

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

QA/QC Specification	Acceptance criteria	Frequency	Corrective action
Leak-check—Sections 8.1.4, 8.3 ...	<2% of Sampling rate	Pre- and Post-sampling	Pre-sampling: Repair leak and re-check Post-sampling: Flag data and repeat run if for regulatory compliance.
Sample flow rate	Between 0.2 and 0.4 L/min	Throughout sampling	Adjust.
VOA vial headspace	No headspace	After sample recovery	Flag data.
Sample preservation	Maintain on ice	After sample recovery	Flag data.
Sample hold time	14 day maximum	After sample recovery	Flag data.
Field Duplicates—Section 8.4.1	Within 20% of mean of original and duplicate sample.	One duplicate per source sample set.	Flag data.
Spiked Sample—Section 8.4.2	Recovery between 80 and 120%	One spike per source sample set	Flag data.
Field Blank—Section 8.4.3	<50% of the lowest calibration standard.	One blank per source sample set	Flag data.
Calibration Linearity—Section 10.1	Correlation coefficient of 0.99 or higher.	Per source sample set	Repeat calibration procedures.
Calibration Check Standard—Section 10.3.	Within 10% of theoretical value	One calibration check per source sample set.	Repeat check, remake standard and repeat, repeat calibration.
Lab Duplicates—Section 11.2.1	Within 10% of mean of original and duplicate sample analysis.	One duplicate per 10 samples	Flag data.
Analytical Blanks—Section 11.2.2	<50% of the lowest calibration standard.	One blank per source sample set	Clean glassware/analytical equipment and repeat.

10.0 Calibration and Standardization

10.1 Spectrophotometer Calibration. Prepare a stock solution of 10 ppm 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. 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_t = target concentration in liquid, ppmw
 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%O₂ = 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
 df = 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 (**Note:** Most spreadsheets are capable of calculating a least squares line.)
 K₁ = 0.3855 °K/mm Hg for metric units, (17.65 °R/in.Hg for English units.)
 MW = molecular weight, 30 g/g-mole, for formaldehyde