

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 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 ppmw. 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^{5,6} for anticipated concentration levels.) 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 5–10 minutes during the sample collection period.

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 5–10 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 rinsate from the sample probe, sample line, and impingers with the impinger catch. In general, combined rinse volumes should not exceed 10 mL. 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.