution can lead to an unrealistic final calculation of overall uncertainty. In contrast, a Monte Carlo simulation has the flexibility to support both assumed distributions along with direct sampling of data sources in cases where the data may not be recognizable as being from a known distribution. While most errors were simulated from a normal distribution, there were cases where non-symmetrical distributions were selected and cases where direct sampling of errors was applied. The model was also built with the flexibility to modify any of these default choices for any error term. Custom distributions can be selected by the user, but these modifications are limited to the normal distribution and uniform distribution cases.

For this project, the Monte Carlo model was set to simulate 10,000 random combinations of error terms. Results from the simulation were interpreted by inspection of the quantiles of the resulting distribution. The 95% confidence interval was obtained by calculating the distance from the 2.5th percentile to the 97.5th percentile, but the model is adjustable to allow the user to calculate any desired confidence interval. The model also calculated the uncertainty for each of the intermediate equations allowing the user to study uncertainty at all levels. For example, the model gives the uncertainty for the calculated dilution factor (DF) (40 CFR 1066.610-2). This allows the user to investigate the impact of calculated DF uncertainty compared to a DF that was directly measured in the test cell.

To populate the model, the user inputs all details specific to their test vehicle, laboratory equipment, test cycle, and final target emission levels for each pollutant. Target emission levels are entered in units of grams per mile (g/mi) so the user can study uncertainty as it relates to regulatory emission levels. From the populated inputs, the model uses an iterative technique to

back calculate all variables required by the CFR equations given in [Table 3](#page-11-0) are given in [Table 4.](#page-12-0) Errors for each term are applied at the appropriate levels as the CFR equations are calculated. For example, the error associated with the linearity of a NO_x analyzer is applied to the phase-level concentration for both sample and ambient measurements, before background correction equations are calculated.

After all error terms are applied, and the CFR calculations are computed, the model calculates the summary statistics of all simulated cases of NMOG, NO_x , and NMGO + NO_x for the target emission levels specified by the user. As previously mentioned, a symmetric 95% confidence interval is the default setting, but a different confidence interval can be specified by the user.

The model also contains a sweep function to allow the user to iteratively step through modifications to individual error terms or even change major model inputs to see how the resulting uncertainty is affected. For example, the user could sweep through different CVS flow rates while holding all other inputs constant. This exercise would show how the overall error is affected as measured concentrations in each sample bag change. The sweep function also allows individual error terms to be turned on, off, or modified to emulate a laboratories' setup.

3.1.2 Example of Model Results

As an example use of the model, [Table 5](#page-13-0) and [Table 6](#page-14-0) show how the overall uncertainty of $NMOG + NO_x$ increases as CVS flowrate increases. For this very simplistic example, the CVS flowrates were selected for a 4-phase FTP-75 test to give a 7:1 dilution factor (DF) for [Table 5](#page-13-0) and a 20:1 DF for [Table 6.](#page-14-0) These DFs represent the lowest and highest acceptable settings allowed by the CFR. The nominal FTP composite NMOG + NO_x result was 0.0162 g/mi for both scenarios, however, the larger DF increased uncertainty. When compared to the nominal value, the upper and lower percentiles both widened by approximately 1.3%. Although the change is small, this example shows how the model can be used to select laboratory settings that will reduce the overall uncertainty of the result.

Monte Carlo Composite Results (g/mi)									
FTP (4-Phase)	Nominal	Mean	Median	Standard Deviation	Lower Percentile	Upper Percentile	Lower Percentile, % of Nominal	Upper Percentile, % of Nominal	
NO _x	0.0070	0.0070	0.0070	0.0001	0.0068	0.0072	$-3.75%$	2.53%	
NMOG	0.0092	0.0091	0.0091	0.0001	0.0089	0.0094	-3.32%	2.40%	
$NMOG + NOx$	0.0162	0.0161	0.0161	0.0002	0.0158	0.0165	$-2.86%$	1.81%	

TABLE 5. MODEL RESULTS WITH 7:1 DILUTION FACTOR

TABLE 6. MODEL RESULTS WITH 20:1 DILUTION FACTOR

3.2 Compile Uncertainty Analysis for Model Inputs

As previously discussed, [Table 1](#page-8-0) shows the 24 individual error terms that were analyzed for uncertainty. The analysis technique used was not the same for all terms, but many of the terms fell into groups that were analyzed in a similar fashion. For example, to understand the error associated with the linearity of a NO_x analyzer, we used historic calibration data collected from SwRI and CRC member labs. We used this same data source for all gaseous analyzers. Similarly, the error associated with the named concentration of all calibration bottles used a more traditional error propagation calculation.

For all error terms, we used the below steps to determine the best approach for understanding uncertainty.

- 1. State the assumed standard practice of emission laboratories.
- 2. Characterize the error of the standard practice using one of the following techniques.
	- a. Assume an uncertainty distribution based on standard lab practices (both shape and size)
	- b. Collect actual data and use it to estimate the uncertainty distribution (both shape and size)
	- c. Collect actual data and sample it directly to determine uncertainty

The following sections describe the selected approach for the various groupings of error terms.

3.2.1 Analyzer Linearity Error

Historical calibration records were obtained from both SwRI and CRC member labs to estimate the error associated with the analyzer linearity of a NO_x analyzer, THC analyzer, CH₄ analyzer, CO analyzer, and $CO₂$ analyzer. Data from multiple representative analyzer ranges were obtained for each analyzer to determine if separate error functions were necessary depending on analyzer range. An example of the data obtained from NO_x analyzer calibrations is shown below in [Figure 2.](#page-15-0)

FIGURE 2. CALIBRATION DATA FOR NO_X ANALYZERS

From the figure, one can readily see both a slight positive bias and that the percentage errors increase as concentrations decrease. After discussion with the committee, the decision was made to assume that the bias was an artifact of limited data rather than an inherent bias attributable to this type of instrument. Therefore, the standard deviations across target concentrations were estimated by assuming that each of the observed errors was equally as likely to be observed with the opposite sign. With this assumption, the concentrations were binned in groups of similar levels and plotted against the percentage errors, as shown below in [Figure 3.](#page-16-0)

FIGURE 3. NO_X ANALYZER ERROR STANDARD DEVIATIONS VS. TARGET **CONCENTRATION**

For this set of errors, there appeared to be no clear ranking of analyzer ranges for very low concentrations. The primary distinction observed was the minimum standard deviation. The 5 ppm and 10 ppm ranges appeared to have a lower standard deviation for concentrations above 2 ppm. The median error standard deviation for the analyzers at concentrations above 2 ppm was 0.47 for the 20-ppm range and 0.34 for the combined 5 ppm and 10 ppm range data. With the above in mind, a quadratic function was fit to the data below 2.5 ppm, as shown in [Figure 4.](#page-16-1)

FIGURE 4. NOX ERROR STANDARD DEVIATION FUNCTION

All three analyzer ranges utilized the standard deviation error function as shown by the fitted line for measured concentrations up until the point where the line intersects minimum threshold, as determined by the median errors stated above. The function line determines the nominal standard deviation for a measured concentration. However, since each point in [Figure 4](#page-16-1) represents a set of data above or below this line, this deviation from the curve was simulated as well for a given test run. Based on inspection of the model residuals and an Anderson Darling Normality test, the dots were observed to be normally distributed around the line. For higher concentrations, the deviations were represented as the difference from the point to the constant nominal value of 0.34 or 0.47, depending on analyzer range. [Figure 5](#page-17-0) shows the distribution of these data points from the fit line, which can be represented by a Normal $(0, 0.084²)$ distribution.

FIGURE 5. DEVIATION OF NOX DATA FROM FIT LINE

Therefore, the final algorithm for determining an error for the NO_x analyzer was as follows:

Algorithm

1. For test phase 1: If analyzer range is 5 ppm or 10 ppm, then if target concentration (x) < 2.14, then $f_1 = 1.50 - 0.97x + 0.20x^2$ else $f_1 = 0.34$. If analyzer range is 20 ppm, if target concentration (x) < 1.57, then $f_1 = 1.50 - 0.97x + 0.20x^2$ else $f_1 = 0.47$. 2. Calculate final standard deviation including the deviation from the function line as $s_1 = f_1 + e_1$, where $e_1 \sim Normal(0,0.084^2)$. 3. Sample $u_1 \sim uniform(0,1)$.
4. The error for Phase 1 is the *i* 4. The error for Phase 1 is the u_1 -th quantile from Normal(0, s_1).
5. For subsequent phases: For subsequent phases: If the analyzer range of a subsequent phase, Phase j is the same as a previous phase, Phase *i*, then calculate f_i , but let $e_i = e_i$ and $u_i = u_i$.

The value of " u " above represents the randomly chosen location on the normal distribution curve, and "e" was the deviation from the function line in determining the standard deviation. It is important to note in the algorithm above that new values of u and e are sampled only if the analyzer range changed for a given phase, while the nominal standard deviation of the normal distribution

always changes depending on concentration. This reflects the understanding that an analyzer error would directionally be similar for test phases which utilized the same analyzer range, even if the normal distribution being sampled from changes.

The error for THC analyzers and CH4 analyzers was determined following the same process as described above for the NO_x analyzer. Calibration data was collected for 5, 10, 25, and 50 ppm ranges for THC and 10 and 20 ppm ranges for CH4. For these analyzers, there were no differences observed between ranges, and therefore all ranges use the same equations in determining the standard deviation, based on concentration.

For THC the equations for determining the standard deviation of the error were as follows:

- If target concentration (x) < 1.59 ppm, $f_i = 1.46 1.16x + 0.31x^2$.

If 1.59 ppm < target concentration (x) < 10 ppm, $f_i = 0.40$.
- If 1.59 ppm < target concentration (x) < 10 ppm, f_i = 0.40.
If target concentration (x) > 10 ppm, f_i = 0.44 0.0044x.
- If target concentration (x) > 10 ppm, $f_i = 0.44 0.0044x$.
The distribution for deviations around these functions was a
- The distribution for deviations around these functions was $e_i \sim Normal(0,0.101)$.

For CH₄ the equations for determining the standard deviation of the error were as follows:

- If target concentration (x) < 10 ppm, $f_i = 0.81 0.135x + 0.0074x^2$.
- If target concentration $(x) > 10$ ppm, $f_i = 0.20$.
• The distribution for deviations around these fun
- The distribution for deviations around these functions was $e_i \sim Normal(0,0.081)$.

Plots of the THC and CH_4 errors used to determine these equations are given in appendix B.

The CO and CO₂ calibration data presented a challenge for determining a representative function or set of functions. A sample of $CO₂$ calibration data is shown in [Figure 6.](#page-19-0) The data indicated a clear level dependent bias which was influenced by analyzer range and also by the order $(2nd$ or $3rd)$ of the polynomial curve used to characterize the analyzer's response. However, even with these considerations, the data was still too inconsistent to confidently model the behaviors observed. For these errors it was therefore decided that direct sampling would be utilized to randomly select from the error pool.

FIGURE 6. SAMPLE OF CO2 CALIBRATION DATA

For CO₂, data was collected for 1%, 2%, 4%, and 5% ranges. For the direct sampling, the algorithm grouped 1% and 2% analyzers together, and 4% and 5% analyzers together. In addition, the list of eligible errors for random sampling was limited to calibration curve cut points which were within 15% comparing to the observed phase level concentration, as a percentage of analyzer range. For example, if an FTP Phase 1 result was measured with a 2% CO₂ range, then the pool of errors was automatically limited to 1% and 2% ranges. Next, if the observed Phase 1 CO₂ concentration was 1.5% (75% of the 2% range), then the pool of errors was further limited to those from 60% to 90% on the calibration curve of the 1% and 2% analyzers. For each run of the Monte Carlo, one error from this reduced set would be randomly chosen. This process of limiting the error pool is repeated independently for each test phase.

The CO analyzer calibration data included ranges of 50, 90, 100, and 450 ppm. The errors were direct sampled in the same manner as the $CO₂$ errors. However, the only analyzer ranges which are combined in the sampling are the 90 and 100 ppm ranges. More information on the CO analyzer errors is provided in the Appendix B.

3.2.2 Analyzer Short-Term Repeatability Error

In addition to the error associated with an analyzer's accuracy, there is also an error associated with precision or repeatability of a measurement. To investigate precision, experiments were conducted to understand the error of short-term repeat measurements of NO_x and THC concentrations. For this experiment, a hand-blend was prepared in a single gaseous emissions collection bag to produce a NO_x and THC concentration expected during an actual vehicle test. This unique bag was connected to each sample or background measurement line of an emissions bench while conducting a mock 4-Phase FTP test. This exercise provided eight individual concentration measurements from the single sample bag over a 20-minute span. After eight measurements were taken, the collection bag was nearly empty, so a new hand-blend was produced

to repeat the process. Each point in [Figure 7](#page-20-0) and [Figure 8](#page-21-0) represents the average of eight individual concentration measurements. Water and carbon dioxide were added to some of the blends to make the mixture more representative of vehicle exhaust. Other blends used only nitrogen as the balance gas.

FIGURE 7. SHORT-TERM NOX MEASUREMENT ERROR

FIGURE 8. SHORT-TERM THC MEASUREMENT ERROR

No clear level dependency was observed in the data for either THC or NO_x . Therefore, the average standard deviation was used for both analyzers. THC analyzer short-term repeatability standard deviation was determined to be 0.0158 ppm, and for NO_x the repeatability standard deviation was 0.0033 ppm. For each phase, these errors are sampled independently and are applied in addition to the analyzer accuracy error.

3.2.3 CVS Flowrate Error

Direct flowrate calibration of a constant volume sampler (CVS) is only required upon initial installation or major maintenance, so very little data is available. Due to the difficulty required for direct calibration, a propane recovery check is used as a surrogate for monitoring the accuracy of CVS flowrate. Although other sources of error can influence the results of a propane recovery check, a better data source could not be identified for this project. Also, propane recovery checks are conducted monthly, so a large amount of historical data is available. [Figure 9](#page-22-0) is a histogram of propane recovery data provided by SwRI and other CRC member labs.

FIGURE 9. FREQUENCY HISTOGRAM FOR PROPANE RECOVERY CHECK DATA

The data exhibited a negative skew, which the committee determined was likely real because both CVS leaks and THC hang-up would push the error in a negative direction. Several distributions were tested to compare their fits. In the end, a Weibull distribution was chosen after considering all factors, such as goodness of fit based on Bayesian Information Criterion (BIC), committee knowledge of the distribution, and simplicity.

To fit the various distributions, including lifetime distributions which have a domain including only positive values, the data had to be shifted $+2\%$ to make all values greater than zero. After the shift, the fitted Weibull distribution had a scale parameter of 1.616 and a shape parameter of 2.050. Therefore, for the Monte Carlo, this error is sampled once per test from the stated Weibull distribution, and then 2% is subtracted from the simulated value (i.e. 1.5% becomes -0.5%).

3.2.4 Fuel Analysis Error

The fuel properties, including carbon, hydrogen, and oxygen weight fractions, along with volume percent ethanol, are measured by standardized American Society for Testing and Materials (ASTM) test methods. All ASTM International standards include information in the procedure about the precision (repeatability and reproducibility) of the test method. One can calculate an approximation to the reproducibility standard deviation (s_R) by dividing the published reproducibility formula (given at the 95% confidence limits) by two. For example, the published reproducibility formula for carbon mass percent in ASTM D5291-21 is $(x + 48.48) * 0.018$, where x is the average of two values being compared. Therefore, if the user inputs a value of 0.80, or 80%, for carbon mass fraction, the standard deviation of the method at this level can be approximated by $(80 + 48.48) * 0.018/2 = 1.156\%$. Therefore, each run of the model would sample an error for carbon from Normal (0,0.0156²). ASTM D5291-21 was similarly used for hydrogen mass fraction, and ASTM 4815-22 was used for oxygen mass fraction. ASTM D5599- 22 was used to obtain the error standard deviation for ethanol volume percent. This ethanol uncertainty took a few additional calculations, as the model uses volume percent, and the reproducibility of the ASTM test method is given in mass percent. Therefore, the approximated error in volume percent was obtained after converting ethanol volume percent to ethanol mass percent by multiplying volume percent by d_f/d_i , where d_f is the density of the fuel at 60°F and

 d_i is the density of ethanol at 60°F. The density of ethanol is 0.7939 and 0.74 was used for the density of the gasoline fuel. Therefore, the following equation shows all parts required to approximate the ethanol volume percent error:

$$
s_R = Ethanol(vol.\%) * \left(\frac{ethanol density}{fuel density}\right) * \frac{(reproduciability)}{2} * \left(\frac{fuel density}{ethanol density}\right)
$$

The ethanol error is then sampled from Normal $(0, s_R^2)$.

3.2.5 Gas Divider Error

Gas dividers are used to reduce full-scale calibration bottle concentrations down to discrete cut points. This allow the response of a gaseous analyzer to be calibrated or linearized over the analyzer's full measurement range. Early generation gas dividers were manually controlled and could only provide a few cut points. For this study, we focused on electronically controlled gas dividers that are assumed to be used when measuring emissions levels relevant to this project. Gas dividers are calibrated yearly, and SwRI "as-found" calibration records were used to assess error.

[Figure 10](#page-24-0) shows five to seven years of "as-found" calibration records from eight different Horiba GDC-703 gas dividers. This gas divider model is still widely used in the industry but is not the current production offering from Horiba. These records indicate a negative bias at low cut points. A Horiba representative confirmed that the negative bias is expected for the older models (GDC-703), but not for the new model (MEXA-ONE). [Figure 11](#page-24-1) shows two yearly calibration records from a single MEXA-ONE gas divider and indicates a more symmetrical error. The data do in fact appear unbiased. However, limited data to estimate the standard deviation of the new MEXA-ONE units, so the standard deviation of the older units was used. For the final gas divider error term, the user of the Monte Carlo chooses "Legacy with Bias" or "Symmetrical Distribution." The only difference currently applied to the model is the bias when choosing the legacy model.

FIGURE 10. ERROR FROM EIGHT HORIBA GDC-703 GAS DIVIDERS

For the bias of the legacy models, a linear equation was used to estimate the median bias for a given sample level and is shown below in [Figure 12.](#page-25-0) Based on the target concentration percentage of the model run, this line determines the mean of the normal error distribution used in the model for the legacy models. Zero is used as the mean for the symmetric case.

FIGURE 12. LEGACY GAS DIVIDER MEDIAN BIAS VS. CUT POINT

The standard deviation of the normal distribution was determined in a manner similar to the gas analyzer linearity errors. The errors were binned into groups and the standard deviation of those errors plotted versus cut point, as shown below in [Figure 13.](#page-26-0)

FIGURE 13. GAS DIVIDER ERROR STANDARD DEVIATION VS. CUT POINT

In [Figure 13,](#page-26-0) the blue line is a moving average line, and the red line shows the quadratic function which was determined to be a reasonable fit to the data. Since the red line starts to increase above 70%, a constant value of 0.04 is used for the standard deviation above 70%.

With this error expected to be directionally the same for all gases (i.e. always high, always low, always close to nominal, etc.), only a single location on the normal distribution curve is sampled per test run in the Monte Carlo. For example, for a THC sample measurement taken with a legacy gas divider, the bias and standard deviation will be different than a THC background measurement, but directionally, we expect the two measurements to be similarly off the mean value. The same assumption about directionality of the errors is true for background and sample measurements of other gases. Therefore, though we determine a different mean (bias) and standard deviation of each of the gaseous emissions separately based on concentration level, we use the same location on the normal distribution curve each time (for example, $60th$ percentile).

3.2.6 Calibration Bottle Concentration Error

Gas calibration bottles are used to conduct monthly linearity checks on emission analyzers, and they are also used to zero and span analyzers before and after each vehicle test. The error associated with a calibration bottle can be estimated multiple ways. Some laboratories simply use the manufacturer-declared concentration (and uncertainty) of a bottle, and some laboratories check or "rename" the bottle's concentration using a naming procedure. For this project, we assumed the second case and followed SwRI's bottle naming procedure to estimate uncertainty. [Figure 14](#page-27-0) shows an example of an uncertainty budget for a Nitric Oxide (NO) calibration bottle. Uncertainty budgets for C_3H_8 , CH₄, CO, and CO₂ are given in Appendix B.

The SwRI bottle naming procedure uses a purpose-built Fourier Transform Infrared Spectroscopy (FTIR) analyzer to name calibration bottles against a National Institute of Standards & Technology (NIST) Standard Reference Material (SRM) primary standard. NIST provides the uncertainty of the SRM standard and historic linearization records were used to characterize the FTIR's linearity, repeatability, and drift. For this example, the SRM and calibration bottle had the same nominal concentration, so a gas divider was not used. However, the error of a gas divider should be considered if the SRM concentration is cut during the naming procedure. The largest uncertainty component in this example came from the SRM itself. It should be noted that 40 CFR 1065 does not account for the uncertainty of the SRM in the specification for calibration bottle accuracy. However, the SRM uncertainty was included in this study to better understand the true uncertainty of this important model input.

FIGURE 14. UNCERTAINTY BUDGET OF A GAS CALIBRATION BOTTLE

The combined standard uncertainties given in these uncertainty budgets were used in the Monte Carlo. For a given gas on a single test case of the Monte Carlo, the same calibration bottle error is carried over to subsequent test phases unless a new analyzer range is used, in which case, a new bottle error is determined.

3.2.7 THC Hang-up Error

THC hang-up is caused by nonmethane hydrocarbon (NMHC) contamination in a laboratory's emission sampling system. NMHC can contaminate emission sample probes, sample lines, sample filters, sample bags, etc. The presence of contamination will produce a NMHC

measurement that is artificially high. 40 CFR 1066.420 covers procedures to reduce the influence of THC hang-up. The first method allows introduction of zero and span gasses into the emission sample probe (or just downstream) rather than directly into the analyzer's calibration port. This method attempts to negate the influence of contamination by offsetting the analyzer response. The second method allows the contamination to be measured before a test and then mathematically subtracted from the sample reading. Both methods assume that NMHC contamination is constant throughout a test and that contamination levels are below 0.5 ppm. Inconsistent contamination throughout a test could lead to measurement errors.

The error introduced by THC hang-up is directly dependent upon the level of contamination present in each individual test site. For this study, the user can adjust the modeled contamination level and determine the influence on the overall uncertainty of the final NMOG result. Although the CFR allows a maximum contamination correction of 0.5 ppm, the model predicts that a much lower level of contamination will have a large influence on NMOG. For example, an uncorrected NMHC contamination of only 0.03 ppm (30 ppb) could introduce an overall NMOG + NOx error of 2% to 5%. Specific vehicle scenarios are discussed in later sections of this report.

3.3 Estimate the Overall Uncertainty for NMOG and NOx

The model was built to accommodate various emission levels and vehicles from both lightduty and medium-duty categories. The model can also accommodate specific equipment or procedures used by a test laboratory. As expected, the estimation of uncertainty will change as inputs to the model are adjusted. For this report, four different vehicle scenarios were modeled, but no major changes were made to laboratory equipment selections outside of analyzer range and CVS flowrate selections. When available, inputs for nominal emission rates and vehicle test weights were taken from certification documents queried from EPA's Transport and Air Quality Document Index System (DIS) or from EPA's Light-Duty Manufacturer-Run In-use Testing Data.

[Table 7](#page-29-0) gives four example scenarios that were used to calculate the overall uncertainty of NMOG + NO_x. A 50% engineering margin was used to determine the nominal NMOG + NO_x emission level. This margin was chosen based on feedback from industry representatives, however, individual manufacturers may choose to calibrate their vehicles using a different margin. The first two examples in the table are current production vehicles. The overall uncertainty width increases by approximately 1.5% when moving from a Tier 3 Bin 30 vehicle down to Bin 20. The test weights were similar for both vehicles so a small adjustment in CVS flowrate was the only adjustment required to keep DF and sample concentrations within acceptable ranges. The increase in uncertainty was primarily driven by increased error of both the THC and NO_x analyzers.

TABLE 7. EXAMPLES OF OVERALL NMOG+NOX UNCERTAINTY, WEIGHTED FTP

The third example is a hypothetical Tier 4 Bin 10 vehicle because this bin does not currently exist. However, the recent NPRM (EPA-HQ-OAR-2022-0829) discusses the intention of adding this bin to the Tier 4 standards. For this example, the nominal NMOG + NO_x result from the Bin 30 example was simply lowered to a level that would be needed for Bin 10 compliance. The CVS flowrate was adjusted downward to maintain reasonable sample concentrations but maintaining an acceptable DF value limited this adjustment. Sample concentrations of both THC and NO_x were reduced significantly and the error from short-term repeatability, for both analyzers, was the primary reason for the increase in overall uncertainty.

The last example is also hypothetical. It simulates a medium-duty class 3 vehicle certified to Bin 70. The NPRM discusses the addition of this Bin for medium-duty vehicles for Tier 4. $CO₂$ emission results from a current production Class 3 vehicle were combined with the NMOG + NO_x results taken from a much lower powered vehicle that currently meets the Bin 70 level. For this scenario, the CVS flowrate was significantly increased to maintain an acceptable DF. The resulting THC and NO_x sample concentrations were like the Tier 4 Bin 10 example. Short-term repeatability for both analyzers were again large contributors to uncertainty.

3.4 Analyze the Model for Sensitivity to Individual Inputs

A sensitivity analysis was conducted using each of the vehicle senarios discussed in the previous section. [Figure 15](#page-30-0) - [Figure](#page-35-0) 18 were created using the model's sweep function. In each bar graph, the first set of upper and lower percentile bars represent the overall uncertainty of NMOG + NO_x when the first twenty-two (22) error terms are enabled (excluding THC hang-up and DF errors). The following paired results give the overall error when only the term listed on the x-axis is enabled. This allows the user to quickly see which terms are large contributors. As shown, a THC hang-up of only 30 ppb would have a very large effect on the measurement and a hang-up of 100 ppb would increase the overall NMOG + NO_x result by 7% to 18%, depending on which example is used. Error in the DF calculation has less of an impact. A 25% error in the DF calculation would change the overall NMOG + NO_x error by 0.2% to 0.6%.

[Table 8](#page-31-0) - [Table 15](#page-36-1) give the rank-order of the twenty-two (22) error terms that were individually analyzed followed by example scenerios were THC hang-up and exhaust dilution

factor errors were introduced. The same error terms generally ranked high, however, the order was not always the same. Short-term repeatability of the NO_x and THC analyzers, CVS flowrate, and linearity of the NO_x analyzer ranked high on all examples. The errors associated with the NO and C_3H_8 calibration bottles also consistantly ranked high.

FIGURE 15. EXAMPLE 1, LD TIER 3 BIN 30 SEN SITIVITY ANALYSIS

TABLE 8. EXAMPLE 1, LD TIER 3 BIN 30 ERROR TERM RANKING

TABLE 9. EXAMPLE 1, LD TIER 3 BIN 30 ADDITIONAL ERROR TERMS

FIGURE 16. EXAMPLE 2, LD TIER 3 BIN 20 SENSITIVITY ANALYSIS

TABLE 10. EXAMPLE 2, LD TIER 3 BIN 20 ERROR TERM RANKING

TABLE 11. EXAMPLE 2, LD TIER 3 BIN 20 ADDITIONAL ERROR TERMS

FIGURE 17. EXAMPLE 3, LD TIER 4 BIN 10 SENSITIVITY ANALYSIS

TABLE 12. EXAMPLE 3, LD TIER 4 BIN 10 ERROR TERM RANKING

TABLE 13. EXAMPLE 3, LD TIER 4 BIN 10 ADDITIONAL ERROR TERMS

FIGURE 18. EXAMPLE 4, MD TIER 4 BIN 70 SENSITIVITY ANALYSIS

TABLE 14. EXAMPLE 4, MD TIER 4 BIN 70 ERROR TERM RANKING

TABLE 15. EXAMPLE 4, MD TIER 4 BIN 70 ADDITIONAL ERROR TERMS

3.5 Recommend Potential Changes to Reduce the Overall Uncertainty of NOx and NMOG Measurements

The below seven (7) error terms consonantly ranked high as substantial contributors to the overall uncertainty of NMOG + NO_x. Below each term are potential ideas for reducing their individual error. Some of the ideas appear to be easily implemented (multiple readings) while others could be challenging (develop very low analyzer range). Investigating the connection between propane recovery check results and actual CVS flowrate error is a task that could reduce measurement uncertainty at all emission levels or prove that this input is actually not a large contributor.

- 2. THC hang-up (measurement contamination)
	- THC hang-up should be measured frequently (weekly)
	- Reduce THC hang-up to below 30 ppb
- 3. THC Short-term Repeatability
	- Average multiple readings from same sample bag
	- Investigate analyzer repeatability drivers
- 4. NO_x Short-term Repeatability
	- Average multiple readings from same sample bag
	- Investigate analyzer repeatability drivers
- 5. NO_x Analyzer linearization
	- Develop an analyzer range at or below 2 ppm with lower uncertainty
	- Improve calibration process (additional low range points, Z/S drift correction, etc.)
- 6. CVS Flowrate
	- Reduce the tolerance of propane recovery test to $+/$ 1%
	- Use MFC propane injection control
	- Investigate how well propane check error represents CVS flow error
- 7. NO Calibration Bottle
	- Use a naming instrument with lower linearity uncertainty
	- Use a NIST bottle with lower uncertainty
- 8. C_3H_8 Calibration Bottle
	- Use a naming instrument with lower linearity uncertainty
	- Use a NIST bottle with lower uncertainty

3.6 Provide the Working Model to CRC

The model will be provided in Microsoft Excel format separate from this report. The spreadsheet will contain instructions for populating the model and using the sweep function to explore changes to error terms and model settings.

4.0 Conclusions

This project developed a model to demonstrate and identify opportunities to reduce the uncertainty of the current technology used to measure oxides of nitrogen (NO_x) and non-methane organic gas (NMOG) for chassis dynamometer light-duty and medium-duty certification testing. Individual uncertainly terms were identified as potential contributors to the overall uncertainty of $NMOG + NO_x$. Individual error terms were vetted and twenty-four (24) were identified for detailed review.

For each individual error term, a source of data was identified and studied to calculate the shape and size of each error term. A model was built using the equations specified in the US Code of Federal Registry (CFR) and individual error terms were introduced at appropriate levels of the calculation. Four (4) example vehicles and laboratory setups were used to populate the model to calculate the overall uncertainty of NMOG + NO_x . The overall uncertainty was approximately 3% to 6%, depending on the vehicle tested and the regulatory emissions certification level. If a THC hang-up of 100 ppb was present, the overall uncertainty could increase by 7 to 18 %.

Setting aside THC hang-up, an overall uncertainty of 3% to 6% does not prevent measurement of NMOG + NO_x , even down at the Tier 4 Bin 10 certification level. For this study, it was assumed that an engineering margin of 50% would be used by the manufacturer when calibrating the vehicle, so the modeled uncertainties would be covered by this margin. However, the 500 ppb CFR limit for THC hang-up is not sufficient and could impact the ability to demonstrate compliance at the Tier 4 levels. In this case, THC hang-up should be limited to 30 ppb.

The model was also used to identify which individual error terms were major contributors to the final result and suggestions were made to reduce uncertainty from each. Below are the seven individual error terms that consistently ranked high as major error contributors. These error terms should be further investigated if a reduction in the NMOG $+$ NO_x uncertainty is needed to meet future emission standards.

- THC hang-up (measurement contamination)
- THC Short-term Repeatability
- NO_x Short-term Repeatability
- NO_x Analyzer linearization
- **CVS** Flowrate
- NO Calibration Bottle
- C₃H₈ Calibration Bottle

APPENDIX A

CFR EQUATIONS USED IN THIS STUDY

CFR Equations for Calculation of NMOG

$$
x_{NMHC} = x_{THC[THC-FID]cor} - RF_{CH4[THC-FID]} \cdot x_{CH4}
$$

\nEq. 1065.660-5
\n
$$
x_{NHAC} = \text{concentration of NMLC.}
$$
\n
$$
x_{HC[THC+FID]cor} = \text{concentration of THC, initial THC contamination and dry-to-wet corrected, as measured by the HC/THC-FIDc} = \text{response factor of THC-FID to CH}_4.
$$
\n
$$
x_{CH4} = \text{concentration of CH}_4 \text{ dry-to-wet corrected, as measured by the GC-FID or FTR.}
$$
\n
$$
x_{NMHC} = x_{THC[THC-FID]cor} - RF_{CH4[THC-FID]} \cdot x_{CH4}
$$
\nEq. 1065.660-5
\nWhere:
\n
$$
x_{NMHC} = \text{concentration of NML.}
$$
\n
$$
x_{HC[THC+DFID]} = \text{response factor of THC, initial THC contamination and dry-to-wet corrected, as measured by the HCFID.}
$$
\n
$$
RF_{CH4[THC-FID]} = \text{response factor of THC-FID to CH}_4
$$
\n
$$
x_{CH4} = \text{concentration of CH}_4 \text{ dry-to-wet corrected, as measured by the GC-FID or FTR.}
$$
\n
$$
DF = \frac{1}{\left(1 + \frac{\alpha}{2} + 3.76 \cdot \left(1 + \frac{\alpha}{4} - \frac{\beta}{2}\right)\right) \cdot (x_{CO2} + x_{NMRC} + x_{CH} + x_{CO})}
$$
\nEq. 1066.610-2
\nWhere:
\n
$$
x_{CO2} = \text{amount of CO}_2 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4} = \text{amount of CH}_4 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4} = \text{amount of CH}_4 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4} = \text{amount of CH}_4 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4} = \text{amount of CH}_4 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4} = \text{amount of CH}_4 \text{ measured in the sample over the test interval.}
$$
\n
$$
x_{CH4}
$$

$$
x_{\text{[emission]}} = x_{\text{[emission]}} - x_{\text{[emission]}} \cdot \left(1 - \left(\frac{1}{DF}\right)\right)
$$

Eq. 1066.610-1

Where:

X_{[emission]dexh} = measured emission concentration in dilute exhaust (after dry-to-wet correction, if applicable). X_{[emission]bkand} = measured emission concentration in the dilution air (after dry-to-wet correction, if applicable). $DF =$ dilution factor, as determined in paragraph (b) of this section.

 $m_{\text{[emission]}} = V_{\text{mix}} \cdot \rho_{\text{[emission]}} \cdot x_{\text{[emission]}} \cdot c$

Eq. 1066.605-2

Where:

 $m_{\text{[emission]}}$ = emission mass over the test interval.

 V_{mix} = total dilute exhaust volume over the test interval, corrected to standard reference conditions, and corrected for any volume removed for emission sampling and for any volume change from adding secondary dilution air.

 $p_{\text{[emission]}}$ = density of the appropriate chemical species as given in § 1066.1005(f).

X_[emission] = measured emission concentration in the sample, after dry-to-wet and background corrections. $c = 10^{-2}$ for emission concentrations in %, and 10⁻⁶ for emission concentrations in ppm.

$$
e_{\text{[emission]}} = \frac{m_{\text{[emission]}}}{D}
$$

Eq. 1066.605-1

Where:

e_[emission] = emission rate over the test interval.

 $m_{\text{femission}}$ = emission mass over the test interval.

 D = the measured driving distance over the test interval.

$$
e_{\text{[emission] - FTPcomp}} = 0.43 \cdot \left(\frac{m_{\text{c}}}{D_{\text{ct}} + D_{\text{cs}}}\right) + 0.57 \cdot \left(\frac{m_{\text{h}}}{D_{\text{ht}} + D_{\text{hs}}}\right)
$$

Eq. 1066.820-1

Where:

 m_c = the combined mass emissions determined from the cold-start UDDS test interval (generally known as bag 1 and bag 2), in grams.

 D_{ct} = the measured driving distance from the transient portion of the cold-start test (bag 1), in miles.

 D_{cs} = the measured driving distance from the stabilized portion of the cold-start test (bag 2), in miles.

 m_h = the combined mass emissions determined from the hot-start UDDS test interval in grams. This is the hotstabilized portion from either the first or second UDDS (bag 2, unless you measure bag 4), in addition

to the hot transient portion (bag 3).

 D_{ht} = the measured driving distance from the transient portion of the hot-start test (bag 3), in miles. D_{hs} = the measured driving distance from the stabilized portion of the hot-start test (bag 4), in miles. Set D_{hs} = D_{cs} for testing where the hot-stabilized portion of the UDDS is not run.

$$
e_{\text{NMOGcomp}} = e_{\text{NMHCcomp}} \cdot (1.0302 + 0.0071 \cdot VP_{\text{EtOH}})
$$

Eq.
$$
1066.635 - 3
$$

Where:

e_{NMOGcomp} = weighted FTP composite mass emission rate of NMOG.

 $e_{NMHCeomp}$ = weighted FTP composite mass emission rate of NMHC, calculated using $\rho_{NMHC-liq}$.

VP_{EtOH} = volume percentage of ethanol in the test fuel. Use good engineering judgment to determine this value either as specified in 40 CFR 1065.710 or based on blending volumes, taking into account any denaturant.

CFR Equations for Calculation of NOx

$$
V_{\rm mix} = V_{\rm CVSstd} + V_{\rm gasstd} + V_{\rm PMstd} - V_{\rm sdastd}
$$

Eq. 1066.605-9

Where:

- V_{CVSstd} = total dilute exhaust volume over the test interval at the flow meter, corrected to standard reference conditions.
- V_{gasstd} = total volume of sample flow through the gaseous emission bench over the test interval, corrected to standard reference conditions.
- V_{PMstd} = total volume of dilute exhaust sampled through the filter over the test interval, corrected to standard reference conditions.

V_{sdastd} = total volume of secondary dilution air flow sampled through the filter over the test interval, corrected to standard reference conditions.

$$
m_{\text{[emission]}} = V_{\text{mix}} \cdot \rho_{\text{[emission]}} \cdot x_{\text{[emission]}} \cdot c
$$

Eq.
$$
1066.605 - 2
$$

Where:

 $m_{[emission]}$ = emission mass over the test interval.

 V_{mix} = total dilute exhaust volume over the test interval, corrected to standard reference conditions, and corrected for any volume removed for emission sampling and for any volume change from adding secondary dilution air.

 $p_{\text{[emission]}}$ = density of the appropriate chemical species as given in § 1066.1005(f).

X_{lemission} = measured emission concentration in the sample, after dry-to-wet and background corrections. $c = 10^{-2}$ for emission concentrations in %, and 10⁻⁶ for emission concentrations in ppm.

$$
e_{\text{[emission]}} = \frac{m_{\text{[emission]}}}{D}
$$

Where:

e_[emission] = emission rate over the test interval.

 $m_{\text{[emission]}}$ = emission mass over the test interval.

 D = the measured driving distance over the test interval.

$$
e_{[emission]-FTPcomp} = 0.43 \cdot \left(\frac{m_c}{D_{ct} + D_{cs}}\right) + 0.57 \cdot \left(\frac{m_h}{D_{ht} + D_{hs}}\right)
$$

Eq. 1066.820-1
Where:
 m_c = the combined mass emissions determined from the cold-start UDDS test interval (generally known as
bag 1 and bag 2), in grams.
 D_{ct} = the measured driving distance from the transient portion of the cold-start test (bag 1), in miles.
 D_{cs} = the measured driving distance from the stabilized portion of the cold-start test (bag 2), in miles.
 m_h = the combined mass emissions determined from the hot-start UDDS test interval in grams. This is the hot-
stabilized portion from either the first or second UDDS (bag 2, unless you measure bag 4), in addition
to the hot transient portion (bag 3).
 D_{ht} = the measured driving distance from the transient portion of the hot-start test (bag 3), in miles.
 D_{hs} = the measured driving distance from the stabilized portion of the hot-start test (bag 4), in miles. Set D_{hs} =

 D_{cs} for testing where the hot-stabilized portion of the UDDS is not run.

APPENDIX B

Additional Detail on Error Terms

Below in [Figure 19](#page-47-0)[-Figure 22](#page-50-0) are the uncertainty budgets for C_3H_8 , CH₄, CO, and CO₂, respectively.

FIGURE 19. PROPANE UNCERTAINTY BUDGET

FIGURE 20. METHANE UNCERTAINTY BUDGET

FIGURE 21. CARBON MONOXIDE UNCERTAINTY BUDGET

FIGURE 22. CARBON DIOXIDE UNCERTAINTY BUDGET

[Figure 23](#page-51-0) is a plot of the standard deviation of the THC analyzer errors by target concentration for 5, 10, 25, and 50 ppm analyzers which were used to determine the equations described in the report, while [Figure 24](#page-51-1) shows a zoomed in view of data below 10 ppm.

FIGURE 23. THC ANALYZER ERROR STANDARD DEVIATIONS VS. TARGET CONCENTRATION

FIGURE 24. THC ANALYZER ERROR STANDARD DEVIATIONS VS. TARGET CONCENTRATION, < 10 PPM ONLY

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[Figure 25](#page-52-0) is a plot of the standard deviation of the $CH₄$ analyzer errors by target concentration for 10 and 20 ppm analyzers which were used to determine the equations described in the report.

FIGURE 25. CH4 ANALYZER ERROR STANDARD DEVIATIONS VS. TARGET CONCENTRATION

[Figure 26](#page-52-1) shows a sample of the CO calibration data which was used in the direct sampling of the CO errors.

FIGURE 26. SAMPLE OF CO CALIBRATION DATA

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