STANDARD OPERATING PROCEDURE (0160 SOP)

DEWATERING OF EMULSION SAMPLES

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0160-SOP

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1.0 SIGNIFICANCE AND USE

This method describes the process of dewatering water and bitumen emulsions through manual distillation of petroleum products. The procedure involves conducting the distillation at atmospheric pressure first, followed by vacuum distillation to ensure the complete removal of water. The method adheres to the guidelines specified in the ASTM D1160 method [1].

2.0 PRINCIPLES AND THEORIES

2.1 PRINCIPLES

The dewatering process of a water-containing hydrocarbon sample involves distillation using the ASTM D1160 apparatus. Heat is applied to the sample in the distillation flask to boil the water and light hydrocarbons, which are then condensed into a receiving flask. A primary distillation under atmospheric pressure removes most of the water. Subsequent vacuum distillation is conducted to allow for lower distillation flask temperatures which will prevent thermal degradation of the sample. Hydrocarbons obtained from the sample through distillation are quantitatively combined prior to further analysis.

2.2 INTERFERENCES

2.2.1 WATER SOLUBLE ORGANICS

Water soluble organics which are distilled into the receiver will partition into the aqueous phase and be counted as water. They will not be recombined into the product.

2.2.2 SOLIDS

Solids will remain in the distillation flask during distillation and will be counted as bitumen. They may not be fully transferred to the product.

2.3 LIMITATIONS AND SCOPE

- If the sample being processed is not homogenous, then entire sample provided needs to be distilled to prevent sampling bias.
- Samples containing hydrocarbons lighter than n-pentane will have some loss due to the efficiency of the dry ice trap.

3.0 SAFETY

3.1 PICTOGRAMS

Pictograms are used throughout the SOP to indicate sources of danger to the operator, equipment, and provide clarification on the use of the SOP and related documents. A key to the pictograms used in this SOP are shown and described in Table 1.

Table 1: Pictogram definitions

	Warning! Failure to comply may result in non-life-threatening injury, damage to the equipment, or irreparable change to the sample or process.
	Outcome. What may happen if the proper procedures are not followed.
	Tips. Information to optimise performance.

3.2 POTENTIAL HAZARDS

This method does not address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

4.0 DEFINITIONS

Acronyms, definitions, or abbreviations contained within the SOP.

- **Atmospheric Equivalent Temperature (AET):** Conversion of a boiling point at reduced pressure to a boiling point at atmospheric pressure.
- **Initial Boiling Point (IBP):** The temperature at which a sample begins to distill.
- **Residue:** Sample remaining in distillation pot flask after distillation.
- **Hydrocarbons:** A mixture of molecules composed primarily of hydrogen and carbon that may also contain nitrogen, sulphur, oxygen, and other trace compounds.
- **Distillation Feed Flask:** A glass distillation feed flask with thermowell used to contain the sample as it is heated.
- **Receiving Flask:** A receiver, also known as a collection flask, is a glass container specifically designed to collect the condensed distillate during a distillation process.
- **Cold Trap Flask:** A trap is glass or metal container which collects material which passes through the condenser.
- **Recombined Sample:** All distilled or residual hydrocarbons blended to recreate the composition of the original sample without water.

5.0 MATERIALS

5.1 MATERIALS

5.1.1 500mL or 1L aluminum cans with vapour tight lids.

5.1.2 100mL amber bottle with septum cap

5.1.3 High temperature silicone based vacuum grease (Fisher Cat# 14-635-5C or equivalent).

5.1.4 Dry ice pellets

5.2 EQUIPMENT

5.2.1 DEWATERING APPARATUS:

5.2.1.1 Distillation column and condenser as described in ASTM D1160

5.2.1.2 Circulating bath capable of maintaining condenser temperature of -5°C

5.2.1.3 Circulating bath capable of maintaining side arm temperature of +5°C

5.2.1.4 Manually controllable upper heating mantle 300W

5.2.1.5 Manually controllable lower heating mantle 300W

5.2.1.6 Vacuum controller configured to allow operation at atmospheric pressure or 10torr (abs)

5.2.1.7 Vacuum pump

5.2.1.8 Magnetic stirrer plate

5.2.1.9 2L distillation feed flask with thermowell

5.2.1.10 1L receiving flask

5.2.1.11 Cold trap with insulated dry-ice container.

5.2.2 LABORATORY EQUIPMENT

5.2.2.1 Oven capable of heating bitumen samples to 60°C

5.2.2.2 Refrigerator 7°C or lower

5.2.2.3 Top loading balance Mettler PB400-S equivalent or better

5.2.2.4 1L separatory funnel

5.2.2.5 Glass funnels

5.2.2.6 Magnetic stir bars

5.2.2.7 Joint clamps

5.3 REAGENTS

5.3.1 Toluene, technical grade – used for cleaning.

5.3.2 Acetone, technical grade – used for cleaning.

5.3.3 Nitrogen, dry - makeup gas for vacuum controller and purge gas

6.0 PROCEDURE

6.1 APPARATUS SETUP

6.1.1 Select an appropriately sized feed flask that is approximately 2x volume of sample.

6.1.2 Add a stir bar to the feed flask, making sure that the thermo-well of the flask does not interfere with the free rotation of the magnetic bar.

6.1.3 Weigh the feed flask, receiving flask and cold trap record the weights in the ASTM D1160 worksheet.

6.1.4 Connect the cold trap to the distillation system. To ensure a secure seal, apply a small amount of vacuum grease to the O-ring. This will create an effective and reliable seal between the distillation components.

6.1.5 Place a thermal bucket around cold trap and fill it with dry-ice pellets.

6.1.6 Turn on the circulating baths and set to -5°C for the condenser and +5°C for side arm and allow the system to come to temperature before heat is applied to the sample.

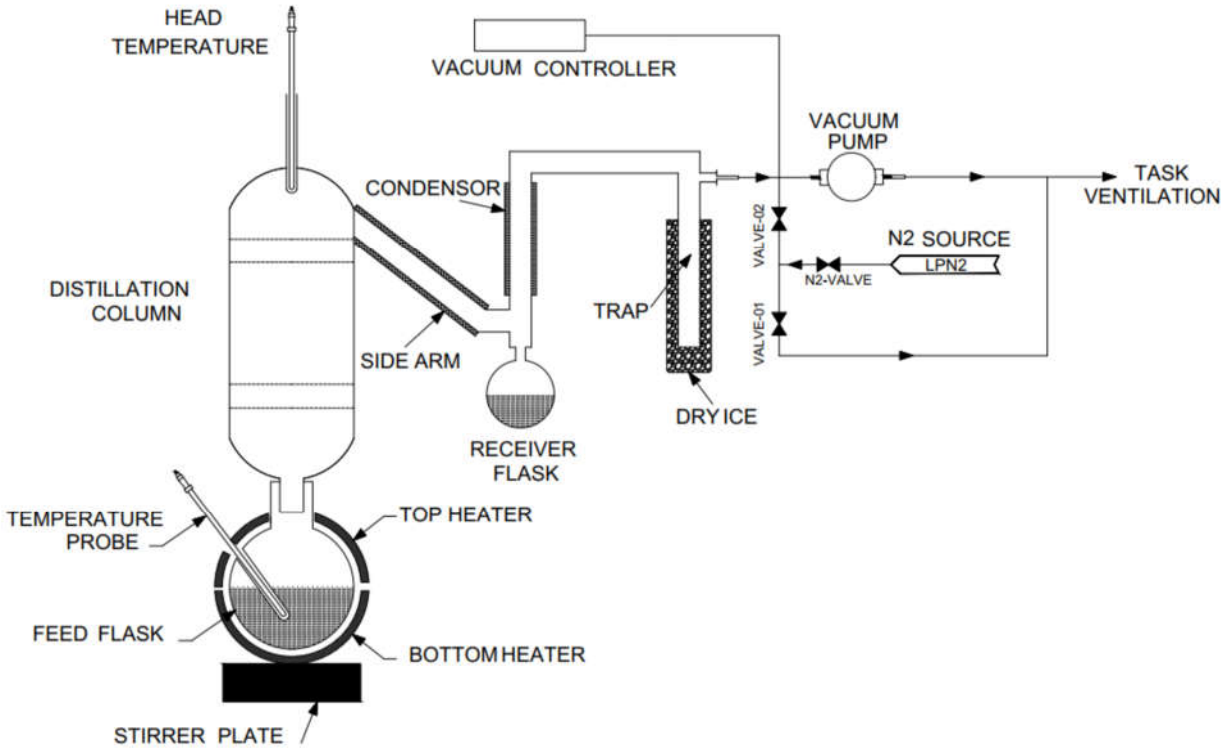

Figure 1: Dewatering apparatus schematic

6.2 Atmospheric Distillation

6.2.1 Preparation of Apparatus

6.2.1.1 Pour any free water and hydrocarbon into the pre-weighed distillation feed flask (6.1.1) using a funnel.

6.2.1.2 When possible, cut the top of the plastic sample container off for easier access to sample.

6.2.1.3 Heat sample container with remaining sample at 60°C in an oven for no more than 15 min to reduce viscosity of the bitumen.

6.2.1.4 Pour and scrape the remaining sample into the flask with a metal spatula.

	Warning! Use as little heat as possible (time x temperature) to not lose any light hydrocarbons.

6.2.1.5 Grease the joints of the receiver flask and the feed flask. Connect the receiver flask and clamp it in place.

6.2.1.6 Insert the feed flask thermocouple into the feed flask thermowell.

6.2.1.7 Place the feed flask into the heating mantle, raise the lab jack until the feed flask is firmly connected to the distillation column and clamp the feed flask in place.

6.2.1.8 Ensure valve-01and valve-02 are open.

6.2.2 Atmospheric Distillation Operation

6.2.2.1 Start the stir plate and adjust the speed to give a maximum agitation. The stirrer may not be capable of maximum rotation while the sample is a room temperature. Stirrer speed should be increased as the sample warms if that is the case.

6.2.2.2 Turn on the heat for both the lower and upper heating mantels. Adjust heat levels as required to initiate the boiling of the sample. 2L of water-bitumen emulsion should boil in 30-60 minutes.

6.2.2.3 Monitor the temperature and observe sample in the feed flask for bumping. If bumping or splashing is observed, please follow the instructions in 6.2.3.

	Warning! Bumping occurs while the sample is first heating up. Sample needs to be constantly monitored until a steady and consistent distillation has been meet.

6.2.2.4 Record the time, feed flask temperature, head temperature and heat rate of the distillation in the D1160 distillation record book. Consistently update the progress of the distillation every 60 min.

6.2.2.5 Continue distillation until no more distillates can be obtained and the feed flask temperature is at least 140°C. It is crucial that the feed flask (liquid) temperature does not exceed 250°C to avoid thermal cracking of the sample. This temperature limitation helps maintain the integrity of the sample during the distillation procedure.

6.2.2.6 When the distillation is complete, turn off the heat and stirring.

6.2.2.7 Untie the upper heating mantle jacket and lower the feed flask away from the distillation column.

6.2.2.8 A stream of air can be applied to cool the feed flask quicker.

6.2.2.9 Remove the receiving flask, wipe off the grease on the joint and weigh. Record the weight of the receiver on worksheet.

6.2.2.10 Transfer contents of the receiver to a separatory funnel and collect the hydrocarbon layer in a pre-weighed amber bottle.

6.2.2.11 Record weight of recovered hydrocarbon on worksheet.

6.2.2.12 Inspect the cold trap for hydrocarbons. If present, transfer to amber bottle used in 6.2.2.10 and record the new weight.

6.2.2.13 Store amber bottle in a fridge at or below 7°C.

	Water should not be present in the cold trap during atmospheric distillation. If found this indicates an issue with the condenser and should be investigated.

6.2.3 How to Handle Sample If Bumping or Splashing Occurs

6.2.3.1 If any violent bubbling or splashing is observed this will lead to sample bumping over into the receiving flask.

6.2.3.2 Turn the heat and stirrer off.

6.2.3.3 If sample was contained in the flask allow the sample to cool and settle. Restart slowly.

6.2.3.4 If sample was lost to the distillation column and/or receiver flask, the sample should be discarded, and the apparatus cleaned when feasible. Repeat the sample.

6.2.3.5 If sample was lost to the distillation column and/or receiver flask and the sample can not be discarded, the distillation column and condenser can be heated to drain the sample back into the feed flask and/or receiver flask. This allows the distillation process to be restarted, this will result in higher than acceptable loss of the sample.

6.3 VACUUM DISTILLATION

6.3.1 APPARATUS PREPARATION

6.3.1.1 Weigh a new receiving flask and record the weight on the worksheet.

6.3.1.2 Add grease to the joint and connect to the distillation unit, clamp it in place.

6.3.1.3 Raise the lab jack and secure the feed flask.

6.3.1.4 Retie the upper heating mantle jacket and turn off any applied cooling air.

6.3.1.5 If the cold trap was disassembled, clean it with toluene, dry with acetone and forced air. Reweigh the trap and record the weight in the worksheet.

6.3.1.6 Start the stir plate and adjust the speed to ensure maximum agitation. The stirrer may not be capable of maximum rotation while the sample is a room temperature. Stirrer speed should be increased as the sample warms.

	**IMPORTANT**: For vacuum distillation, to avoid boil over and excessive foaming, reduce the pressure slowly. The feed flask temperature MUST be <70°C before applying vacuum. Constantly check for foaming.

6.3.1.7 On the vacuum controller, set the pressure set point at 10torr.

6.3.1.8 Open N2-valve for the nitrogen supply (Figure 1) and turn the vacuum pump **ON.**

6.3.1.9 Close valve-01 (Figure 1) to the exhaust. Monitor for sample in the feed flask for foaming.

6.3.1.10 Slowly close valve-02 (Figure 1) to seal the apparatus to vacuum, monitor the feed flask for sample foaming.

6.3.1.11 Check to see if 10torr pressure was achieved, pressure should stabilize within a few seconds. Proceed with section 6.3.2.

6.3.1.12 If 10torr can not be achieved turn off vacuum pump, open both valves-01 and-02 then check for leaks. Restart at 6.3.1.7.

6.3.2 VACUUM DISTILLATION OPERATION

6.3.2.1 Turn on the lower and upper heating mantels to the same settings identified in 6.2.2.2.

6.3.2.2 Record time, feed flask and head temperatures, heat rate, and pressure in the D1160 distillation record book.

6.3.2.3 As soon as the head temperature hits 80.5°C, turn off heat to the feed flask. Head temp may continue to rise slightly due to residual heat in the system.

	Dewatering should be done to a 204°C AET. At 10torr this equates to 80.5°C head temperature. If a different pressure is achieved, head temperature target should be recalculated using annex A7 in ASTM D1160.

6.3.2.4 Record time, temperatures, and pressure in the logbook.

6.3.2.5 Remove the upper heating mantle.

6.3.2.6 When head temperature begins to decrease and no distillate is coming over to the receiving flask, break the vacuum in the system.

6.3.2.7 Slowly open valve-02.

6.3.2.8 Slowly open valve-01.

6.3.2.9 Turn off the vacuum pump.

6.3.2.10 Turn off the nitrogen by closing the N2-valve.

6.3.2.11 Allow the sample to cool for at least 15 min to ensure all vapours have recondensed into the feed flask.

6.3.2.12 Remove the receiver flask, clean off vacuum grease with a cloth and weigh the receiver. Record the weight in worksheet.

6.3.2.13 Place receiving flask on dry ice for 2-5 mins to freeze any small amount of water.

6.3.2.14 Transfer hydrocarbon in the receiving flask to the amber collection bottle in step 6.2.2.13. Re-weigh the bottle and record weight in worksheet.

6.3.2.15 Remove trap from unit and inspect for liquids.

6.3.2.16 If the trap contains liquids, place the trap on dry ice to freeze water as in 6.3.2.13 and carefully pipette out the hydrocarbons. Add any additional light hydrocarbons collected from the cold trap to the amber collection bottle. Re-weigh bottle and record weight in worksheet.

6.3.2.17 Lower the feed flask from the distillation column and remove the flask.

6.3.2.18 Clean off vacuum grease with a cloth and weigh the flask while still warm. Record weight in logbook.

6.3.2.19 Pre-weigh a metal can, record the weight in worksheet. Carefully transfer the contents of the feed flask into the can. Retrieve the stir bar.

6.3.2.20 Allow the feed flask and the metal can come to room temperature. Record final weights in the D1160 worksheet.

6.4 RECOMBINE HYDROCARBONS

6.4.1 Calculate the amount of light hydrocarbons to add using the calculation in Equation 1. Due to transfer losses it is not possible to recombine all recovered light ends with the residue transferred to the can.

6.4.2 Warm the residual bitumen can in an oven. 60°C for 20 mins is suggested. This should be modified to ensure good mixing when the sample is warm without exceeding the expected IBP of the recombined sample.

6.4.3 Add the calculated amount of light hydrocarbons to residual bitumen can. Mix carefully and thoroughly using a spatula or stir rod.

	**NOTE**: The temperature used for residue heating must be enough that the sample can be easily mixed, but low enough that there will be no evaporation of the recovered hydrocarbons. Residue temperature must be below the IBP of the light hydrocarbons. For de-watered bitumen this is generally between 40°C and 60°C. Any power mixing must not create or conduct heat into the sample.

6.5 CLEANUP

6.5.1 CLEAN DISTILLATION UNIT.

6.5.1.1 Add a small amount of toluene to a distillation feed flask.

6.5.1.2 Add a new receiving flask. Assemble the apparatus following 6.1 to 6.2.2.3.

6.5.1.3 Turn on the heating mantels and allow toluene to come to a boil. Once you observe at least 50ml of toluene in the receiving flask, turn off the heat and allow the unit to cool.

6.5.1.4 Rinse the unit with acetone through the head temperature thermowell and allow to air dry.

6.5.2 CLEAN DISTILLATION FEED FLASK AND RECEIVER

6.5.2.1 Place feed flask and receiver in the burning oven overnight.

6.5.2.2 When the flasks are cooled the next morning, wash with soap and water and rinse with type 1 water.

6.5.2.3 Dry both flasks at 110°C in an oven for 1-2hours.

6.5.3 CLEAN COLD TRAP

6.5.3.1 Rinse the cold trap with toluene followed by acetone and allow to air dry.

7.0 QUALITY CONTROL

7.1 EQUIPMENT VERIFICATION

7.1.1 Test head temperature reading using toluene. When cleaning, the head temperature should read 110.6°C. If this is not reached, check positioning and calibration of thermocouple.

7.1.2 Test vacuum controllers either following manufacturer's recommendations, or by distilling a known product under vacuum and comparing to expected yields.

7.2 DATA VERIFICATION

7.2.1 When properly performed, this method should have 98% or greater recovery. If loss is greater than 2%, investigate potential errors.

8.0 CALCULATIONS

Equation 1: Recombination Calculation

$$F2 = \frac{F1\ x\ R2}{R1}$$

F2= the weight of the fraction needed to be added back

F1 = total weight of light fraction recovered

R2 = weight of residue transferred into container

R1 = total weight of residual

9.0 PRECISION AND BIAS

This method was designed primarily as a sample preparation method. Precision and bias of this method have not been determined because there is not accepted reference standard. Site precision can be determined using a homogenous sample stream if required.

10.0 REPORTING

Report water recovered total hydrocarbons and loss in wt% to two decimal places or as appropriate based on the precision of the balance(s) used.

11.0 REFERENCES AND RESOURCES

11.1 REFERENCES

11.1.1 ASTM Standard D1160-18 “Standard Test Method for Distillation of Petroleum Products at Reduced Pressure” ASTM International, West Conshohocken, PA, 2003, DOI: 10.1520/D1160-18, www.astm.org

11.2 FORMS

Distillation Worksheet

Date: _____ Lims #: _____ Description: _____

Cut	Pressure (mmHg)	Flask (g)	Flask + Sample (g)	Sample (g)	Weight % (m/m)
POT					
FR1+H20	ATM				
FR1	ATM				
H20	ATM				
FR1+H20	Vac				
FR1	Vac				
H20	Vac				
Trap					
Final FR1					
Final H20					
RESIDUE					
LOSS					

COMMENTS: _____ RESULTS: _____

Figure 2: Example distillation worksheet

12.0 HISTORICAL REVISION LOG

Table 2: Revision log

Revision Date	Revision Description	Revised By	Reviewed By
May 21st 2023	External distribution edits made	ADH/JS	**MM**

13.0 CONTACT INFORMATION

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