Method 204F - Volatile Organic Compounds Content in Liquid Input Stream (Distillation Approach)

1. Introduction

1.1 Applicability. This procedure is applicable for determining the input of volatile organic compounds (VOC). It is intended to be used as a segment in the development of liquid/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The amount of VOC introduced to the process (L) is the sum of the products of the weight (W) of each VOC containing liquid (ink, paint, solvent, etc.) used, and its VOC content (V), corrected for a response factor (RF).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

2. Summary of Method

A sample of each coating used is distilled to separate the VOC fraction. The distillate is used to prepare a known standard for analysis by a flame ionization analyzer (FIA), calibrated against propane, to determine its RF.

3. Safety

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

4. Equipment and Supplies

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Liquid Weight.

4.1.1 Balances/Digital Scales. To weigh drums of VOC containing liquids to within 0.2 lb or 1.0 percent of the total weight of VOC liquid used.

4.1.2 Volume Measurement Apparatus (Alternative). Volume meters, flow meters, density measurement equipment, etc., as needed to achieve the same accuracy as direct weight measurements.

4.2 Response Factor Determination (FIA Technique). The VOC distillation system and Tedlar gas bag generation system apparatuses are shown in Figures 204F–1 and 204F–2, respectively. The following equipment is required:

4.2.1 Sample Collection Can. An appropriately-sized metal can to be used to collect VOC containing materials. The can must be constructed in such a way that it can be grounded to the coating container.

4.2.2 Needle Valves. To control gas flow.

4.2.3 Regulators. For calibration, dilution, and sweep gas cylinders.

4.2.4 Tubing and Fittings. Teflon and stainless steel tubing and fittings with diameters, lengths, and sizes determined by the connection requirements of the equipment.

4.2.5 Thermometer. Capable of measuring the temperature of the hot water and oil baths to within 1 °C.

4.2.6 Analytical Balance. To measure ±0.01 mg.

4.2.7 Microliter Syringe. 10–µl size.

4.2.8 Vacuum Gauge or Manometer. 0– to 760–mm (0– to 30–in.) Hg U-Tube manometer or vacuum gauge.

4.2.9 Hot Oil Bath, With Stirring Hot Plate. Capable of heating and maintaining a distillation vessel at 110 ±3°C.

4.2.10 Ice Water Bath. To cool the distillation flask.

4.2.11 Vacuum/Water Aspirator. A device capable of drawing a vacuum to within 20 mm Hg from absolute.

4.2.12 Rotary Evaporator System. Complete with folded inner coil, vertical style condenser, rotary speed control, and Teflon sweep gas delivery tube with valved inlet. Buchi Rotavapor or equivalent.

4.2.13 Ethylene Glycol Cooling/Circulating Bath. Capable of maintaining the condenser coil fluid at −10°C.

4.2.14 Dry Gas Meter (DGM). Capable of measuring the dilution gas volume within 2 percent, calibrated with a spirometer or bubble meter, and equipped with a temperature gauge capable of measuring temperature within 3°C.

4.2.15 Activated Charcoal/Mole Sieve Trap. To remove any trace level of organics picked up from the DGM.

4.2.16 Gas Coil Heater. Sufficient length of 0.125-inch stainless steel tubing to allow heating of the dilution gas to near the water bath temperature before entering the volatilization vessel.

4.2.17 Water Bath, With Stirring Hot Plate. Capable of heating and maintaining a volatilization vessel and coil heater at a temperature of 100 ±5°C.

4.2.18 Volatilization Vessel. 50–ml midget impinger fitted with a septum top and loosely filled with glass wool to increase the volatilization surface.

4.2.19 Tedlar Gas Bag. Capable of holding 30 liters of gas, flushed clean with zero air, leak tested, and evacuated.

4.2.20 Organic Concentration Analyzer. An FIA with a span value of 1.5 times the expected concentration as propane; however, other span values may be used if it can be demonstrated that they would provide equally accurate measurements. The FIA instrument should be the same instrument used in the gaseous analyses adjusted with the same fuel, combustion air, and sample back-pressure (flow rate) settings. The system shall be capable of meeting or exceeding the following specifications:

4.2.20.1 Zero Drift. Less than ±3.0 percent of the span value.

4.2.20.2 Calibration Drift. Less than ±3.0 percent of the span value.

4.2.20.3 Calibration Error. Less than ±3.0 percent of the calibration gas value.

4.2.21 Integrator/Data Acquisition System. An analog or digital device or computerized data acquisition system used to integrate the FIA response or compute the average response and record measurement data. The minimum data sampling frequency for computing average or integrated value is one measurement value every 5 seconds. The device shall be capable of recording average values at least once per minute.

4.2.22 Chart Recorder (Optional). A chart recorder or similar device is recommended to provide a continuous analog display of the measurement results during the liquid sample analysis.

5. Reagents and Standards

5.1 Zero Air. High purity air with less than 1 ppm of organic material (as propane) or less than 0.1 percent of the span value, whichever is greater. Used to supply dilution air for making the Tedlar bag gas samples.

5.2 THC Free N_2. High purity N_2 with less than 1 ppm THC. Used as sweep gas in the rotary evaporator system.

5.3 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to ±1 percent of the tag value. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.3.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent H_2/60 percent He, or 40 percent H_2/60 percent N_2 mixture is recommended to avoid fuels with oxygen to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.3.2 Combustion Air. High purity air with less than 1 ppm of organic material (as propane) or less than 0.1 percent of the span value, whichever is greater.

5.3.3 FIA Linearity Calibration Gases. Low-, mid-, and high-range gas mixture standards with nominal propane concentration of 20–30, 45–55, and 70–80 percent of the span value in air, respectively. Other calibration values and other span values may be used if it can be shown that equally accurate measurements would be achieved.

5.3.4 System Calibration Gas. Gas mixture standard containing propane in air, approximating the VOC concentration expected for the Tedlar gas bag samples.

6. Quality Control

6.1 Required instrument quality control parameters are found in the following sections:

6.1.1 The FIA system must be calibrated as specified in section 7.1.

6.1.2 The system drift check must be performed as specified in section 7.2.

6.2 Precision Control. A minimum of one sample in each batch must be distilled and analyzed in duplicate as a precision control. If the results of the two analyses differ by more than ±10 percent of the mean, then the system must be reevaluated and the entire batch must be redistilled and analyzed.

7. Calibration and Standardization

7.1 FIA Calibration and Linearity Check. Make necessary adjustments to the air and fuel supplies for the FIA and ignite the burner. Allow the FIA to warm up for the period recommended by the manufacturer. Inject a calibration gas into the measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero-and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low-and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system. A calibration curve consisting of zero gas and two calibration levels must be performed at the beginning and end of each batch of samples.

7.2 Systems Drift Checks. After each sample, repeat the system calibration checks in section 7.1 before any adjustments to the FIA or measurement system are made. If the zero or calibration drift exceeds ±3 percent of the span value, discard the result and repeat the analysis. Alternatively, recalibrate the FIA as in section 7.1 and report the results using both sets of calibration data (i.e., data

determined prior to the test period and data determined following the test period). The data that results in the lowest CE value shall be reported as the results for the test run.

8. Procedures

8.1 Determination of Liquid Input Weight

8.1.1 Weight Difference. Determine the amount of material introduced to the process as the weight difference of the feed material before and after each sampling run. In determining the total VOC containing liquid usage, account for: (a) The initial (beginning) VOC containing liquid mixture; (b) any solvent added during the test run; (c) any coating added during the test run; and (d) any residual VOC containing liquid mixture remaining at the end of the sample run.

8.1.1.1 Identify all points where VOC containing liquids are introduced to the process. To obtain an accurate measurement of VOC containing liquids, start with an empty fountain (if applicable). After completing the run, drain the liquid in the fountain back into the liquid drum (if possible), and weigh the drum again. Weigh the VOC containing liquids to ±0.5 percent of the total weight (full) or ±1.0 percent of the total weight of VOC containing liquid used during the sample run, whichever is less. If the residual liquid cannot be returned to the drum, drain the fountain into a preweighed empty drum to determine the final weight of the liquid.

8.1.1.2 If it is not possible to measure a single representative mixture, then weigh the various components separately (e.g., if solvent is added during the sampling run, weigh the solvent before it is added to the mixture). If a fresh drum of VOC containing liquid is needed during the run, then weigh both the empty drum and fresh drum.

8.1.2 Volume Measurement (Alternative). If direct weight measurements are not feasible, the tester may use volume meters and flow rate meters (and density measurements) to determine the weight of liquids used if it can be demonstrated that the technique produces results equivalent to the direct weight measurements. If a single representative mixture cannot be measured, measure the components separately.

8.2 Determination of VOC Content in Input Liquids

8.2.1 Collection of Liquid Samples.

8.2.1.1 Collect a 1-pint or larger sample of the VOC containing liquid mixture at each application location at the beginning and end of each test run. A separate sample should be taken of each VOC containing liquid added to the application mixture during the test run. If a fresh drum is needed during the sampling run, then obtain a sample from the fresh drum.

8.2.1.2 When collecting the sample, ground the sample container to the coating drum. Fill the sample container as close to the rim as possible to minimize the amount of headspace.

8.2.1.3 After the sample is collected, seal the container so the sample cannot leak out or evaporate.

8.2.1.4 Label the container to identify clearly the contents.

8.2.2 Distillation of VOC.

8.2.2.1 Assemble the rotary evaporator as shown in Figure 204F–1.

8.2.2.2 Leak check the rotary evaporation system by aspirating a vacuum of approximately 20 mm Hg from absolute. Close up the system and monitor the vacuum for approximately 1 minute. If the vacuum falls more than 25 mm Hg in 1 minute, repair leaks and repeat. Turn off the aspirator and vent vacuum.

8.2.2.3 Deposit approximately 20 ml of sample (inks, paints, etc.) into the rotary evaporation distillation flask.

8.2.2.4 Install the distillation flask on the rotary evaporator.

8.2.2.5 Immerse the distillate collection flask into the ice water bath.

8.2.2.6 Start rotating the distillation flask at a speed of approximately 30 rpm.

8.2.2.7 Begin heating the vessel at a rate of 2 to 3°C per minute.

8.2.2.8 After the hot oil bath has reached a temperature of 50°C or pressure is evident on the mercury manometer, turn on the aspirator and gradually apply a vacuum to the evaporator to within 20 mm Hg of absolute. Care should be taken to prevent material burping from the distillation flask.

8.2.2.9 Continue heating until a temperature of 110°C is achieved and maintain this temperature for at least 2 minutes, or until the sample has dried in the distillation flask.

8.2.2.10 Slowly introduce the N_2 sweep gas through the purge tube and into the distillation flask, taking care to maintain a vacuum of approximately 400-mm Hg from absolute.

8.2.2.11 Continue sweeping the remaining solvent VOC from the distillation flask and condenser assembly for 2 minutes, or until all traces of condensed solvent are gone from the vessel. Some distillate may remain in the still head. This will not affect solvent recovery ratios.

8.2.2.12 Release the vacuum, disassemble the apparatus and transfer the distillate to a labeled, sealed vial.

8.2.3 Preparation of VOC standard bag sample.

8.2.3.1 Assemble the bag sample generation system as shown in Figure 204F–2 and bring the water bath up to near boiling temperature.

8.2.3.2 Inflate the Tedlar bag and perform a leak check on the bag.

8.2.3.3 Evacuate the bag and close the bag inlet valve.

8.2.3.4 Record the current barometric pressure.

8.2.3.5 Record the starting reading on the dry gas meter, open the bag inlet valve, and start the dilution zero air flowing into the Tedlar bag at approximately 2 liters per minute.

8.2.3.6 The bag sample VOC concentration should be similar to the gaseous VOC concentration measured in the gas streams. The amount of liquid VOC required can be approximated using equations in section 9.2. Using Equation 204F–4, calculate C_{VOC} by assuming RF is 1.0 and selecting the desired gas concentration in terms of propane, C_{C3}. Assuming B_V is 20 liters, M_L, the approximate amount of liquid to be used to prepare the bag gas sample, can be calculated using Equation 204F–2.

8.2.3.7 Quickly withdraw an aliquot of the approximate amount calculated in section 8.2.3.6 from the distillate vial with the microliter syringe and record its weight from the analytical balance to the nearest 0.01 mg.

8.2.3.8 Inject the contents of the syringe through the septum of the volatilization vessel into the glass wool inside the vessel.

8.2.3.9 Reweigh and record the tare weight of the now empty syringe.

8.2.3.10 Record the pressure and temperature of the dilution gas as it is passed through the dry gas meter.

8.2.3.11 After approximately 20 liters of dilution gas have passed into the Tedlar bag, close the valve to the dilution air source and record the exact final reading on the dry gas meter.

8.2.3.12 The gas bag is then analyzed by FIA within 1 hour of bag preparation in accordance with the procedure in section 8.2.4.

8.2.4 Determination of VOC response factor.

8.2.4.1 Start up the FIA instrument using the same settings as used for the gaseous VOC measurements.

8.2.4.2 Perform the FIA analyzer calibration and linearity checks according to the procedure in section 7.1. Record the responses to each of the calibration gases and the back-pressure setting of the FIA.

8.2.4.3 Connect the Tedlar bag sample to the FIA sample inlet and record the bag concentration in terms of propane. Continue the analyses until a steady reading is obtained for at least 30 seconds. Record the final reading and calculate the RF.

8.2.5 Determination of coating VOC content as VOC (V_{IJ}).

8.2.5.1 Determine the VOC content of the coatings used in the process using EPA Method 24 or 24A as applicable.

9. Data Analysis and Calculations

9.1. Nomenclature.

B_V = Volume of bag sample volume, liters.

C_{C3} = Concentration of bag sample as propane, mg/liter.

C_{VOC} = Concentration of bag sample as VOC, mg/liter.

K = 0.00183 mg propane/(liter-ppm propane)

L = Total VOC content of liquid input, kg propane.

M_L = Mass of VOC liquid injected into the bag, mg.

M_V = Volume of gas measured by DGM, liters.

P_M = Absolute DGM gas pressure, mm Hg.

P_{STD} = Standard absolute pressure, 760 mm Hg.

R_{C3} = FIA reading for bag gas sample, ppm propane.

RF = Response factor for VOC in liquid, weight VOC/weight propane.

RF_J = Response factor for VOC in liquid J, weight VOC/weight propane.

T_M = DGM temperature, °K.

T_{STD} = Standard absolute temperature, 293°K.

V_{IJ} = Initial VOC weight fraction of VOC liquid J.

V_{FJ} = Final VOC weight fraction of VOC liquid J.

V_{AJ} = VOC weight fraction of VOC liquid J added during the run.

W_{IJ} = Weight of VOC containing liquid J at beginning of run, kg.

W_{FJ} = Weight of VOC containing liquid J at end of run, kg.

W_{AJ} = Weight of VOC containing liquid J added during the run, kg.

9.2 Calculations.

9.2.1 Bag sample volume.

$$B_V = \frac{M_V T_{STD} P_M}{T_M P_{STD}} \qquad \text{Eq. 204F-1}$$

9.2.2 Bag sample VOC concentration.

$$C_{VOC} = \frac{M_I}{B_V} \qquad \text{Eq. 204F-2}$$

9.2.3 Bag sample VOC concentration as propane.

$$C_{C_3} = R_{C_3} K \qquad \text{Eq. 204F-3}$$

9.2.4 Response Factor.

$$RF = \frac{C_{VOC}}{C_{C_3}} \qquad \text{Eq. 204F-4}$$

9.2.5 Total VOC Content of the Input VOC Containing Liquid.

$$L = \sum_{j=1}^{n} \frac{V_{ij} W_{ij}}{RF_J} - \sum_{j=1}^{n} \frac{V_{ij} W_{ij}}{RF_J} + \sum_{j=1}^{n} \frac{V_{Aj} W_{Aj}}{RF_J} \qquad \text{Eq. 204F-5}$$
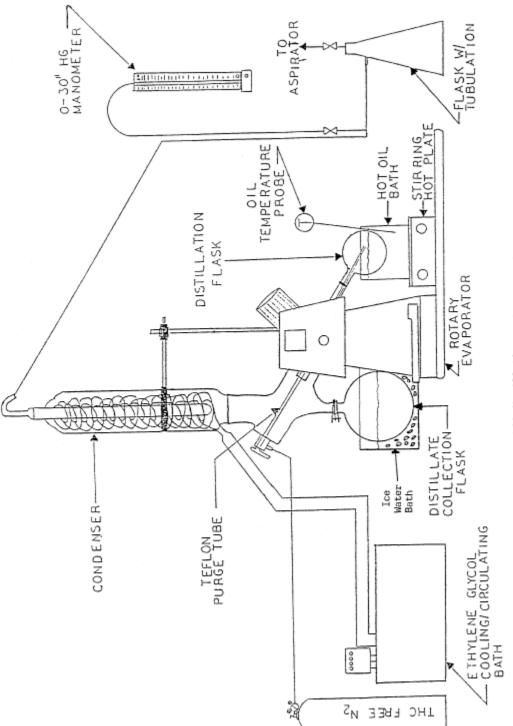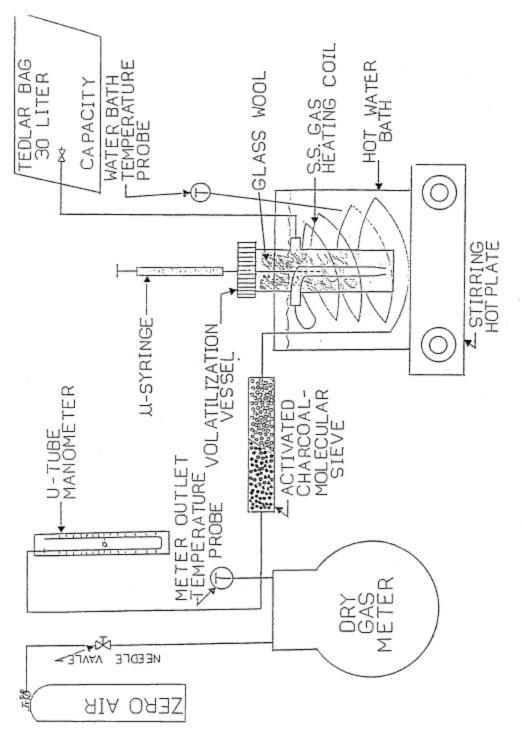
10. Diagrams

Figure 2D4F-1. VOC distillation system apparatus.

Figure 204F-2. Tedlar gas bag generation system apparatus.