Appendix D
Vapor Pressure Analysis Using Minivap Method
Standard Operating Procedure

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(Ver. 1.0)

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Project Background and Objectives

1.1. *Project Description*

The US EPA uses models to predict the amount of emissions from 6 oil and liquid asphalt storage and blending tanks using the vapor pressure of the mixture. However, the vapor pressure is difficult to measure from these highly viscous materials. Classic techniques like ASTM D2879 and others require degassing steps that may eliminate relatively lower molecular weight species from the vapor pressure measurement.

1.1.1. Objective

The objective of this project is to test the viability of the minivap method for the measurement of vapor pressure from heavy petroleum liquids such as 6 oil and liquid asphalt.

1.1.2. Background

Distillation of crude oil yields a multitude of products that fuel our modern machinery. Light fuel oils and gasoline are very profitable products from this process. Heavy liquid fuel oils and asphalt are considered the bottom of the barrel products from the distillation of crude oil. They are the remaining portions of crude oil after all other lighter and more useable fractions are stripped away in the distillation column. In the early days of refining crude oil the lower products of the process could be used directly as fuel for marine vessels and was called 6 oil or bunker C. The 6 oil became unusable as a direct marine fuel as the refining processes became more efficient and effective at stripping away lower molecular weight fractions creating a new product called vacuum residual. Vacuum residual still has energy that can be useful in powering ships. Today it is common practice to mix other blending stocks to the vacuum residual to make it usable in the internal combustion engines in marine vessels.

Blending takes place in large, sometimes insulated tanks that are open to the air and are kept at 120-140°F. The mixture must remain heated to allow the product to flow and prevent plugging of pumps and lines. Air sparging and circulator pumps are utilized to stir the tanks as each blending stock is added to the mixture.

The blending tanks that hold upwards of 300,000 barrels of 6 Oil are vented to the atmosphere. Volatile organics, if present in the mixture, have a direct route to the environment and can be released into the air. There is some question as to how much material is released to the air from these tanks.

1.1.3. Validating that the objective is met

An automated minimethod machine is available that will be used to measure the vapor pressure of 6 oil and liquid asphalt at 5 different temperatures. The variability of repeated measurements will be used to test the stability of the analytical instrumentation. Curves will be generated using the data and will be compared to vapor pressure data generated from several commercial laboratories using ASTM methods.

It is understood that the heavy liquids will vary from each other in the concentration and types of light ends that would be most at risk of being lost during the analytical process. In the course of the project, each material will be analyzed using the minimethod five times (except for the first heavy refinery liquid, which is analyzed ten times). In order to assess the possibility that the first heavy refinery liquid happened to be one that was less sensitive to volatile loss than other heavy refinery liquids, the first two dispensed samples and final three dispensed samples of the heavy refinery liquids will be analyzed using the minimethod.

1.2. *Procedure*

Figure 1 shows one of the minivap instruments used in this project.

Figure 1. Apparatus for dispensing sample material into smaller containers.

1.2.1. Instrument Setup

Grabner VP Vision

Set up the instrument according to the instructions in section 7.0 of the operator's manual with the following exceptions.

1. The outlet tube and waste container will not be used for this testing. Instead a cloth or towel will be used to catch expended fluids from the VPV.
2. Remove sample filter screen and O-ring.
3. Assemble and test a vacuum pump with inline knockout flask for connection with the outlet during bake outs and air purging.
4. Solvent rinse the instrument using pressure on the syringe to help the solvent move through the cell and out the exhaust. Do repeatedly at least 5 times and until no visible trace of sample is observed at the exhaust. Petroleum Ether will be used for all solvent rinses.
5. Run 1 check with n-Pentane.
6. Bake out at 120°F with vacuum pump attached to remove residuals.
7. Run 5 air rinses with vacuum pump attached to remove residuals.
8. Instrument is now ready for first sample.

Eralytics ERAVAP

Set up the instrument according to the instructions in section 3 of the operator's manual with the following exceptions.

1. The outlet tube and waste container will not be used for this testing. Instead a cloth or towel will be used to catch expended fluids from the ERAVAP.
2. Assemble and test a vacuum pump with inline knockout flask for connection with the outlet during bake outs and air purging.
3. Solvent rinse the instrument using pressure on the syringe to help the solvent move through the cell and out the exhaust. Do repeatedly at least 5 times and until no visible trace of sample is observed at the exhaust. Petroleum Ether will be used for all solvent rinses.
4. Run 1 check with n-Pentane.
5. Bake out at 120°F with vacuum pump attached to remove residuals.
6. Run 5 air rinses with vacuum pump attached to remove residuals.
7. Instrument is now ready for first sample.

1.2.2. Sample Preparation

1. Select the sample vial to be analyzed using the "Heavy Liquids Sample Receipt Logbook".

2. Locate and retrieve the vial from the flammables storage refrigerator.
3. Record the date the vial was received, the instrument used for the analysis, and the method used to perform the analysis in the “Heavy Liquids Sample Receipt Logbook”.
4. Record on the vial label the method to be run and a “G” for the Grabner and an “E” for Eralytics matching the instrument type used in the sample’s analysis.
5. Assemble a cleaned syringe and place it in a large beaker plunger side up.
6. Place the beaker and the syringe in a 60°C oven to preheat.
    a. 120°F to 140°F for 6 oil samples.
7. Remove any tape from the sample vile lid and place the vial in the 60°C oven to preheat.
8. Remove one set of toe warmers from their sealed packaging to allow the oxidation process to start and preheat. Do not put toe warmers in the oven. They will preheat nicely outside on a clean counter.
9. After the sample becomes liquid (usually after 5-10min) load the syringe with the sample by slowly pulling on the plunger with the vial inverted and attached with the filling cap.
10. Once the full liquid volume is loaded on the syringe, carefully expel any headspace.
11. Cap the syringe and place back in the oven until the instrument is ready for injection.

4 System Operation

1. Login to the VPV according to the instructions in section 8.0 of the operator’s manual using the following parameters.
2. Fill out the laboratory log on page 37 and 42 for the Grabner and Eralytics instruments, respectively.
3. Run a QA check with Pentane and ASTM single point measurement at 100°F.
    a. Use gentle force on the syringe to maintain ambient pressure in the chamber during all filling cycles.
    b. Minimum of 3 sample rinses of Pentane
    c. Injection temperature at 68°F
    d. Passes if Pabs is 15.48 to 15.82 psig
4. Bake out instrument at 120°F with vacuum.
5. Remove the syringe from the oven and apply toe warmers.
6. Attach the syringe to the sample port of the instrument. Use a single layer of pig mat absorptive sheeting to insulate the syringe/port area.
7. Fill out the laboratory log on page 37 and 42 for the Grabner and Eralytics instruments, respectively.

a. Use gentle force on the syringe to maintain ambient pressure in the chamber
b. Minimum of 3 sample rinses
c. Injection temperature at 77°F for hydraulic fluid.
d. Injection temperature at 100°F for known.
e. Injection temperature at 120°F to 140°F for 6 oil samples.
    i. Actual temperature determined when sample liquefies during sample preparation.

8. Perform an instrument cleaning described in section 2 “Instrument Setup”