

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_e = 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, 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., $V_u/(V_u + V_s)$, where $V_u + V_s$ should = 2.0 mL]
 Z_s = volume fraction of spike solution contained in the final spiked aliquot [e.g., $V_s/(V_u + V_s)$]
 R = 0.02405 dscm per g-mole, for metric units
 Y = Dry Gas Meter calibration factor

12.2 Pretest Design

$$C_1 = \frac{B \cdot t \cdot D \cdot 30}{24.05 \cdot E} \quad \text{Eq. 323-1}$$

12.3 Exhaust Flow Rate

$$Q = \frac{F_d Q_g GCV_g}{10^6} \left[\frac{20.9}{20.9 - O_{2d}} \right] \quad \text{Eq. 323-2}$$

12.4 Percent Difference.—(Applicable to Field and Lab Duplicates)

$$PD = \frac{(X_1 - X_2)}{\left(\frac{X_1 + X_2}{2} \right)} * 100 \quad \text{Eq. 323-3}$$

12.5 Percent Recovery of Spike

$$\%R = \frac{(C_{sm} - Z_u C_u)}{Z_s C_s} * 100 \quad \text{Eq. 323-4}$$

12.6 Mass of Formaldehyde in Liquid Sample

$$m = K_c AF \left(\frac{V_t}{V_a} \right) \quad \text{Eq. 323-5}$$

12.7 Dry Sample Gas Volume, Corrected to Standard Conditions

$$V_{m(std)} = \frac{(V_m Y T_{std} P_{bar})}{(T_m P_{std})} \quad \text{Eq. 323-6}$$

$$= \frac{K_i Y V_m P_{bar}}{T_m}$$

12.8 Formaldehyde Concentration in Gas Stream

$$C_{form} = \frac{R}{MW} \left(\frac{m}{V_{m(std)}} \right) \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) (1 \times 10^6 \text{ ppm}) \quad \text{Eq. 323-7}$$

12.9 Formaldehyde Concentration, Corrected to 15% Oxygen

$$C_{form@15\%O_2} = C_{form} * \frac{(20.9 - 15)}{(20.9 - O_{2d})} \quad \text{Eq. 323-8}$$

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 ppmw 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/rinsate 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

¹ National Council of the Paper Industry for Air and Stream Improvement, Inc., "Volatile Organic Emissions from Pulp and Paper Mill Sources, Part X—Test Methods, Quality Assurance/Quality Control Procedures, and

Data Analysis Protocols," Technical Bulletin No. 684, December 1994.

² National Council of the Paper Industry for Air and Stream Improvement, Inc., "Field Validation of a Source Sampling Method for Formaldehyde, Methanol, and Phenol at Wood Products Mills," 1997 TAPPI International Environmental Conference.

³ Roy F. Weston, Inc., "Formaldehyde Sampling Method Field Evaluation and Emission Test Report for Georgia-Pacific Resins, Inc., Russellville, South Carolina," August 1996.

⁴ Hoechst Celanese Method CL 8-4, "Standard Test Method for Free Formaldehyde in Air Using Acetyl acetone," Revision 0, September 1986.

⁵ Shareef, G.S., *et al.* "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities." Report No. GRI-96/0009.1, Gas Research Institute, Chicago, Illinois, February 1996.

⁶ Gundappa, M., *et al.* "Characteristics of Formaldehyde Emissions from Natural Gas-Fired Reciprocating Internal Combustion Engines in Gas Transmission. Volume I: Phase I Predictive Model for Estimating Formaldehyde Emissions from 2-Stroke Engines." Report No. GRI-97/0376.1, Gas