



Heptane or Toluene Insoluble Matter in Petroleum Oils Using Vacuum Filtration

UOP Method 614-18

Scope

This method is for the determination of either heptane or toluene insoluble material in petroleum oils. This method covers the range of 0.01 to 25 mass-% insolubles. Solid particulate materials interfere. More viscous or solid materials such as asphalts may be analyzed using this method but will require using a heated sonicating bath (up to 60°C). 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.

Outline of Method

A weighed sample is dispersed in ambient temperature solvent, either *n*-heptane or toluene, refluxed nominally at 80°C for 2 hours, and filtered through a weighed glass microfiber filter using vacuum. Samples that cannot be completely dispersed should not be analyzed by this method. The glass microfiber filter is dried at 100°C and reweighed to obtain the weight of insoluble matter.

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 and 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 that require extended digestion time for separation. The terms "heptane-insolubles", "toluene-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, readable to 0.0001 g

Clamp, for ring stand and sample cylinders. minimum opening 38.1-mm, VWR International, Cat. No. C6088-12

Clamp holder, for ring stand and clamp, VWR International, Cat. No. C6088-2

Condenser, glass 300mm with 24/40 fittings, VWR, Cat. No. KT431500-2430

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Cylinder, graduated, 250-mL, Fisher Scientific, Cat. No. 08-559EC

Desiccator, to hold Petri dishes

Dishes, Petri, borosilicate glass, 60-mm diameter, Fisher Scientific, Cat. No. 08-746A

Electromantle with stirrer, 250ml, VWR, Cat. No. 33749-326

Filter apparatus (300-mL glass filter holder and 1-L filtering flask), VWR, Cat. No. KT953825-0000

Findenser, Heidolph Radleys, Model RR31100, 400mm long, Cat. No. 015610003

Flask, round bottom 250-mL with 24/40 fitting, VWR, Cat. No. 80068-778

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

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

Hot plate, stirring, capable of 80°C

- must have round base plate to work with Starfish Work Station, such as Heidolph MR Hei-Tec, Cat. No. 036110582

Oven, capable of operation at 100°C

Pipet, volumetric transfer, disposable, 2-mL, Fisher Scientific, Cat. No. 13-650-2C

Pump, vacuum, Welch Director Direct Drive Pump, Fisher Scientific, Cat. No. 01-115-4

Ring stand, with rectangular base, 140- x 229-mm with 610-mm rod, VWR International Cat. No. 470104-060

StarFish Work Station, Heidolph Radley, works with round-top stirring hot plates; includes base plate Cat. No. 015890020, monoblock for 250-mL flasks Cat. No. 015890070, rod support Cat. No. 015890410, 5-way clamp for Findenser Cat. No. 015892140

Stir bars, egg shape 1 inch x ½, VWR, Cat. No. 80062-140

Stir bar retriever, polyethylene, VWR, Cat. No. 80062-180

Tubing, Tygon, ⅜ inch ID x ½ inch OD, 1/16-inch wall, VWR International, Cat. No. 89403-882

Ultrasonic bath, heated, 1.5-L capacity, VWR, Cat. No. 89375-494

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.

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

n-Heptane, 99% minimum purity, Honeywell Burdick & Jackson, Cat. No. 207-4

Glass Microfiber filters, 1.2-µm pore size, 47-mm diameter, white, plain, VWR cat. No. 28333-139

Toluene, 99% minimum purity, Honeywell Burdick & Jackson, Cat. No. AH347-4PC

Sampling

The sampling procedure varies according to the fluidity of the sample. If the sample is sufficiently fluid at room temperature to draw into a pipet, take the sample from the container. If the sample is too viscous, or is waxy, it must be heated.

1. Remove the cap or stopper of the sample container and place sample in the 100°C oven.
2. Heat sample until sufficiently liquid for pouring or transferring with a pipet. Never heat for more than 2 hours as prolonged or overheating can cause oxidative or thermal polymerization of asphaltene precursors that result in a higher insoluble content.
3. Very high boiling samples, such as asphalts, should be sampled by heating until the sample is liquid enough to be stirred and a small portion poured into the flask. Stir the sample with a spatula for 10 to 30 seconds. If the material is too thick to cleanly pour into the flask, the stirred sample can be poured out into a clean glass or aluminum petri dish, allowed to cool, and then chipped and the pieces placed into the flask.

The size of the sample taken for the test is determined by the fluidity of the material and the expected insoluble concentration, with larger sample amounts being used for lower expected insolubles. A sample size of 1-10 grams can be used for most samples which are fluid at room temperature. For most samples that are solid at room temperature, a sample size of 0.5-2g can be used. Sample size should not exceed an amount that can be dispersed in the solvent (generally, more sample can be used for toluene insolubles than heptane insolubles). *See Table 1.*

Table 1
Sample Size

<u>Approximate Matter, mass-%</u>	<u>Range of Insoluble Sample Size, g</u>
0.01 to 0.25	10
0.25 to 5	2 to 5
5 to 25	0.5 to 1

Procedure

The analyst is expected to be familiar with general laboratory practices and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

1. Weigh an empty 250-mL round bottom flask to the nearest 0.0001 g.
2. Tighten the stopper or cap on the sample container and shake the sample vigorously for 10 to 30 seconds. Stir heavier samples with a spatula for 10 to 30 seconds. Quickly remove the stopper or cap.
 - Use heat resistant gloves when handling hot samples
3. Using a disposable pipet, transfer appropriate amount of sample into the flask. Avoid getting sample on the ground glass joint.
 - Use heat resistant gloves when handling hot samples

4. Allow the flask to come to room temperature and reweigh it to the nearest 0.0001 g.
5. Add 200 mL of room temperature solvent, *n*-heptane or toluene, to the flask. Stopper and shake the flask for at least 2 minutes or until sample is completely dispersed. For hot samples, be sure to vent the flask every 30 seconds.
6. 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 5 minutes. Use a ring stand and clamp to suspend the flask in the bath. Continue this procedure until the sample appears to be completely dispersed.
 - The sample must be completely dispersed in the solvent or the test is invalid.
7. Place a stir bar in the flask, place flask into the monoblock which has been set on the hot plate, and connect the Findenser. Adjust the stir rate to maintain a moderate vortex, and set heating to achieve 80°C, $\pm 5^\circ\text{C}$. Apparatus set-up is pictured in Figure 1.
 - An electromantle may also be used for heating/stirring, and water-cooled condensers can be used in place of Findenser. See apparatus set-up in Figure 2.
 - As a best practice use of an over-temperature device that will cut power if any of the positions exceed 100°C is recommended.
8. Reflux the sample on the stirring hot plate for 2 hours.
9. Place a glass microfiber filter disc (rough side up) in a clean, dry, previously numbered Petri dish and place both the petri dish and filter paper in the oven at 100°C for 30 minutes to remove moisture. Remove from petri dish and filter paper from oven and place in a desiccator to cool.
10. Add about 180 mL of diluent solvent, either *n*-heptane or toluene, to a 250-mL Erlenmeyer flask, place on hot plate and connect to a Findenser or water condenser. Heat to approximately 80°C. Approximately 25-30 mL of warm solvent will be used for the final rinse for each sample in steps 17 to 20.
11. Weigh petri dish and filter paper to the nearest 0.0001 g.
12. Insert the base of the filter holder in the filtering flask.
13. Place the filter disc on the frit with rough side up in the base of the filter holder.
14. Attach the top (funnel) of the filter holder and clamp in place.
15. Apply a slight vacuum to the filter (see *Note 1*). Wet the filter with solvent to ensure good seal.
16. Raise and secure Findenser or water condenser and remove the flask containing the sample from the hot plate. Use a stir bar retriever to remove the stir bar from the sample flask. Rinse off the stir bar and retriever with the diluent solvent wash bottle.
 - If using water condensers, turn off the water prior to removing flask.
 - Wear heat resistant gloves when handling hot flasks
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.
18. Rinse stopper into the funnel with diluent solvent to collect any residual sample.

19. When the level of the solution has receded to the throat of the funnel, rinse the funnel using warm diluent (about 80°C) solvent, washing down the sides of the funnel to rinse any sediment onto the filter (see *Note 2*).
 - **CAUTION:** Heptane and toluene have low flash points.
20. Continue with vacuum until the solids on the filter appear to be dry.
21. Unclamp the filter holder and gently remove the funnel. If the sediment is unusually heavy (greater than 40 to 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 using diluent solvent.
22. 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 diluent solvent to remove any oil that may have seeped under the edge of the holder until the filter appears dry.
23. Turn off the vacuum and carefully transfer filter to the Petri dish in which the disc was originally weighed.
24. Discard the filtrate.
25. Place the dish containing the filter in the oven at 100°C for 30 minutes to evaporate any residual solvent.
26. Remove the dish and filter, and cool in a desiccator until it reaches ambient temperature, approximately 30 to 45 minutes.
27. Reweigh to the nearest 0.0001 g. Note and report if any solid particles appear to be present on the filter.

Calculations

Calculate the concentration of heptane or toluene insolubles using the Equation.

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

where:

- G** = gross weight of dish, filter and residue, g
- T** = tare weight of dish and filter, g
- L** = weight of round bottom flask and sample, g
- M** = weight of round bottom flask, g

Note the solvent used when reporting insolubles results. For values from 0.01 mass-% to 10.0 mass-%, report to two decimal places. For values 10.0 mass-% and higher, report to one decimal place.

Notes

1. Do not use more vacuum than what is necessary because evaporation of solvent and consequent chilling of the mixture may occur and cause the wax to precipitate.
2. Rinsing the funnel is best done by using hot solvent. Do not allow the filter cake to become dry when rinsing as cracks may develop, allowing the solvent to flow through the cracks and not through the filter cake. This incomplete washing could cause high results.
3. Scope of the method allows for determination of up to 25% insoluble material. Higher levels may be determined; however, precision has not been determined above the method scope.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods".

Repeatability and Site Precision

A nested design was carried out for determining heptane or toluene insolubles in four samples by two analysts. Each analyst carried out tests on two separate days, performing two tests each day for a total of 32 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated for the components at the concentration levels listed in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 1 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 1 with 95% confidence.

Table 2
Repeatability and Site Precision, Insolubles, mass-%

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
"A" Heptane Insolubles	11.5	0.36	1.4	0.42	2.6
"B" Heptane Insolubles	0.46	0.019	0.07	0.023	0.09
"C" Toluene Insolubles	2.69	0.077	0.30	0.102	0.40
"D" Toluene Insolubles	22.0	0.12	0.5	0.15	0.6

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.

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

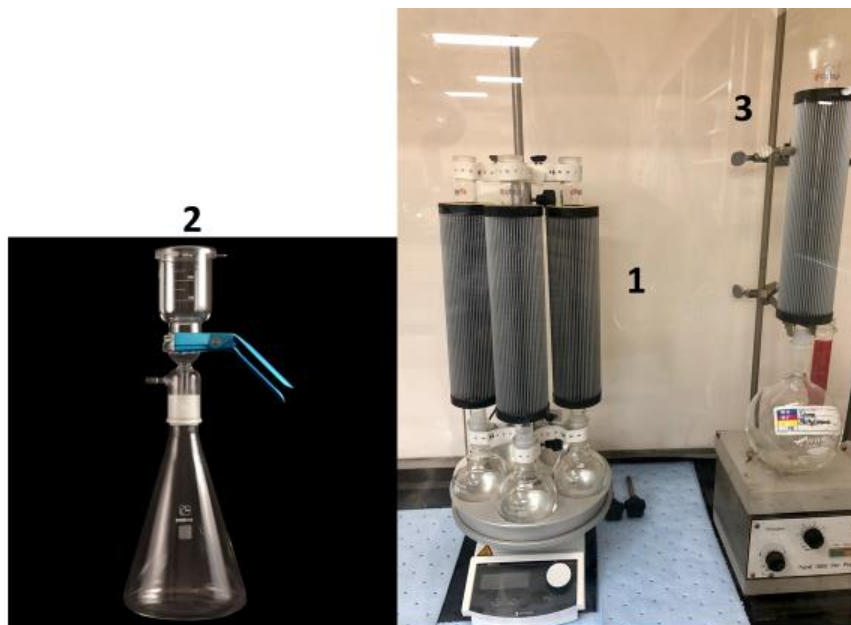
Burdick and Jackson, 1953 S. Harvey Street, Muskegon, MI 49442, USA, 1-800-322-2766,
www.labchemicals-honeywell.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Millipore Corp., Prescott Road, Jaffrey, NH 03452 USA, 1-603-532-8711, www.millipore.com

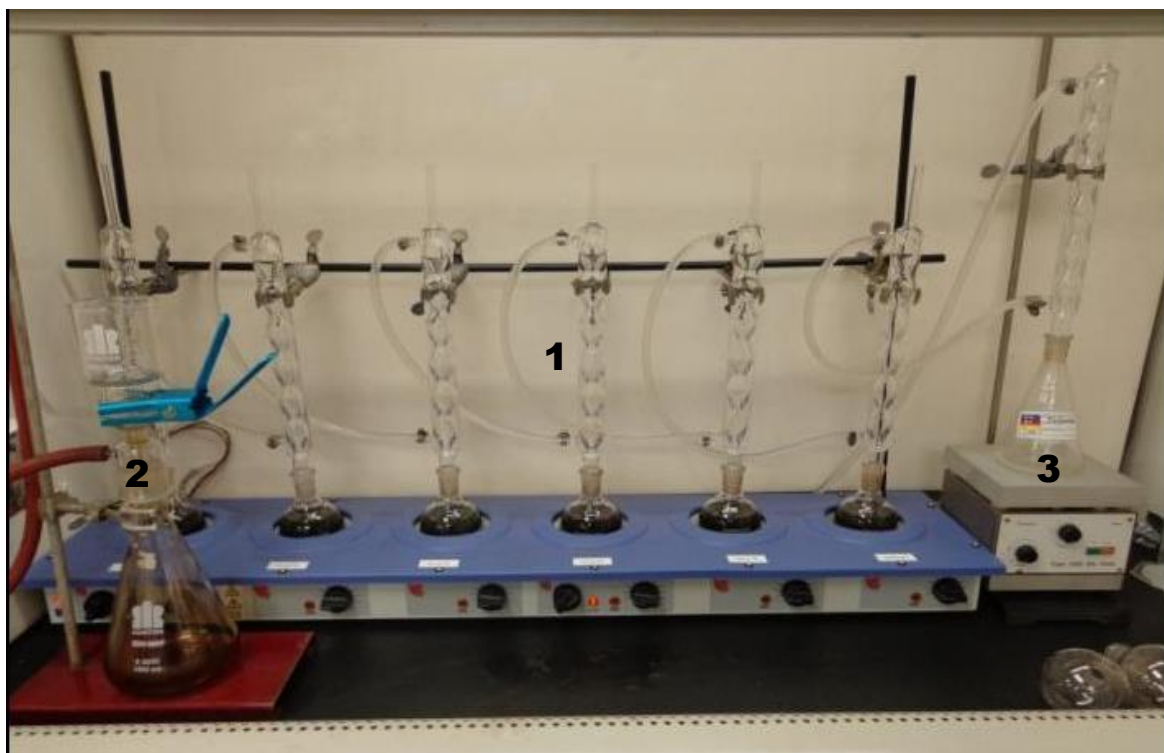
VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

Figure 1
Insolubles Apparatus using Starfish Work Station with Findensers



Set up of apparatus for Insolubles determination using Starfish Work Station and Findensers. (1) Heidolph hot plate with monoblock and Findensers, (2) Filtration unit, (3) Solvent heating apparatus.

Figure 2
Insolubles Apparatus using Electromantle and Water Condensers



Set up of apparatus for Insolubles determination. (1) Reflux apparatus and Electromantle, (2) Filtration unit, (3) Solvent heating apparatus.