



A Honeywell Company

Pentane-Insoluble Matter in Petroleum Oils Using a Membrane Filter

UOP Method 99-07

Scope

This method is for the determination of pentane-insolubles in petroleum oils and is applicable to samples that are fluid at about 37°C or lower temperatures. This method covers the range of 0.01 to about 20 mass-% pentane-insolubles. Solid particulate materials interfere. The data provided by this method may be used as an index to coking tendency of petroleum oils when considering their suitability as charge stocks to cracking or other processes.

More viscous or solid materials such as asphalts may be handled by using the modification described in the *Appendix*.

A similar test method for heptane-insolubles, for samples that are fluid at 80°C, is UOP Method 614, "Heptane-Insoluble Matter in Petroleum Oils by Membrane Filtration," which also mentions toluene-insolubles in a *Note*. ASTM Method D 4055, "Pentane Insolubles by Membrane Filtration," is also similar in technique, but is written for particulates in lubricating oils rather than asphaltenes.

References

ASTM Method D 56, "Flash Point by Tag Closed Cup Tester," www.astm.org

ASTM Method D 4055, "Pentane Insolubles by Membrane Filtration," www.astm.org

UOP Method 614, "Heptane-Insoluble Matter in Petroleum Oils by Membrane Filtration," www.astm.org

Outline of Method

A weighed sample is dispersed at ambient temperature in *n*-pentane, digested at 37°C, and filtered through a weighed membrane filter. Samples that cannot be completely dispersed cannot be analyzed. The membrane filter is dried and reweighed to obtain the weight of insoluble matter.

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Definition

Asphaltenes are defined as the material present in oil fractions that is not soluble in light paraffinic solvents. They are fine, powdery, black-brown solids which are polymeric materials spanning a wide range of molecular weights. Their chemical composition is quite complicated. They appear to be closely associated with high molecular weight semi-polar naphthenic materials. The terms “pentane-insolubles” and “asphaltenes” are often used synonymously.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Balance, readability 0.1-mg, capacity 200-g

Clamps, for 250-mL flasks in shaker bath, Fisher Scientific, Cat. No. 15-455-15E

Cylinder, graduated, 250-mL, Fisher Scientific, Cat. No. 08-557E

Desiccator, with plate, to hold Petri dishes, Fisher Scientific, Cat. No. 08-615A

Dishes, Petri, borosilicate glass, 60-mm diameter

Filter holder, stainless steel, "Millipore Hydrosol" filter holder, Millipore Corp., Cat. No. XX 20 047 20

Flask, filtering, with sidearm, 2-L, Fisher Scientific, Cat No. K953760-2000

Flask, Erlenmeyer, narrow neck, 250-mL, with pennyhead, ground-glass, standard taper stopper, Fisher Scientific, Cat. No. 10-100E

Forceps, stainless steel, with flat, polished tips for handling filters, Millipore Corp., Cat. No. XX62 000 06

Gloves, thermal resistant, Fisher Scientific, Cat No. 11-462-56

Oven, capable of operation at 95°C, Fisher Scientific, Cat No. 13-247-637G

Pipet, volumetric transfer, 2-mL, Fisher Scientific, Cat. No. 13-650-2C. Cut 4-5 mm off the tip to obtain a large-bore tip.

Pipet, 25-mL graduated serological, large tip opening, Fisher Scientific, Cat. No. 13-671-108E

Pipet filler, Fisher Scientific, Cat. No. 03-692-35

Pump, vacuum, Welch Rotovap, Fisher Scientific, Cat. No. 01-129-19. If the pump is to be located in the hood, or anywhere near the warmed pentane, an explosion proof model such as Fisher Scientific, Cat. No. 01-182-003 must be used.

Shaker water bath, Precision Scientific Model 50, Fisher Scientific, Cat. No. 15-455-5

Thermometer, for oven, without mercury, Fisher Scientific, Cat. No. 15-041-6C

Ultrasonic bath, 9-L capacity, 185 watt, Fisher Scientific, Cat. No. 15-335-110

Wash Bottle, 500-mL, fluorinated HDPE, Fisher Scientific, Cat. No. 03-409-17B

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Depth filter disc, 35-mm diameter, Millipore Corp., Cat. No. AP2503500, if needed, see *Procedure*, Step 10

Dessicant, indicating Drierite, Fisher Scientific, Cat. No. 07-578-3A

n-pentane, 99% minimum purity, residue after evaporation <0.001%, Acros Organics, Cat. No. 16787 0025, Fisher Scientific

Membrane filter discs, 0.8 μm and 5.0 μm pore sizes, 47-mm diameter, white, plain, MF, Millipore Corp., Cat. Nos. AAWP04700 and SMWP04700, respectively

Sampling

Samples for this test should be taken in clean containers under a blanket of nitrogen or other inert gas. The container should be filled only about 3/4 full so that the sample can be shaken vigorously before testing. No other tests or analyses should be made on this sample until after the pentane-insoluble content is determined. Samples under an inert gas blanket can usually be kept a few days at room temperature. However, for best results, test the sample the same day it is taken.

Sample Preparation

The sampling procedure varies according to two conditions: the expected pentane-insoluble matter content, and the fluidity of the sample. If the sample is sufficiently fluid to withdraw into a pipet, take the sample from the container at room temperature. If the sample is too viscous, or is waxy, it must be heated.

1. Loosen the cap or stopper of the sample container to vent it and place it in the 95°C oven along with the appropriate pipet.
 - *CAUTION:* If there is any possibility of the sample containing light ends, or if it is of unknown origin, test it for flash point by ASTM Method D 56, "Flash Point by Tag Closed Cup Tester," before placing it in the oven. If it flashes, do not use the oven to heat the sample.
2. Heat small bottles (pint or less) 30 minutes before sampling. Allow one hour of heating for a gallon container. Never heat for more than about 2 hours, because some oils can form additional insoluble compounds on prolonged heating (see *Note 1*). Very high boiling samples, such as asphalts, should be sampled as described in the *Appendix*.

The size of the sample taken for the test and the size of the pores of the membrane filter disc to be used are determined by the expected content of insolubles in the sample. If the insolubles content is expected to be less than 1.0 mass-% use the 25-mL graduated pipet with the large tip opening to take about 12-13 mL (approximately 10 g) of sample. Use the 0.8 μm pore size filter disc for filtering. If the insolubles content is expected to be above 1.0 mass-%, use the tipless 2-mL pipet to take a 0.5-1.5 g sample (Table 1) and use the 5.0 μm disc filter for filtering.

Procedure

The analyst is expected to be familiar with general laboratory procedures and with the equipment being used. *CAUTION:* All steps involving heated pentane shall be performed in a fume hood.

1. Weigh a 250-mL Erlenmeyer flask to the nearest 0.0001 g.
2. Following the *Sample Preparation* above, tighten the stopper or cap on the sample container and shake the sample vigorously for 30-50 seconds.
3. Quickly remove the stopper or cap.

Table 1
Sample Size and Filter Selection

<u>Range of Pentane-Insoluble Matter, mass-%</u>	<u>Approx. Sample Size, g</u>	<u>Filter Pore Size, μm</u>
0.01-1.0	10	0.8
1-5	1.5	5.0
5-20	0.5	5.0

4. Insert the end of the pipet into the center of the oil sample and draw an aliquot. Drain the pipet into the flask. Avoid getting sample on the ground glass joint.
 - Use gloves if the sample is hot.
5. Allow the flask to come to room temperature and reweigh it to the nearest 0.0001 g.
6. Using a graduated cylinder, add 200 mL of cool (room temperature) *n*-pentane to the flask. Stopper and shake the flask vigorously for at least 2 minutes.
7. Place the flask, loosely stoppered, into the ultrasonic bath for 5 minutes. Remove the flask from the ultrasonic bath after approximately two minutes and again after four minutes, swirl it by hand, and return it to the bath. Observe the bottom of the flask; there should be no sample left clinging to the bottom. If the sample is not completely dispersed, place the flask in the ultrasonic bath for an additional 5 minutes, swirling it occasionally. Continue this procedure until the sample appears to be completely dispersed.
 - The sample must be thoroughly dispersed or the test is invalid.
8. Place the loosely stoppered flask in the shaker water bath maintained at 37°C. Operate the shaker at the maximum rate possible without splashing. Observe the sample several times over a period of 15 minutes. If the sample tends to settle out, place the flask in the ultrasonic bath and redisperse the sample.
 - Viscous samples may require extended heating and shaking time in the water bath with intermittent ultrasonic treatment to obtain complete dispersal of the sample.
9. Leave the flask in the shaker water bath for a minimum of 60 minutes total digestion time at 37°C. Operate the shaker at the maximum rate possible, without splashing, during the entire digestion period (see *Note 2*).
10. Place a membrane filter disc, and depth filter if used, in a clean, dry, previously numbered Petri dish and weigh it to the nearest 0.0001 g. Always handle the filter discs with smooth-tipped forceps.
 - The depth filter disc is used with black oil samples, which tend to plug the regular filter. The depth filter is weighed along with the regular filter and then placed in the throat of the funnel after the regular filter is in place (Step 13). The analysis then continues as described in the method using both filters.
11. Insert the base of the filter holder in the filtering flask.
12. Place the filter disc on the screen in the base of the filter holder.
13. Attach the top (funnel) of the filter holder and screw it on tightly.
14. Electrically ground both the top and the base of the filter holder to a suitable common ground. The apparatus must be grounded in this fashion to prevent an electrostatic charge from accumulating on the filter cake.

- The presence of a static charge could cause problems with transferring the filter cake to the balance without loss of insolubles, as well as being a potential safety hazard should a spark be generated.
15. Apply a slight vacuum to the filter, just sufficient to see the filter pulled down onto the plate.
 - Do not use more vacuum than what is absolutely necessary because evaporation of solvent and consequent chilling of the mixture may occur and cause the wax to precipitate.
 - For convenience, the vacuum pump may be placed outside the hood, with just the vacuum line running into the hood. Vent the outlet of the pump to the hood or other laboratory exhaust.
 16. Remove the flask containing the sample from the water bath. Wipe the water from the outside of the flask.
 17. Stopper and shake the flask, then pour the contents on the filter. If the amount of insoluble material is high, pour the contents on the filter in aliquots. When the level of the solution has receded to the throat of the funnel, rinse the flask at least 3 times, using 100 mL of warm (about 37°C) pentane the first time, and 50-mL portions subsequently, pouring the washings down the sides of the funnel to wash any sediment onto the filter. The last wash should be colorless; if it is not, continue washing until the washings are colorless.
 - **CAUTION:** Pentane has a low flash point. KEEP AWAY FROM OPEN FLAMES.
 18. Rinse, with about 100 mL of warm pentane, the sides of the funnel and filter cake until the solids on the filter appear to be dry (see *Note 3*).
 19. With the vacuum still on, unscrew the filter holder and gently remove the funnel. If the sediment is unusually heavy (greater than 40-50 mg) some of it may tend to cling to the throat of the funnel at the bottom where it meets the filter. Wash this material onto the filter.
 20. Examine the filter disc. The outer edge should be only lightly discolored if it was properly gripped by the holder. Wash the edge of the filter disc with a fine stream of warm pentane to remove any oil that may have seeped under the edge of the holder until the filter appears dry.
 21. Turn off the vacuum and disconnect the vacuum line. Hold the Petri dish, in which the disc was originally weighed, next to and level with the filter. Gently loosen the filter supporting the pentane-insolubles with the tip of the forceps and carefully slide it into the dish.
 22. Discard the filtrate in an environmentally safe manner.
 23. Place the dish containing the filter into the oven at 95°C and heat 10 to 15 minutes.
 24. Remove the dish and filter, and cool in a desiccator in order to prevent the filter cake from absorbing moisture, about one hour.
 25. Reweigh to the nearest 0.1 mg (see *Note 4*).

Calculations

Calculate the concentration of pentane-insolubles using the Equation.

$$\text{Pentane-Insoluble Matter, mass-\%} = \frac{100(G - T)}{S}$$

where:

G = gross weight of dish, filter (and depth filter, if used) and residue, g

S = weight of sample, g

T = tare weight of dish and filter (and depth filter, if used), g

For values less than 0.10 mass-%, report to three decimal places. For values from 0.10 to 10.0 mass-%, report to two decimal places. For values 10.0 mass-% and higher, report to one decimal place.

Notes and Precautions

1. Many waxy or viscous materials can be safely heated prior to transferring the desired amount into the flask. However, prolonged or overheating can often cause oxidative or thermal polymerization of asphaltene precursors. This will result in a higher insolubles content.
2. The importance of proper dispersion, the correct digestion time and continuous shaking cannot be overemphasized. Digestion time cannot be reduced by raising the bath temperature above 37°C because samples tend to degrade if overheated, thereby increasing the asphaltene content.
3. Rinsing the funnel is best done by using a wash bottle containing warm pentane. When in doubt, use plenty of warm pentane. Do not allow the filter cake to become dry when rinsing as cracks may develop. *n*-Pentane will flow through the cracks and not through the filter cake. This incomplete washing could cause high results.
4. Vacuum tower bottoms may contain fine sand particles. These will show on the filter as minute, glittering specks. Report their presence.

Precision

Intermediate Precision

n-Pentane insolubles were determined on three samples with one analyst in one laboratory. Each sample was analyzed six times. The precision data are summarized in Table 2. Two tests performed by the same analyst should not differ by more than the intermediate precision allowable difference with 95% confidence.

The data in Table 2 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table 2
Intermediate Precision, mass-%

<u>Sample</u>	<u>Mean Level</u>	<u>Intermediate Precision</u>	
		<u>Within-Lab esd</u>	<u>Allowable Difference</u>
1	0.49	0.014	0.05
2	2.28	0.08	0.28
3	22.3	1.01	3.7

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for a single analysis is 3.5 hours. The labor requirement is 1 hour.

Suggested Suppliers

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com

Millipore Corp., Prescott Road, Jaffrey, NH 03452 (603-532-8711) www.millipore.com

APPENDIX

Pentane-Insoluble Matter in Heavy Oils, Tars, Asphalts, and Hard Asphaltic Solids

Scope

The sampling and dispersion techniques described in this Appendix extend the useful range of the Method to asphaltic materials which are not fluid at 37°C and become hard and brittle at -78°C. The techniques are directed specifically toward the plant sampling of vacuum tower bottoms but can be extended to any heavy petroleum fraction that becomes hard and brittle at dry ice temperature (-78°C) and can be readily shattered at this temperature.

Outline of Method

A small amount of hot sample is poured into a metal box placed in a bucket of powdered dry ice and allowed to solidify. The frozen sample is shattered and a portion of it is weighed into a flask. *n*-Pentane at room temperature is added to this flask and the sample is dispersed in an ultrasonic bath. The procedure described in the body of the Method is then followed.

Apparatus

The following items are in addition to those listed in the body of the Method.

Box, metal, seamless, round, with paper-labeled lid, approx. 120-mL, Fisher Scientific, Cat. No. 03-490D

Bucket, any convenient size

Ladle, long handle

Pan, round, approximately 20-cm diameter by 3.5-cm deep, Fisher Scientific, Cat. No. 15-242A

Spatula, semi-micro, scoop style with plastic handle, Fisher Scientific, Cat. No. 21-401-15

Reagents and Materials

The following item is in addition to those listed in the body of the Method.

Dry ice, powdered or granulated, local supply

Sampling

Sampling of vacuum tower bottoms is described below. Sampling for other streams would be performed similarly.

1. Prepare a clean metal box for the sample receiver as illustrated in the Figure.
2. Flush the sample tap thoroughly with sample at a fast rate into a slop bucket. Reduce the flow of sample. Flush the long-handled ladle (usually used for taking samples of vacuum tower bottoms) 3 times with sample before taking the analytical sample.
3. Pour just enough sample into the metal box to cover the bottom of the box 2.5- to 5-mm deep (about 5-20 g). Avoid getting any sample on the rim of the box where it will interfere with the lid. Mark the identity of the sample on the paper-labeled lid and place the lid on the box.
4. Carry the sample in the bucket of dry ice to the laboratory.

5. Put about $\frac{3}{4}$ -inch of granulated dry ice in a round pan. Bury the tip of the micro-spatula deeply into the dry ice. Prepare an indentation in the dry ice about $\frac{1}{2}$ -inch deep and big enough to receive the box.

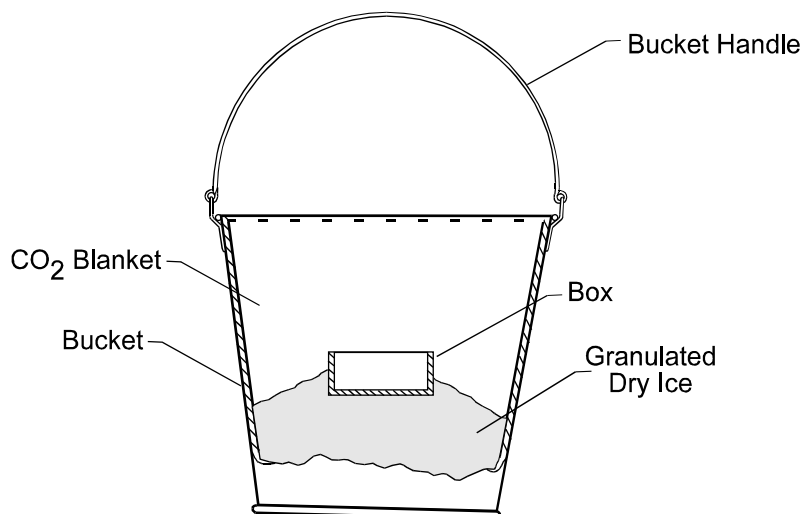


Figure
Sample Receiver

6. Remove the box from the bucket (use a glove or heavy towel). Immediately strike the bottom of the box very vigorously several times on a hard surface.
7. Remove the lid and examine the sample. If the sample is not adequately shattered, refreeze the sample in the box, then repeat the striking. When about 20% or more of the sample is found to be finely divided, put the box (with lid on) in the dry ice inside the round pan, and pile up the dry ice around the box.
8. Place the round pan near the analytical balance. Weigh an empty 250-mL Erlenmeyer flask to the nearest 0.0001 g.
9. Remove the lid of the box and pick up some of the frozen powdered sample with the cold micro-spatula. Insert the tip of the spatula halfway into the tilted flask and tap or shake it to scatter the sample particles on the bottom and lower portion of the flask. Then bury the spatula tip in the dry ice again. Rotate the flask 45°.
10. Repeat this process until slightly over 0.5 g of sample has been added to the flask. The particles should be evenly spread out over the bottom and lower half of the sides of the flask; solid patches, or blobs, will be much more difficult to disperse in the *n*-pentane.
11. Let the flask warm up for several minutes to equilibrate.
12. Obtain and record the weight of the sample and the flask. The analytical balance will remain steady if the sample has reached equilibrium.
13. Add 200-mL of *n*-pentane at room temperature to the flask, stopper it, and shake vigorously. Place the flask in the ultrasonic bath and thoroughly disperse the sample in the *n*-pentane without heating. Verify that the sample remains dispersed by following the procedure described in the body of the Method (*Procedure*, Steps 8 and 9). When the sample is

completely dispersed, leave the flask in the shaker water bath (without shaking) at 37°C for a digestion time of three hours.

14. Proceed with filtration as described in the body of the Method.

Time for Analysis

The elapsed time for a single analysis, including sampling and determination of pentane-insolubles, is about 8 hours. The labor requirement is about 5 hours.