Method 323—Measurement of Formaldehyde Emissions From Natural Gas-Fired Stationary Sources—Acetyl Acetone Derivitization Method

1.0 Introduction. This method describes the sampling and analysis procedures of the acetyl acetone colorimetric method for measuring formaldehyde emissions in the exhaust of natural gas-fired, stationary combustion sources. This method, which was prepared by the Gas Research Institute (GRI), is based on the Chilled Impinger Train Method for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone, and Formaldehyde (Technical Bulletin No. 684) developed and published by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). However, this method has been prepared specifically for formaldehyde and does not include specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) for methanol, acetone, acetaldehyde, and methyl ethyl ketone. To obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 1 and 2 of 40 CFR part 60, appendix A-1; Method 3 of 40 CFR part 60, appendix A-2; and Method 4 of 40 CFR part 60, appendix A-3.

1.1 Scope and Application

1.1.1 Analytes. The only analyte measured by this method is formaldehyde (CAS Number 50-00-0).

1.1.2 Applicability. This method is for analyzing formaldehyde emissions from uncontrolled and controlled natural gas-fired, stationary combustion sources.

1.1.3 Data Quality Objectives. If you adhere to the quality control and quality assurance requirements of this method, then you and future users of your data will be able to assess the quality of the data you obtain and estimate the uncertainty in the measurements.

2.0 Summary of Method. An emission sample from the combustion exhaust is drawn through a midget impinger train containing chilled reagent water to absorb formaldehyde. The formaldehyde concentration in the impinger is determined by reaction with acetyl acetone to form a colored derivative which is measured colorimetrically.

3.0 Definitions

[Reserved]

4.0 Interferences. The presence of acetaldehyde, amines, polymers of formaldehyde, periodate, and sulfites can cause interferences with the acetyl acetone procedure which is used to determine the formaldehyde concentration. However, based on experience gained from extensive testing of natural gas-fired combustion sources using FTIR to measure a variety of compounds, GRI
expects only acetaldehyde to be potentially present when combusting natural gas. Acetaldehyde has been reported to be a significant interference only when present at concentrations above 50 ppmv. However, GRI reports that the concentration of acetaldehyde from gas-fired sources is very low (typically below the FTIR detection limit of around 0.5 ppmv); therefore, the potential positive bias due to acetaldehyde interference is expected to be negligible.

5.0 Safety

5.1 Prior to applying the method in the field, a site-specific Health and Safety Plan should be prepared. General safety precautions include the use of steel-toed boots, safety glasses, hard hats, and work gloves. In certain cases, facility policy may require the use of fire-resistant clothing while on-site. Since the method involves testing at high-temperature sampling locations, precautions must be taken to limit the potential for exposure to high-temperature gases and surfaces while inserting or removing the sample probe. In warm locations, precautions must also be taken to avoid dehydration.

5.2 Potential chemical hazards associated with sampling include formaldehyde, nitrogen oxides (NOx), and carbon monoxide (CO). Formalin solution, used for field spiking, is an aqueous solution containing formaldehyde and methanol. Formaldehyde is a skin, eye, and respiratory irritant and a carcinogen, and should be handled accordingly. Eye and skin contact and inhalation of formaldehyde vapors should be avoided. Natural gas-fired combustion sources can potentially emit CO at toxic concentrations. Care should be taken to minimize exposure to the sample gas while inserting or removing the sample probe. If the work area is enclosed, personal CO monitors should be used to insure that the concentration of CO in the work area is maintained at safe levels.

5.3 Potential chemical hazards associated with the analytical procedures include acetyl acetone and glacial acetic acid. Acetyl acetone is an irritant to the skin and respiratory system, as well as being moderately toxic. Glacial acetic acid is highly corrosive and is an irritant to the skin, eyes, and respiratory system. Eye and skin contact and inhalation of vapors should be avoided. Acetyl acetone and glacial acetic acid have flash points of 41 °C (105.8 °F) and 43 °C (109.4 °F), respectively. Exposure to heat or flame should be avoided.

6.0 Equipment and Supplies

6.1 Sampling Probe. Quartz glass probe with stainless steel sheath or stainless steel probe.

6.2 Teflon Tubing. Teflon tubing to connect the sample probe to the impinger train. A heated sample line is not needed since the sample transfer system is rinsed to recover condensed formaldehyde and the rinsate combined with the impinger contents prior to sample analysis.

6.3 Midget Impingers. Three midget impingers are required for sample collection. The first impinger serves as a moisture knockout, the second impinger contains 20 mL of reagent water, and the third impinger contains silica gel to remove residual moisture from the sample prior to the dry gas meter.
6.4 Vacuum Pump. Vacuum pump capable of delivering a controlled extraction flow rate between 0.2 and 0.4 L/min.

6.5 Flow Measurement Device. A rotameter or other flow measurement device is required to indicate consistent sample flow.

6.6 Dry Gas Meter. A dry gas meter is used to measure the total sample volume collected. The dry gas meter must be sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).

6.7 Spectrophotometer. A spectrophotometer is required for formaldehyde analysis, and must be capable of measuring absorbance at 412 nm.

7.0 Reagents and Standards

7.1 Sampling Reagents

7.1.1 Reagent water. Deionized, distilled, organic-free water. This water is used as the capture solution, for rinsing the sample probe, sample line, and impingers at the completion of the sampling run, in reagent dilutions, and in blanks.

7.1.2 Ice. Ice is necessary to pack around the impingers during sampling in order to keep the impingers cold. Ice is also needed for sample transport and storage.

7.2 Analysis

7.2.1 Acetyl acetone Reagent. Prepare the acetyl acetone reagent by dissolving 15.4 g of ammonium acetate in 50 mL of reagent water in a 100-mL volumetric flask. To this solution, add 0.20 mL of acetyl acetone and 0.30 mL of glacial acetic acid. Mix the solution thoroughly, then dilute to 100 mL with reagent water. The solution can be stored in a brown glass bottle in the refrigerator, and is stable for at least two weeks.

7.2.2 Formaldehyde. Reagent grade.

7.2.3 Ammonium Acetate

7.2.4 Glacial Acetic Acid

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-test

8.1.1 Collect information about the site characteristics such as exhaust pipe diameter, gas flow rates, port location, access to ports, and safety requirements during a pre-test site survey. You should then decide the sample collection period per run and the target sample flow rate based on
your best estimate of the formaldehyde concentration likely to be present. You want to assure
that sufficient formaldehyde is captured in the impinger solution so that it can be measured
precisely by the spectrophotometer. You may use Equation 323-1 to design your test program.
As a guideline for optimum performance, if you can, design your test so that the liquid
concentration \((C_l)\) is approximately 10 times the assumed spectrophotometer detection limit of
0.2 µg/mL. However, since actual detection limits are instrument specific, we also suggest that
you confirm that the laboratory equipment can meet or exceed this detection limit.

8.1.2 Prepare and then weigh the midget impingers prior to configuring the sampling train. The
first impinger is initially dry. The second impinger contains 20 mL of reagent water, and the
third impinger contains silica gel that is added before weighing the impinger. Each prepared
impinger is weighed and the pre-sampling weight is recorded to the nearest 0.5 gm.

8.1.3 Assemble the sampling train (see Figure 1). Ice is packed around the impingers in order to
keep them cold during sample collection. A small amount of water may be added to the ice to
improve thermal transfer.

8.1.4 Perform a sampling system leak check (from the probe tip to the pump outlet) as follows:
Connect a rotameter to the outlet of the pump. Close off the inlet to the probe and observe the
leak rate. The leak rate must be less than 2 percent of the planned sampling rate of 0.2 or 0.4
L/min.

8.1.5 Source gas temperature and static pressure should also be considered prior to field
sampling to ensure adequate safety precautions during sampling.

8.2 Sample Collection

8.2.1 Set the sample flow rate between 0.2-0.4 L/min, depending upon the anticipated
concentration of formaldehyde in the engine exhaust. (You may have to refer to published data
for anticipated concentration levels—see References 5 and 6.) If no information is available for
the anticipated levels of formaldehyde, use the higher sampling rate of 0.4 L/min.

8.2.2 Record the sampling flow rate every 5 to 10 minutes during the sample collection period.

NOTE: It is critical that you do not sample at a flow rate higher than 0.4 L/min. Sampling at
higher flow rates may reduce formaldehyde collection efficiency resulting in measured
formaldehyde concentrations that are less than the actual concentrations.

8.2.3 Monitor the amount of ice surrounding the impingers and add ice as necessary to maintain
the proper impinger temperature. Remove excess water as needed to maintain an adequate
amount of ice.

8.2.4 Record measured leak rate, beginning and ending times and dry gas meter readings for
each sampling run, impinger weights before and after sampling, and sampling flow rates and dry
gas meter exhaust temperature every 5 to 10 minutes during the run, in a signed and dated
notebook.
8.2.5 If possible, monitor and record the fuel flow rate to the engine and the exhaust oxygen concentration during the sampling period. This data can be used to estimate the engine exhaust flow rate based on the Method 19 approach. This approach, if accurate fuel flow rates can be determined, is preferred for reciprocating IC engine exhaust flow rate estimation due to the pulsating nature of the engine exhaust. The F-Factor procedures described in Method 19 may be used based on measurement of fuel flow rate and exhaust oxygen concentration. One example equation is Equation 323-2.

8.3 Post-test. Perform a sampling system leak-check (from the probe tip to pump outlet). Connect a rotameter to the outlet of the pump. Close off the inlet to the probe and observe the leak rate. The leak rate must be less than 2 percent of the sampling rate. Weigh and record each impinger immediately after sampling to determine the moisture weight gain. The impinger weights are measured before transferring the impinger contents, and before rinsing the sample probe and sample line. The moisture content of the exhaust gas is determined by measuring the weight gain of the impinger solutions and volume of gas sampled as described in Method 4. Rinse the sample probe and sample line with reagent water. Transfer the impinger catch to an amber 40-mL VOA bottle with a Teflon-lined cap. If there is a small amount of liquid in the dropout impinger (<10 mL), the impinger catches can be combined in one 40 mL VOA bottle. If there is a larger amount of liquid in the dropout impinger, use a larger VOA bottle to combine the impinger catches. Rinse the impingers and combine the rinsings from the sample probe, sample line, and impingers with the impinger catch. In general, combined rinse volumes should not exceed 10 mL. However, in cases where a long, flexible extension line must be used to connect the sample probe to the sample box, sufficient water must be used to rinse the connecting line to insure that any sample that may have collected there is recovered. The volume of the rinses during sample recovery should not be excessive as this may result in your having to use a larger VOA bottle. This in turn would raise the detection limit of the method since after combining the rinses with the impinger catches in the VOA bottle, the bottle should be filled with reagent water to eliminate the headspace in the sample vial. Keep the sample bottles over ice until analyzed on-site or received at the laboratory. Samples should be analyzed as soon as possible to minimize possible sample degradation. Based on a limited number of previous analyses, samples held in refrigerated conditions showed some sample degradation over time.

8.4 Quality Control Samples

8.4.1 Field Duplicates. During at least one run, a pair of samples should be collected concurrently and analyzed as separate samples. Results of the field duplicate samples should be identified and reported with the sample results. The percent difference in exhaust (stack) concentration indicated by field duplicates should be within 20 percent of their mean concentration. Data are to be flagged as suspect if the duplicates do not meet the acceptance criteria.

8.4.2 Spiked Samples. An aliquot of one sample from each source sample set should be spiked at 2 to 3 times the formaldehyde level found in the unspiked sample. It is also recommended that a second aliquot of the same sample be spiked at around half the level of the first spike; however, the second spike is not mandatory. The results are acceptable if the measured spike recovery is
80 to 120 percent. Use Equation 323-4. Data are to be flagged as suspect if the spike recovery do not meet the acceptance criteria.

8.4.3 Field Blank. A field blank consisting of reagent water placed in a clean impinger train, taken to the test site but not sampled, then recovered and analyzed in the same manner as the other samples, should be collected with each set of source samples. The field blank results should be less than 50 percent of the lowest calibration standard used in the sample analysis. If this criteria is not met, the data should be flagged as suspect.

9.0 Quality Control

<table>
<thead>
<tr>
<th>QA/QC</th>
<th>Acceptance</th>
<th>Frequency</th>
<th>Corrective action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leak-check—Sections 8.1.4, 8.3</td>
<td>&lt;2% of Sampling rate</td>
<td>Pre- and Post-sampling</td>
<td>Pre-sampling: Repair leak and recheck</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Post-sampling: Flag data and repeat run if for regulatory compliance.</td>
</tr>
<tr>
<td>Sample flow rate</td>
<td>Between 0.2 and 0.4 L/min</td>
<td>Throughout sampling</td>
<td>Adjust.</td>
</tr>
<tr>
<td>VOA vial headspace</td>
<td>No headspace</td>
<td>After sample recovery</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Sample preservation</td>
<td>Maintain on ice</td>
<td>After sample recovery</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Sample hold time</td>
<td>14 day maximum</td>
<td>After sample recovery</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Field Duplicates— Section 8.4.1</td>
<td>Within 20% of mean of original and duplicate sample</td>
<td>One duplicate per source sample set</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Spiked Sample—Section 8.4.2</td>
<td>Recovery between 80 and 120%</td>
<td>One spike per source sample set</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Field Blank—Section 8.4.3</td>
<td>&lt;50% of the lowest calibration standard</td>
<td>One blank per source sample set</td>
<td>Flag data.</td>
</tr>
<tr>
<td>Calibration Linearity—Section 10.1</td>
<td>Correlation coefficient of 0.99 or higher</td>
<td>Per source sample set</td>
<td>Repeat calibration procedures.</td>
</tr>
<tr>
<td>Calibration Check Standard—Section 10.3</td>
<td>Within 10% of theoretical value</td>
<td>One calibration check per source sample set</td>
<td>Repeat check, remake standard and repeat, repeat calibration.</td>
</tr>
<tr>
<td>Lab Duplicates—Section 11.2.1</td>
<td>Within 10% of mean of original and duplicate sample analysis</td>
<td>One duplicate per 10 samples</td>
<td>Flag data.</td>
</tr>
</tbody>
</table>
### 10.0 Calibration and Standardization

10.1 Spectrophotometer Calibration. Prepare a stock solution of 10 µg/mL formaldehyde. Prepare a series of calibration standards from the stock solution by adding 0, 0.1, 0.3, 0.7, 1.0, and 1.5 mL of stock solution (corresponding to 0, 1.0, 3.0, 7.0, 10.0, and 15.0 µg formaldehyde, respectively) to screw-capped vials. Adjust each vial's volume to 2.0 mL with reagent water. At this point the concentration of formaldehyde in the standards is 0.0, 0.5, 1.5, 3.5, 5.0, and 7.5 µg/mL, respectively. Add 2.0 mL of acetyl acetone reagent, thoroughly mix the solution, and place the vials in a water bath (or heating block) at 60 °C for 10 minutes. Remove the vials and allow to cool to room temperature. Transfer each solution to a cuvette and measure the absorbance at 412 nm using the spectrophotometer. Develop a calibration curve from the analytical results of these standards. The acceptance criteria for the spectrophotometer calibration is a correlation coefficient of 0.99 or higher. If this criteria is not met, the calibration procedures should be repeated.

10.2 Spectrophotometer Zero. The spectrophotometer should be zeroed with reagent water when analyzing each set of samples.

10.3 Calibration Checks. Calibration checks consisting of analyzing a standard separate from the calibration standards must be performed with each set of samples. The calibration check standard should not be prepared from the calibration stock solution. The result of the check standard must be within 10 percent of the theoretical value to be acceptable. If the acceptance criteria are not met, the standard must be reanalyzed. If still unacceptable, a new calibration curve must be prepared using freshly prepared standards.

### 11.0 Analytical Procedure

11.1 Sample Analysis. A 2.0-mL aliquot of the impinger catch/rinsate is transferred to a screw-capped vial. Two mL of the acetyl acetone reagent are added and the solution is thoroughly mixed. Once mixed, the vial is placed in a water bath (or heating block) at 60 °C for 10 minutes. Remove the vial and allow to cool to room temperature. Transfer the solution to a cuvette and measure the absorbance using the spectrophotometer at 412 nm. The quantity of formaldehyde present is determined by comparing the sample response to the calibration curve. Use Equation 323-5. If the sample response is out of the calibration range, the sample must be diluted and reanalyzed. Such dilutions must be performed on another aliquot of the original sample before the addition of the acetyl acetone reagent. The full procedure is repeated with the diluted sample.

11.2 Analytical Quality Control

11.2.1 Laboratory Duplicates. Two aliquots of one sample from each source sample set should be prepared and analyzed (with a minimum of one pair of aliquots for every 10 samples). The percent difference between aliquot analysis should be within 10 percent of their mean. Use Equation 323-3. Data are flagged if the laboratory duplicates do not meet this criteria.
11.2.2 Analytical blanks. Blank samples (reagent water) should be incorporated into each sample set to evaluate the possible presence of any cross-contamination. The acceptance criteria for the analytical blank is less than 50 percent of the lowest calibration standard. If the analytical blank does not meet this criteria, the glassware/analytical equipment should be cleaned and the analytical blank repeated.

12.0 Calculations and Data Analysis

12.1 Nomenclature

\( A = \) measured absorbance of 2 mL aliquot

\( B = \) estimated sampling rate, Lpm

\( C_l = \) target concentration in liquid, \( \mu g/mL \)

\( D = \) estimated stack formaldehyde concentration (ppmv)

\( E = \) estimated liquid volume, normally 40 mL (the size of the VOA used)

\( c_{form} = \) formaldehyde concentration in gas stream, ppmvd

\( c_{form} @15\%O_2 = \) formaldehyde concentration in gas stream corrected to 15\% oxygen, ppmvd

\( C_{sm} = \) measured concentration of formaldehyde in the spiked aliquot

\( C_u = \) measured concentration of formaldehyde in the unspiked aliquot of the same sample

\( C_s = \) calculated concentration of formaldehyde spiking solution added to the spiked aliquot

\( F = \) dilution factor, 1 unless dilution of the sample was needed to reduce the absorbance into the calibration range

\( F_d = \) dry basis F-factor from Method 19, dscf per million btu

\( GCV_g = \) Gross calorific value (or higher heating value), btu per scf

\( K_c = \) spectrophotometer calibration factor, slope of the least square regression line, \( \mu g/\text{absorbance} \) (Note: Most spreadsheets are capable of calculating a least squares line.)

\( K_1 = 0.3855^\circ K/mm \text{ Hg for metric units, (17.65}^\circ R/\text{in.Hg for English units.})\)

\( MW = \) molecular weight, 30 g/g-mole, for formaldehyde 24.05 = mole specific volume constant, liters per g-mole

\( m = \) mass of formaldehyde in liquid sample, mg

\( P_{std} = \) Standard pressure, 760 mm Hg (29.92 in.Hg)

\( P_{bar} = \) Barometric pressure, mm Hg (in.Hg)
PD = Percent Difference

Q_c = exhaust flow rate, dscf per minute
Q_g = natural gas fuel flow rate, scf per minute

T_m = Average DGM absolute temperature, °K (°R).
T_std = Standard absolute temperature, 293 °K (528 °R).

t = sample time (minutes)

V_m = Dry gas volume as measured by the DGM, dcm (dcf).

V_m(std) = Dry gas volume measured by the DGM, corrected to standard conditions of 1 atmosphere and 20 °C, dscm (dscf).

V_t = actual total volume of impinger catch/rinsate, mL

V_a = volume (2.0) of aliquot analyzed, mL

X_1 = first value

X_2 = second value

O_2d = oxygen concentration measured, percent by volume, dry basis

%R = percent recovery of spike

Z_u = volume fraction of unspiked (native) sample contained in the final spiked aliquot
    [e.g., Vu/(Vu + Vs), where Vu + Vs should = 2.0 mL]

Z_s = volume fraction of spike solution contained in the final spiked aliquot [e.g., Vs/(Vu + Vs)]

R = 0.02405 dscm per g-mole, for metric units at standard conditions of 1 atmosphere and 20 °C

Y = Dry Gas Meter calibration factor

12.2 Pretest Design

\[ C_1 = \frac{B \times t \times D \times 30}{24.05 \times E} \]  
Eq. 323-1

12.3 Exhaust Flow Rate

\[ Q = \frac{F_d Q_g GCV_g}{10^6} \left[ \frac{20.9}{20.9 - O_2d} \right] \]  
Eq. 323-2

12.4 Percent Difference—(Applicable to Field and Lab Duplicates)
\[ PD = \left( \frac{X_1 - X_2}{X_1 + X_2} \right) \times 100 \]  \hspace{1cm} \text{Eq. 323-3}

12.5  Percent Recovery of Spike

\[ \% R = \left( \frac{C_{sm} - Z_u C_u}{Z_s C_s} \right) \times 100 \]  \hspace{1cm} \text{Eq. 323-4}

12.6  Mass of Formaldehyde in Liquid Sample

\[ m = K_c \times A \times P \left( \frac{V_t}{V_a} \right) \left( \frac{1 \text{mg}}{1000 \text{ } \mu \text{g}} \right) \]  \hspace{1cm} \text{Eq. 323-5}

12.7  Dry Gas Sample Volume Corrected to Standard Conditions

\[ V_{m(\text{std})} = \frac{V_m \gamma_{\text{std}} P_{\text{bar}}}{T_m P_{\text{std}}} \]  \hspace{1cm} \text{Eq. 323-6}

\[ = \frac{K_c \gamma V_m P_{\text{bar}}}{T_m} \]

12.8  Formaldehyde Concentration in gas Stream

\[ c_{\text{form}} = \frac{R}{MW} \left( \frac{m}{V_{m(\text{std})}} \right) \left( \frac{1 \text{ } \text{g}}{1000 \text{ } \text{mg}} \right) \left( 1 \times 10^6 \text{ ppmv} \right) \]  \hspace{1cm} \text{Eq. 323-7}

12.9  Formaldehyde Concentration Corrected to 15% Oxygen

\[ C_{\text{form} @ 15\%O_2} = C_{\text{form}} \frac{(20.9 - 15)}{(20.9 - 0.2d)} \]  \hspace{1cm} \text{Eq. 323-8}
13.0 Method Performance

13.1 Precision. Based on a Method 301 validation using quad train arrangement with post sampling spiking study of the method at a natural gas-fired IC engine, the relative standard deviation of six pairs of unspiked samples was 11.2 percent at a mean stack gas concentration of 16.7 ppmvd.

13.2 Bias. No bias correction is allowed. The single Method 301 validation study of the method at a natural gas-fired IC engine, indicated a bias correction factor of 0.91 for that set of data. An earlier spiking study got similar average percent spike recovery when spiking into a blank sample. This data set is too limited to justify using a bias correction factor for future tests at other sources.

13.3 Range. The range of this method for formaldehyde is 0.2 to 7.5 µg/mL in the liquid phase. (This corresponds to a range of 0.27 to 10 ppmv in the engine exhaust if sampling at a rate of 0.4 Lpm for 60 minutes and using a 40-mL VOA bottle.) If the liquid sample concentration is above this range, perform the appropriate dilution for accurate measurement. Any dilutions must be taken from new aliquots of the original sample before reanalysis.

13.4 Sample Stability. Based on a sample stability study conducted in conjunction with the method validation, sample degradation for 7- and 14-day hold times does not exceed 2.3 and 4.6 percent, respectively, based on a 95 percent level of confidence. Therefore, the recommended maximum sample holding time for the underivatized impinger catch/rinsings is 14 days, where projected sample degradation is below 5 percent.

14.0 Pollution Prevention

Sample gas from the combustion source exhaust is vented to the atmosphere after passing through the chilled impinger sampling train. Reagent solutions and samples should be collected for disposal as aqueous waste.

15.0 Waste Management

Standards of formaldehyde and the analytical reagents should be handled according to the Material Safety Data Sheets.

16.0 References


17.0 Tables, Diagrams, Flowcharts, and Validation Data