METHOD 305: MEASUREMENT OF EMISSION POTENTIAL OF INDIVIDUAL VOLATILE ORGANIC COMPOUNDS IN WASTE

NOTE: This method does not include all of the specifications (*e.g.,* equipment and supplies) and procedures (*e.g.,* sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in 40 CFR Part 60, Appendix A. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 25D.

1.0 Scope and Application.

1.1 Analyte. Volatile Organics. No CAS No. assigned.

1.2 Applicability. This procedure is used to determine the emission potential of individual volatile organics (VOs) in waste.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method.

2.1 The heated purge conditions established by Method 25D (40 CFR Part 60, Appendix A) are used to remove VOs from a 10 gram sample of waste suspended in a 50/50 solution of polyethylene glycol (PEG) and water. The purged

VOs are quantified by using the sample collection and analytical techniques (e.g. gas chromatography) appropriate for the VOs present in the waste. The recovery efficiency of the sample collection and analytical technique is determined for each waste matrix. A correction factor is determined for each compound (if acceptable recovery criteria requirements are met of 70 to 130 percent recovery for every target compound), and the measured waste concentration is corrected with the correction factor for each compound. A minimum of three replicate waste samples shall be analyzed.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies.

6.1 Method 25D Purge Apparatus.

6.1.1 Purge Chamber. The purge chamber shall accommodate the 10 gram sample of waste suspended in a matrix of 50 mL of PEG and 50 mL of deionized, hydrocarbon-free water. Three fittings are used on the glass chamber top. Two #7 Ace-threads are used for the purge gas inlet and outlet connections. A #50 Ace-thread is used to connect the top of the chamber to the base (see Figure 305-1). The base of the chamber has a side-arm equipped with a #22 Sovirel fitting to allow for easy sample introductions into the chamber. The dimensions of the chamber are shown in Figure 305-1.

6.1.2 Flow Distribution Device (FDD). The FDD enhances the gas-to-liquid contact for improved purging efficiency. The FDD is a 6 mm OD (0.2 in) by 30 cm (12 in) long glass tube equipped with four arm bubblers as shown in Figure 305-1. Each arm shall have an opening of 1 mm (0.04 in) in diameter.

6.1.3 Coalescing Filter. The coalescing filter serves to discourage aerosol formation of sample gas once it leaves the purge chamber. The glass filter has a fritted disc mounted 10 cm (3.9 in) from the bottom. Two #7 Ace-threads are used for the inlet and outlet connections. The dimensions of the chamber are shown in Figure 305-2.

6.1.4 Oven. A forced convection airflow oven capable of maintaining the purge chamber and coalescing filter at 75 ± 2°C (167 ± 3.6°F).

6.1.5 Toggle Valve. An on/off valve constructed from brass or stainless steel rated to 100 psig. This valve is placed in line between the purge nitrogen source and the flow controller.

6.1.6 Flow Controller. High-quality stainless steel flow controller capable of restricting a flow of nitrogen to 6 ± 0.06 L/min (0.2 ± 0.002 ft^3/min) at 40 psig.

6.1.7 Polyethylene Glycol Cleaning System.

6.1.7.1 Round-Bottom Flask. One liter, three-neck glass round-bottom flask for cleaning PEG. Standard taper 24/40 joints are mounted on each neck.

6.1.7.2 Heating Mantle. Capable of heating contents of the 1-L flask to 120 °C (248 °F).

6.1.7.3 Nitrogen Bubbler. Teflon® or glass tube, 0.25 in OD (6.35 mm).

6.1.7.4 Temperature Sensor. Partial immersion glass thermometer.

6.1.7.5 Hose Adapter. Glass with 24/40 standard tapered joint.

6.2 Volatile Organic Recovery System.

6.2.1 Splitter Valve (Optional). Stainless steel cross-pattern valve capable of splitting nominal flow rates from the purge flow of 6 L/min (0.2 ft^3/min). The valve shall be maintained at 75 $\pm$ 2°C (167 ± 3.6°F) in the heated zone and shall be placed downstream of the coalescing filter. It is recommended that 0.125 in OD (3.175 mm) tubing be used to direct the split vent flow from the heated zone. The back pressure caused by the 0.125 in OD (3.175 mm) tubing is critical for maintaining proper split valve operation.

NOTE: The splitter valve design is optional; it may be used in cases where the concentration of a pollutant would saturate the adsorbents.

6.2.2 Injection Port. Stainless steel 1/4 in OD (6.35 mm) compression fitting tee with a 6 mm (0.2 in) septum fixed on the top port. The injection port is the point of entry for the recovery study solution. If using a gaseous standard to determine recovery efficiency, connect the gaseous standard to the injection port of the tee.

6.2.3 Knockout Trap (Optional but Recommended). A 25 mL capacity glass reservoir body with a full-stem impinger (to avoid leaks, a modified midget glass impinger with a screw cap and ball/socket clamps on the inlet and outlet is recommended). The empty impinger is placed in an ice water

bath between the injection port and the sorbent cartridge.
Its purpose is to reduce the water content of the purge gas
(saturated at 75 °C (167 °F)) before the sorbent cartridge.

6.2.4   Insulated Ice Bath.   A 350 mL dewar or other
type of insulated bath is used to maintain ice water around
the knockout trap.

6.2.5   Sorbent Cartridges.   Commercially available
glass or stainless steel cartridge packed with one or more
appropriate sorbents.   The amount of adsorbent packed in the
cartridge depends on the breakthrough volume of the test
compounds but is limited by back pressure caused by the
packing (not to exceed 7 psig).   More than one sorbent
cartridge placed in series may be necessary depending upon
the mixture of the measured components.

6.2.6   Volumetric Glassware.   Type A glass 10 mL
volumetric flasks for measuring a final volume from the
water catch in the knockout trap.

6.2.7   Thermal Desorption Unit.   A clam-shell type
oven, used for the desorption of direct thermal desorption
sorbent tubes.   The oven shall be capable of increasing the
temperature of the desorption tubes rapidly to recommended
desorption temperature.

6.2.8   Ultrasonic Bath.   Small bath used to agitate
sorbent material and desorption solvent.   Ice water shall be

used in the bath because of heat transfer caused by
operation of the bath.

6.2.9 Desorption Vials. Four-dram (15 mL) capacity
borosilicate glass vials with Teflon-lined caps.

6.3 Analytical System. A gas chromatograph (GC) is
commonly used to separate and quantify compounds from the
sample collection and recovery procedure. Method 18 (40 CFR
Part 60, Appendix A) may be used as a guideline for
determining the appropriate GC column and GC detector based
on the test compounds to be determined. Other types of
analytical instrumentation may be used (HPLC) in lieu of GC
systems as long as the recovery efficiency criteria of this
method are met.

6.3.1 Gas Chromatograph (GC). The GC shall be
equipped with a constant-temperature liquid injection port
or a heated sampling loop/valve system, as appropriate. The
GC oven shall be temperature-programmable over the useful
range of the GC column. The choice of detectors is based on
the test compounds to be determined.

6.3.2 GC Column. Select the appropriate GC column
based on (1) literature review or previous experience,
(2) polarity of the analytes, (3) capacity of the column, or
(4) resolving power (*e.g.,* length, diameter, film thickness)
required.

6.3.3 Data System. A programmable electronic integrator for recording, analyzing, and storing the signal generated by the detector.

7.0 Reagents and Standards.

7.1 Method 25D Purge Apparatus.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure organic polymer with an average molecular weight of 400 g/mol. Volatile organics are removed from the PEG prior to use by heating to 120 $\pm$ 5°C (248 ± 9°F) and purging with pure nitrogen at 1 L/min (0.04 ft^3/min) for 2 hours. After purging and heating, the PEG is maintained at room temperature under a nitrogen purge maintained at 1 L/min (0.04 ft^3/min) until used. A typical apparatus used to clean the PEG is shown in Figure 305-3.

7.1.2 Water. Organic-free deionized water is required.

7.1.3 Nitrogen. High-purity nitrogen (less than 0.5 ppm total hydrocarbons) is used to remove test compounds from the purge matrix. The source of nitrogen shall be regulated continuously to 40 psig before the on/off toggle valve.

7.2 Volatile Organic Recovery System.

7.2.1 Water. Organic-free deionized water is required.

7.2.2 Desorption Solvent (when used). Appropriate high-purity (99.99 percent) solvent for desorption shall be used. Analysis shall be performed (utilizing the same analytical technique as that used in the analysis of the waste samples) on each lot to determine purity.

7.3 Analytical System. The gases required for GC operation shall be of the highest obtainable purity (hydrocarbon free). Consult the operating manual for recommended settings.

8.0 Sample Collection, Preservation, Storage, and Transport.

8.1 Assemble the glassware and associated fittings (see Figures 305-3 and 305-4 , as appropriate) and leak-check the system (approximately 7 psig is the target pressure). After an initial leak check, mark the pressure gauge and use the initial checkpoint to monitor for leaks throughout subsequent analyses. If the pressure in the system drops below the target pressure at any time during analysis, that analysis shall be considered invalid.

8.2 Recovery Efficiency Determination. Determine the individual recovery efficiency (RE) for each of the target compounds in duplicate before the waste samples are analyzed. To determine the RE, generate a water blank (Section 11.1) and use the injection port to introduce a known volume of spike solution (or certified gaseous standard) containing all of the target compounds at the levels expected in the waste sample. Introduce the spike solution immediately after the nitrogen purge has been started (Section 8.3.2). Follow the procedures outlined in Section 8.3.3. Analyze the recovery efficiency samples using the techniques described in Section 11.2. Determine the recovery efficiency (Equation 305-1, Section 12.2) by comparing the amount of compound recovered to the

theoretical amount spiked. Determine the RE twice for each

compound; the relative standard deviation, (RSD) shall be

$\leq$ 10 percent for each compound. If the RSD for any compound

is not $\leq$ 10 percent, modify the sampling/analytical

procedure and complete an RE study in duplicate, or continue

determining RE until the RSD meets the acceptable criteria.

The average RE shall be 0.70 $\leq$ RE $\leq$ 1.30 for each compound.

If the average RE does not meet these criteria, an

alternative sample collection and/or analysis technique

shall be developed and the recovery efficiency determination

shall be repeated for that compound until the criteria are

met for every target compound. Example modifications of the

sampling/analytical system include changing the adsorbent

material, changing the desorption solvent, utilizing direct

thermal desorption of test compounds from the sorbent tubes,

utilizing another analytical technique.

8.3 Sample Collection and Recovery.

8.3.1 The sample collection procedure in Method 25D

shall be used to collect (into a preweighed vial) 10 g of

waste into PEG, cool, and ship to the laboratory. Remove

the sample container from the cooler and wipe the exterior

to remove any ice or water. Weigh the container and sample

to the nearest 0.01 g and record the weight. Pour the

sample from the container into the purge flask. Rinse the

sample container three times with approximately 6 mL of PEG

(or the volume needed to total 50 mL of PEG in the purge

flask), transferring the rinses to the purge flask. Add

50 mL of organic-free deionized water to the purge flask.

Cap the purge flask tightly in between each rinse and after

adding all the components into the flask.

8.3.2 Allow the oven to equilibrate to 75 ± 2°C

(167 ± 3.6°F). Begin the sample recovery process by turning

the toggle valve on, thus allowing a 6 L/min flow of pure

nitrogen through the purge chamber.

8.3.3 Stop the purge after 30 min. Immediately

remove the sorbent tube(s) from the apparatus and cap both

ends. Remove the knockout trap and transfer the water catch

to a 10 mL volumetric flask. Rinse the trap with organic-

free deionized water and transfer the rinse to the

volumetric flask. Dilute to the 10 mL mark with water.

Transfer the water sample to a sample vial and store at 4 °C

(39.2 °F) with zero headspace. The analysis of the contents

of the water knockout trap is optional for this method. If

the target compounds are water soluble, analysis of the

water is recommended; meeting the recovery efficiency

criteria in these cases would be difficult without adding

the amount captured in the knockout trap.

9.0   Quality Control.

9.1 Miscellaneous Quality Control Measures.

Section	Quality Control Measure	Effect
8.1	Sampling equipment leak-check	Ensures accurate measurement of sample volume.
8.2	Recovery efficiency (RE) determination for each measured compound.	Ensures accurate sample collection and analysis.
8.3	Calibration of analytical instrument with at least 3 calibration standards.	Ensures linear measurement of compounds over the instrument span.

10.0 Calibration and Standardization.

10.1 The analytical instrument shall be calibrated with a minimum of three levels of standards for each compound whose concentrations bracket the concentration of test compounds from the sorbent tubes. Liquid calibration standards shall be used for calibration in the analysis of the solvent extracts. The liquid calibration standards shall be prepared in the desorption solvent matrix. The calibration standards may be prepared and injected individually or as a mixture. If thermal desorption and focusing (onto another sorbent or cryogen focusing) are used, a certified gaseous mixture or a series of gaseous standards shall be used for calibration of the instrument. The gaseous standards shall be focused and analyzed in the same manner as the samples.

10.2 The analytical system shall be certified free from contaminants before a calibration is performed (see

Section 11.1). The calibration standards are used to determine the linearity of the analytical system. Perform an initial calibration and linearity check by analyzing the three calibration standards for each target compound in triplicate starting with the lowest level and continuing to the highest level. If the triplicate analyses do not agree within 5 percent of their average, additional analyses will be needed until the 5 percent criteria is met. Calculate the response factor (Equation 305-3, Section 12.4) from the average area counts of the injections for each concentration level. Average the response factors of the standards for each compound. The linearity of the detector is acceptable if the response factor of each compound at a particular concentration is within 10 percent of the overall mean response factor for that compound. Analyze daily a mid-level calibration standard in duplicate and calculate a new response factor. Compare the daily response factor average to the average response factor calculated for the mid-level calibration during the initial linearity check; repeat the three-level calibration procedure if the daily average response factor differs from the initial linearity check mid-level response factor by more than 10 percent. Otherwise, proceed with the sample analysis.

11.0 Analytical Procedure.

11.1 Water Blank Analysis. A water blank shall be
analyzed daily to determine the cleanliness of the purge and
recovery system. A water blank is generated by adding 60 mL
of organic-free deionized water to 50 mL of PEG in the purge
chamber. Treat the blank as described in Sections 8.3.2 and
8.3.3. The purpose of the water blank is to insure that no
contaminants exist in the sampling and analytical apparatus
which would interfere with the quantitation of the target
compounds. If contaminants are present, locate the source
of contamination, remove it, and repeat the water blank
analysis.

11.2 Sample Analysis. Sample analysis in the context
of this method refers to techniques to remove the target
compounds from the sorbent tubes, separate them using a
chromatography technique, and quantify them with an
appropriate detector. Two types of sample extraction
techniques typically used for sorbents include solvent
desorption or direct thermal desorption of test compounds to
a secondary focusing unit (either sorbent or cryogen based).
The test compounds are then typically transferred to a GC
system for analysis. Other analytical systems may be used
(*e.g.,* HPLC) in lieu of GC systems as long as the recovery
efficiency criteria of this method are met.

11.2.1 Recover the test compounds from the sorbent tubes that require solvent desorption by transferring the adsorbent material to a sample vial containing the desorption solvent. The desorption solvent shall be the same as the solvent used to prepare calibration standards. The volume of solvent depends on the amount of adsorbed material to be desorbed (1.0 mL per 100 mg of adsorbent material) and also on the amount of test compounds present. Final volume adjustment and or dilution can be made so that the concentration of test compounds in the desorption solvent is bracketed by the concentration of the calibration solutions. Ultrasonicate the desorption solvent for 15 min in an ice bath. Allow the sample to sit for a period of time so that the adsorbent material can settle to the bottom of the vial. Transfer the solvent with a pasteur pipet (minimizing the amount of adsorbent material taken) to another vial and store at 4 °C (39.2 °F).

11.2.2 Analyze the desorption solvent or direct thermal desorption tubes from each sample using the same analytical parameters used for the calibration standard. Calculate the total weight detected for each compound (Equation 305-4, Section 12.5). The slope (area/amount) and y-intercept are calculated from the line bracketed between the two closest calibration points. Correct the

concentration of each waste sample with the appropriate recovery efficiency factor and the split flow ratio (if used). The final concentration of each individual test compound is calculated by dividing the corrected measured weight for that compound by the weight of the original sample determined in Section 8.3.1 (Equation 305-5, Section 12.6).

11.2.3 Repeat the analysis for the three samples collected in Section 8.3. Report the corrected concentration of each of the waste samples, average waste concentration, and relative standard deviation (Equation 305-6, Section 12.7).

12.0 Data Analysis and Calculations.

12.1 Nomenclature.

A_S = Mean area counts of test compound in standard.

A_U = Mean area counts of test compound in sample desorption solvent.

b = Y-intercept of the line formed between the two closest calibration standards that bracket the concentration of the sample.

C_T = Amount of test compound (µg) in calibration standard.

C_F = Correction for adjusting final amount of sample detected for losses during individual sample runs.

F_P = Nitrogen flow through the purge chamber (6 L/min).

F_S = Nitrogen split flow directed to the sample recovery system (use 6 L/min if split flow design was not used).

PPM = Final concentration of test compound in waste sample [μg/g (which is equivalent to parts per million by weight (ppmw))].

RE = Recovery efficiency for adjusting final amount of sample detected for losses due to inefficient trapping and desorption techniques.

R.F. = Response factor for test compound, calculated from a calibration standard.

S = Slope of the line (area counts/C_T) formed between two closest calibration points that bracket the concentration of the sample.

W_C = Weight of test compound expected to be recovered in spike solution based on theoretical amount (μg).

W_E = Weight of vial and PEG (g).

W_F = Weight of vial, PEG and waste sample (g).

W_S = Weight of original waste sample (g).

W_T = Corrected weight of test compound measured (µg) in sample.

W_X = Weight of test compound measured during analysis of recovery efficiency spike samples (µg).

12.2 Recovery efficiency for determining trapping/desorption efficiency of individual test compounds in the spike solution, decimal value.

$$RE = \frac{W_X}{W_C}$$ **Eq. 305-1**

12.3 Weight of waste sample (g).

$$W_S = W_F - W_E$$ **Eq. 305-2**

12.4 Response factor for individual test compounds.

$$RF = \frac{C_T}{A_S}$$ **Eq. 305-3**

12.5 Corrected weight of a test compound in the sample, in µg.

$$W_T = \frac{A_u - b}{S} \times \frac{1}{RE} \times \frac{F_p}{F_s}$$ **Eq. 305-4**

12.6 Final concentration of a test compound in the sample in ppmw.

$$PPM = \frac{W_T}{W_S}$$ **Eq. 305-5**

12.7 Relative standard deviation (RSD) calculation.

$$RSD = \frac{100}{\overline{PPM}}\sqrt{\frac{\sum_{i=1}^{n}(PPM_i - \overline{PPM})^2}{n-1}}$$ **Eq. 305-6**

13.0 Method Performance. [Reserved].

14.0 Pollution Prevention. [Reserved].

15.0 Waste Management. [Reserved].

16.0 References. [Reserved].
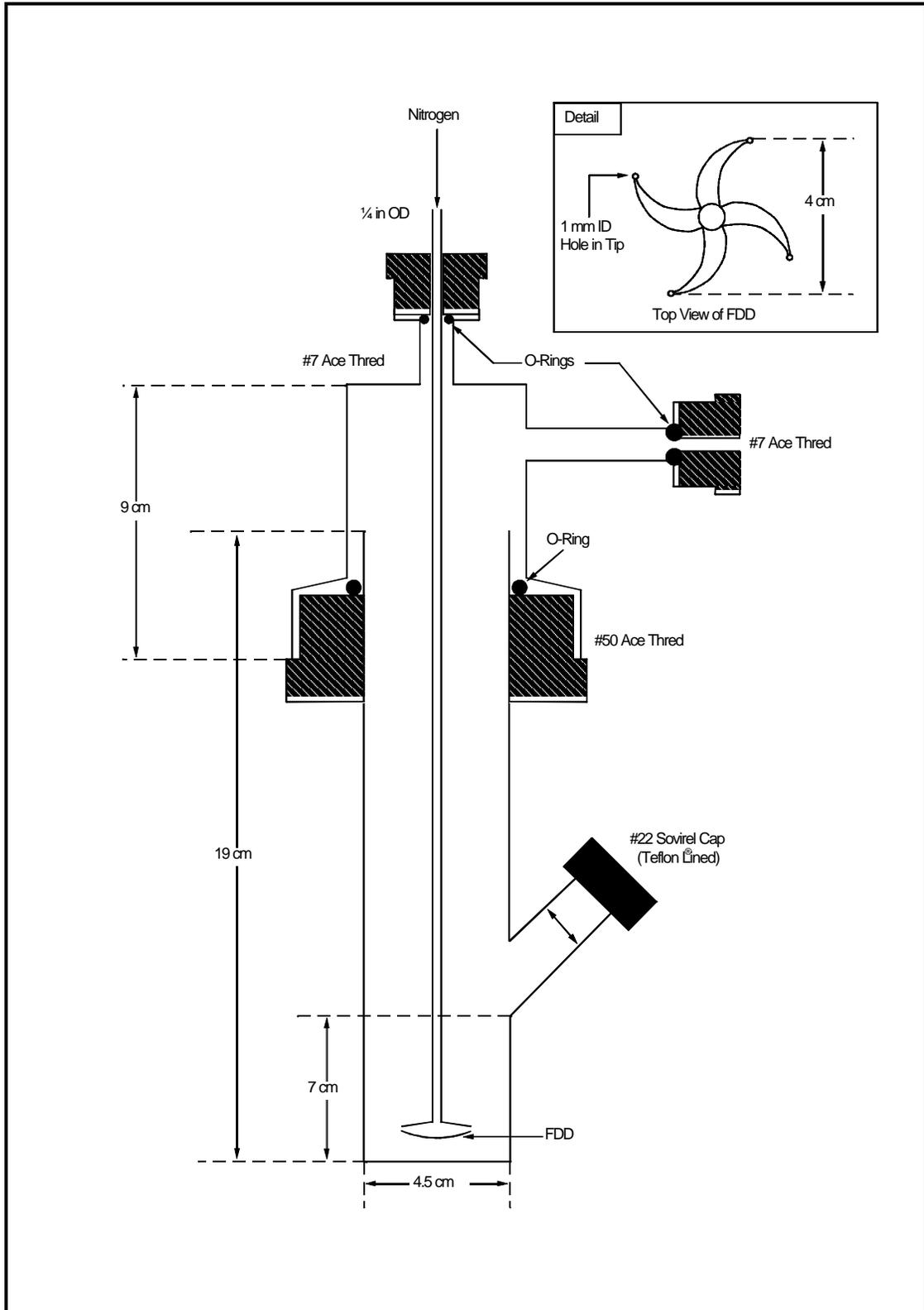
17.0 Tables, Diagrams, Flowcharts, and Validation Data.

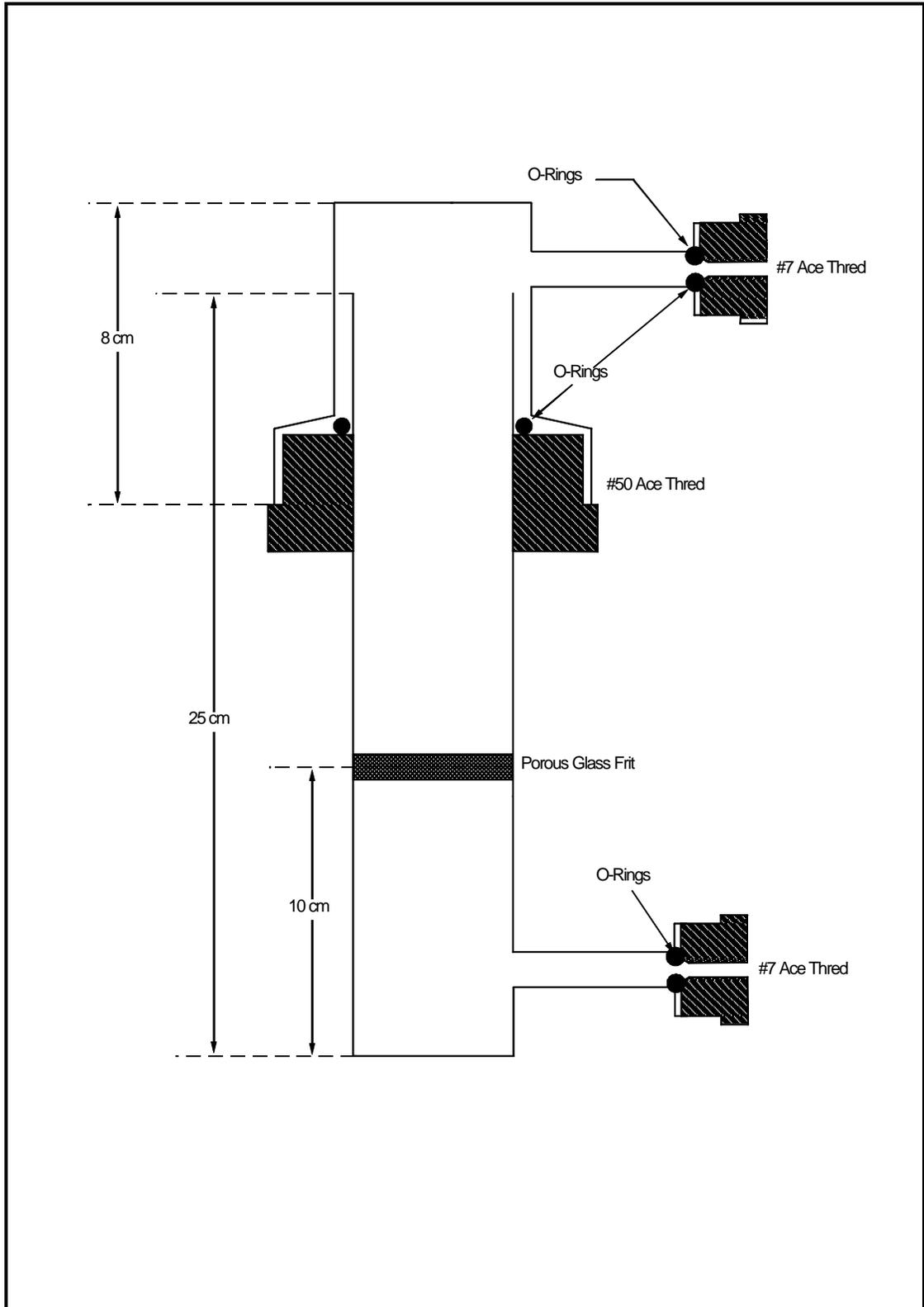Figure 305-1.   Schematic of Purge Chamber.

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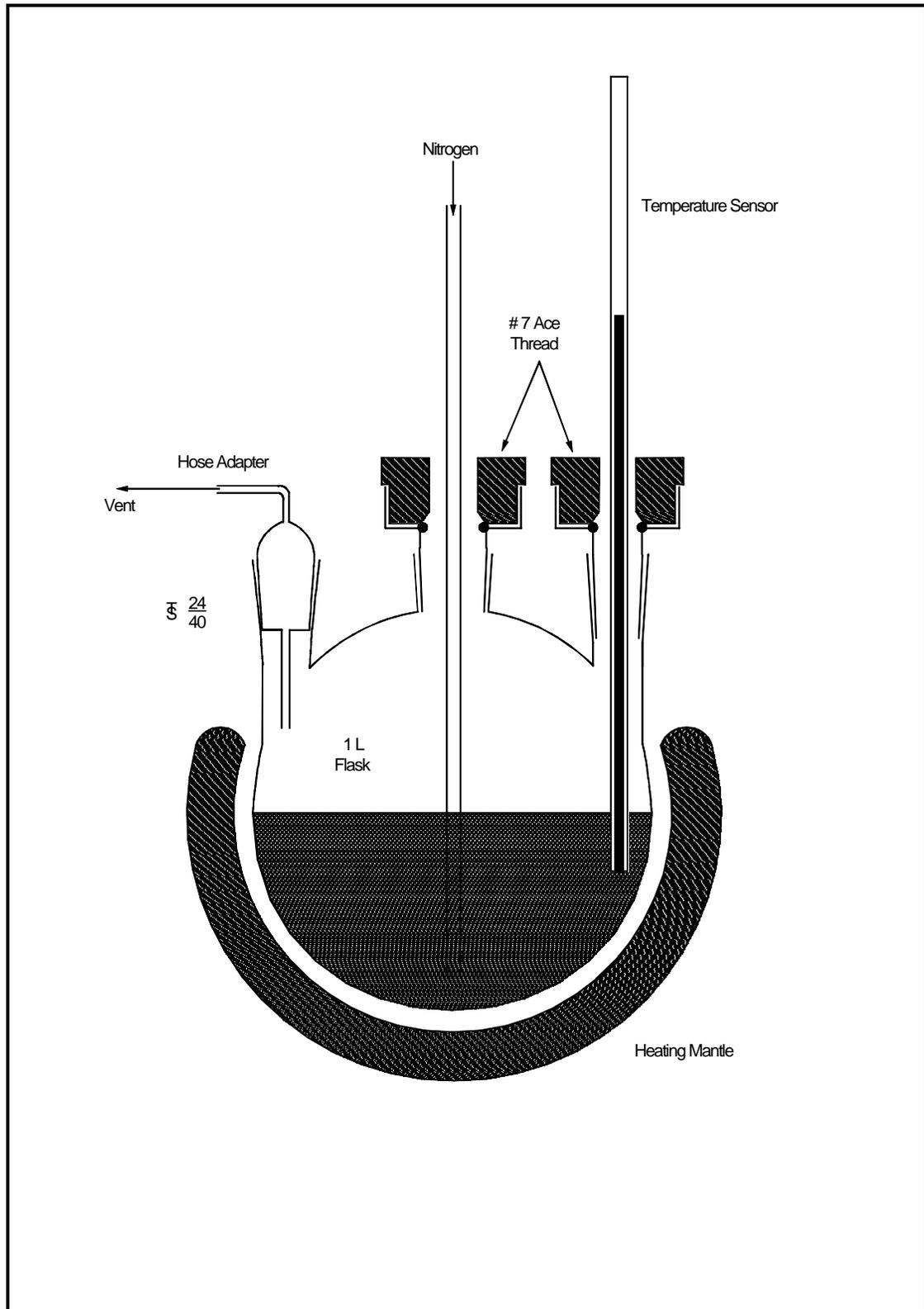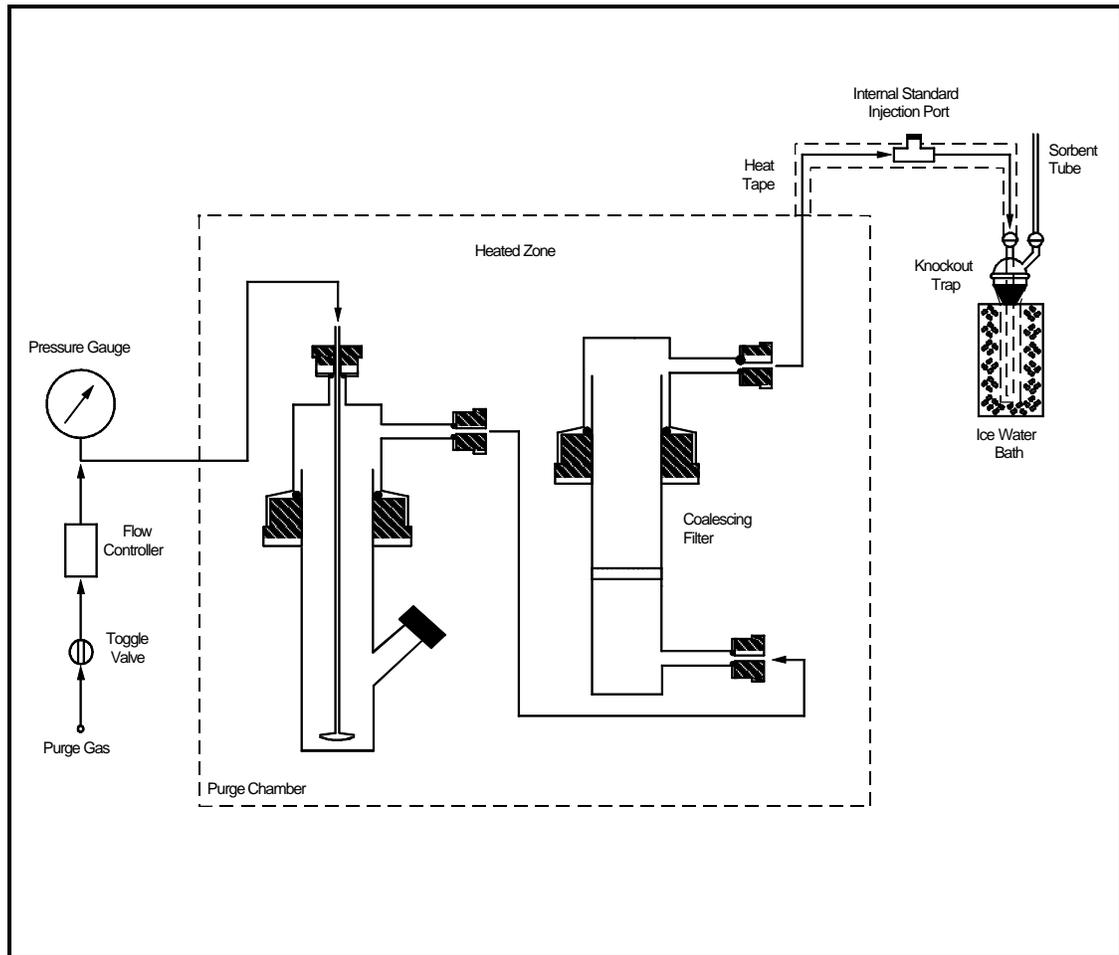**Figure 305-2.   Schematic of Coalescing Filter.**

Figure 305-3. Schematic of PEG Cleaning System.

Figure 305-4. Schematic of Purge and Recovery Apparatus.