Appendix A
Procedure for Dispensing Samples

Dispensing Large Samples of Heavy Refinery Liquids into Smaller Containers
Standard Operating Procedure
(Ver. 1.0)

Prepared by
Vince Torres, Kirsten Sinclair Rosselot, and Jarett Spinhirne

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Project Background and Objectives

1.1. Project Description

The objective of this procedure is to dispense samples that are uniform with respect to vapor pressure from 1 liter bulk flasks to 10 mL and 100 mL sample vials.

1.2. Background

The heavy refinery liquid (fuel oil no. 6 and liquid asphalt) samples for this project are typically contained in jars that are 1 L or larger. This material needs to be transferred to dozens of smaller containers that will be sent to commercial labs or used in the automated minimethod vapor pressure analyzer obtained for the project. This material does not flow at room temperature and must be heated before dispensing. Because of the need to have all the samples of each material be uniform with respect to vapor pressure, the handling, preparation, and dispensing of samples to be analyzed needs to be done uniformly and quickly to minimize the potential for loss of any volatile components and provide uniformity of samples with respect to vapor pressure.

1.3. Validating that the objective is met

An automated minimethod machine is available, it will be used to understand the effect of any volatiles lost during the process of separating the sample into smaller containers. This will be done by comparing measurements of the vapor pressure of the first heavy refinery liquid material at the beginning and at the end of the dispensing process. Part of the identification for each sample will be the order in which it was dispensed. It is understood that there will be some variability in the measured vapor pressure, even among samples that are identical. Thus, the first sample and last sample from each heavy refinery liquid batches that are dispensed using the apparatus will be analyzed using the automated minimethod. If the average vapor pressure of the last sample is below the average vapor pressure of the first sample and is below the lower limit of the 95% confidence interval for the first sample, a loss of volatiles during dispensing will be suspected.

It is also 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 dispensing 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. As soon as the minimethod results for all of the heavy refinery liquids are available, the ratio of the average of the early dispensed samples and late dispensed samples will be calculated for each material. If there is no vapor pressure bias introduced during dispensing, it is expected that the average of these ratios would be a number near one. If any of the refinery liquids has a ratio that is below the lower

limit of the 67% confidence interval for the ratios as a whole, a loss of volatiles for that material will be suspected.

Table 2. Sample Vial Matrix

FIRST MATERIAL DISPENSED: HYDRAULIC FLUID
Dispense 1.5 L of material.

Order of dispensing	**Purpose of vials/containers**
eight 30-ml vials labeled HY-ddmmyy-1 to HY-ddmmyy-8	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 in reserve
six 10-ml vials labeled HY-ddmmyy-9 to HY-ddmmyy-14	3 for D2879 analysis (1 to Savant, 1 to Petro-Lubricant Testing, 1 to Alcor Petrolab), 3 in reserve
two 125-ml containers labeled HY-ddmmyy-15 and HY-ddmmyy-16	1 for D323 Procedure A at Fesco, 1 in reserve
two 200-ml containers labeled HY-ddmmyy-17 and HY-ddmmyy-18	1 for E1719 at Analytical Testing, 1 in reserve
fourteen 30-ml vials labeled HY-ddmmyy-19 to HY-ddmmyy-32 (fill at least eight but no more than 14)	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 to 10 in reserve

SECOND MATERIAL DISPENSED: "KNOWN" RECIPE
Make up enough for 1.5 L of material (20 mol % octane and 80 mol % nonadecane) and dispense it.

Order of dispensing	**Purpose of vials/containers**
eight 30-ml vials labeled KR-ddmmyy-01 to KR-ddmmyy-08	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 in reserve
six 10-ml vials labeled KR-ddmmyy-09 to KR-ddmmyy-14	3 for D2879 analysis (1 to Savant, 1 to Petro-Lubricant Testing, 1 to Alcor Petrolab), 3 in reserve
two 125-ml containers labeled KR-ddmmyy-15 and KR-ddmmyy-16	1 for D323 Procedure A at Fesco, 1 in reserve
two 200-ml containers labeled KR-ddmmyy-17 and KR-ddmmyy-18	1 for E1719 at Analytical Testing, 1 in reserve
fourteen 30-ml vials labeled KR-ddmmyy-19 to KR-ddmmyy-32 (fill at least eight but no more than 14)	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 to 10 in reserve

THIRD MATERIAL DISPENSED: SOURCE B SIX OIL
Combine material from Source B jars until there are 2 L total. There will be about 500 ml of BOSTCO material left over.

Order of dispensing	**Purpose of vials/containers**
eight 30-ml vials labeled BT-ddmmyy-01 to BT-ddmmyy-08	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 in reserve
eight 10-ml vials labeled BT-ddmmyy-09 to BT-ddmmyy-16	3 for D2879 analysis (1 to Savant, 1 to Petro-Lubricant Testing, 1 to Alcor Petrolab), 1 to BP for their vapor pressure project, 4 in reserve
four 50-ml containers labeled BT-ddmmyy-17 to BT-ddmmyy-20	1 for D445 analysis (viscocity) at Petro-Lubricant Testing, 1 for D2522 (sulfur) at Petro-Lubricant Testing, 2 in reserve
four 100-ml containers labeled BT-ddmmyy-21 to BT-ddmmyy-24	1 for D93 Procedure B (flash) at Petro-Lubricant Testing, 1 for D95 (water) at Petro-Lubricant Testing, 2 in reserve
two 125-ml containers labeled BT-ddmmyy-25 and BT-ddmmyy-26	1 for D323 Procedure A at Fesco, 1 in reserve
two 200-ml containers labeled BT-ddmmyy-27 and BT-ddmmyy-28	1 for E1719 at Analytical Testing, 1 in reserve
fourteen 30-ml vials labeled BT-ddmmyy-29 to BT-ddmmyy-42	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 10 in reserve
one 500-ml vial for leftovers labeled BT-ddmmyy-43 (or two 250-ml vials labeled BT-ddmmyy-43 and BT-ddmmyy-44, etc.)	So we can store the leftovers without a lot of head space.

FOURTH MATERIAL DISPENSED: SECOND AND THIRD SAMPLES OF SIX OIL

Combine all of the material from the second sample delivery with material from the third sample delivery from Source M until there are 2 L total. There will be about 750 ml of Source M's third sample delivery left over.

Order of dispensing	**Purpose of vials/containers**
eight 30-ml vials labeled MM-ddmmyy-01 to MM-ddmmyy-08	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 in reserve
eight 10-ml vials labeled MM-ddmmyy-09 to MM-ddmmyy-16	3 for D2879 analysis (1 to Savant, 1 to Petro-Lubricant Testing, 1 to Alcor Petrolab), 1 to BP for their vapor pressure project, 4 in reserve
four 50-ml containers labeled MM-ddmmyy-17 to MM-ddmmyy-20	1 for D445 analysis (viscocity) at Petro-Lubricant Testing, 1 for D2522 (sulfur) at Petro-Lubricant Testing, 2 in reserve
four 100-ml containers labeled MM-ddmmyy-21 to MM-ddmmyy-24	1 for D93 Procedure B (flash) at Petro-Lubricant Testing, 1 for D95 (water) at Petro-Lubricant Testing, 2 in reserve
two 125-ml containers labeled MM-ddmmyy-25 and MM-ddmmyy-26	1 for D323 Procedure A at Fesco, 1 in reserve
two 200-ml containers labeled MM-ddmmyy-27 and MM-ddmmyy-28	1 for E1719 at Analytical Testing, 1 in reserve
fourteen 30-ml vials labeled MM-ddmmyy-29 to MM-ddmmyy-42	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 10 in reserve
one 750-ml vial for leftovers labeled MM-ddmmyy-43 (or three 250-ml vials labeled MM-ddmmyy-44 to MM-ddmmyy-46, etc.)	So we can store the leftovers without a lot of head space.

FIFTH MATERIAL DISPENSED: FIRST SAMPLE OF SIX OIL FROM SOURCE M MIXED WITH SOURCE B SAMPLE

Combine all of the material from Source M's first sample delivery with material from Source B jar(s) until there is a total of 2 L of material. Get a good measurement of the volume of Source M's first sample delivery so we have that for our records. There will be little to no material left over.

Order of dispensing	**Purpose of vials/containers**
eight 30-ml vials labeled MB-ddmmyy-01 to MB-ddmmyy-08	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 in reserve
eight 10-ml vials labeled MB-ddmmyy-09 to MB-ddmmyy-16	3 for D2879 analysis (1 to Savant, 1 to Petro-Lubricant Testing, 1 to Alcor Petrolab), 1 to BP for their vapor pressure project, 4 in reserve
four 50-ml containers labeled MB-ddmmyy-17 to MB-ddmmyy-20	1 for D445 analysis (viscocity) at Petro-Lubricant Testing, 1 for D2522 (sulfur) at Petro-Lubricant Testing, 2 in reserve
four 100-ml containers labeled MB-ddmmyy-21 to MB-ddmmyy-24	1 for D93 Procedure B (flash) at Petro-Lubricant Testing, 1 for D95 (water) at Petro-Lubricant Testing, 2 in reserve
two 125-ml containers labeled MB-ddmmyy-25 and MB-ddmmyy-26	1 for D323 Procedure A at Fesco, 1 in reserve
two 200-ml containers labeled MB-ddmmyy-27 and MB-ddmmyy-28	1 for E1719 at Analytical Testing, 1 in reserve
fourteen 30-ml vials labeled MB-ddmmyy-29 to MB-ddmmyy-42 (fill at least eight but no more than 14)	3 for the Grabner (for D6378, D6377, and indirect VOC), 1 for the Eralytics (for D6378), 4 to 10 in reserve

1.4. Procedure

Figure 1 shows the elements of the procedure. The bulk supply bottle will be used to fill a 2 quart mixing vessel that will be quickly stoppered with a stopper that has two ports:

1) a dip tube
2) an air inlet and thermocouple

The bulk supply bottle will be heated slowly in a warm oil bath with a magnetic stirrer until the contents begin to flow adequately (~100°F). Then air will be introduced using a manual hand pump at about 5 psi (gauge), pushing the contents out of the dip tube and into the smaller containers, which will be filled until full and sealed. The minimum pressure will be used necessary to flow the sample into the vials. This will be conducted until the bulk supply bottle is empty. A weight will prevent the bottle from floating in the oil bath.

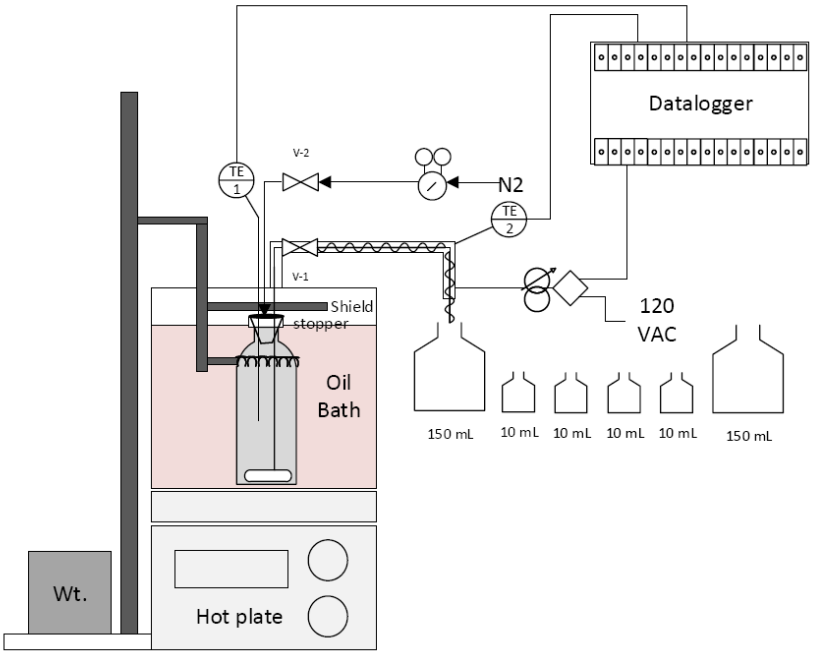

Figure 1. Apparatus for dispensing sample material into smaller containers.

1.5. Vial Preparation

Vials will be purchased to accommodate a headspace not more than 20% of the total volume of the vial once loaded with sample. All vials will be marked with the appropriate level marker prior to dispensing so that the operator can concentrate on the filling process without the need to make volumetric measurements during the process. Labels will be applied to all vials after the stock bottle is completely depleted. Extra sample material remaining after filling of the predetermined vials will be dispensed in volumes required for the minimethod analysis until the stock bottle is depleted.

1.6. Dispensing

1. The magnetic stir bar is added to the stock mixing bottle.
2. The bottle is positioned on top of a stainless steel spacer ring within the oil bath container.
3. The bottle is positioned in a manner that the magnetic stir bar move freely in the center.
4. The lid of the oil bath is placed on top without adjusting the position of the now aligned bottle.
5. The ring stand claw is now used to mark the correct position of the bottle.
6. The mixing bottle is now filled with all the material that is indicated in the mixing batch and sample vial matrix.

7. Be careful not to overfill the mixing bottle. The sample material will expand as it is heated.
8. The top portion of the dispensing apparatus is now carefully placed in and on top of the mixing bottle.
9. Secure the apparatus in place using slight downward pressure from the ring stand claw.
10. The oil bath is now charged with oil.
11. The feedback thermocouple probe tip associated with the hotplate is to be in contact with the heated oil in the oil bath at all times that the hotplate is turned on.
12. The power to the hotplate is turned on and temperature is set to 100°F. Reasonable RPMS are set for the magnetic stir bar.
13. The temperatures should be monitored.
14. The power to the dispensing transfer line is turned on and set to 100°F.
15. Absorbent towels or a catch pan should be placed under the outlet just in case there is overflow during expansion of the sample in the mixing bottle.
16. The hand air pump and gauge is now attached to the system.
    a. The mixing bottle should remain at ambient pressure until the hand pump is manipulated. A buildup of pressure indicates a problem and power to all heaters should be terminated until the cause of the buildup can be remedied.
17. Once the mixing bottle internal thermocouple indicates 100°F dispensing can start.
    a. Set point for the hotplate temperature will need to be increased to a point higher than the internal temperature of the sample to maintain target temperature.
18. After dispensing all power to heated zones should be turned off.
19. Oil should be drained from the oil bath and at a safe handling temperature and only if necessary for the safe introduction of the next mixing batch.
20. It may be determined that the next sample can be added to the mixing bottle without cleaning.
21 If cleaning of the apparatus is needed, all wetted parts will be cleansed with enough petroleum ether, purged with dry nitrogen within the hood area, and baked out for 1 hour in a drying oven at 212°F.towards the heater wall