

Standard Procedure for Separating Asphaltenes from Crude Oils

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The ASTM recommended procedure for separating asphaltenes from crude oil (ASTM D2007-80) is a widely-recognized standard. We follow this procedure, with some modifications, in order to ensure that our results are comparable to those obtained in other laboratories. The ASTM procedure specifies adding a volume of n-pentane that is 40 times the volume of the aliquot of oil. Varying either the ratio or the precipitant changes the amount of asphaltene that separates from a given oil. Our principal modification is to use n-heptane instead of n-pentane as the standard precipitant. Step-by-step instructions for asphaltene separation are provided in this standard procedure.

Determine sample size

Most crude oils contain from 1 to 10 grams of n-heptane asphaltenes per 100 ml of oil. To ensure accurate determination of asphaltene content, as much oil should be used as possible. In most cases, 20 ml of oil should be adequate.

Mix crude oil with precipitant

- 1) Accurately measure a volume of oil into a glass flask.
- 2) Add 40 times that volume of n-heptane (or other asphaltene precipitant, as needed) to the flask. Seal the flask with a stopper and shake the mixture thoroughly. If a rubber stopper is used, wrap it with aluminum foil to avoid direct contact of stopper with the solvent or its vapor.
- 3) Equilibrate the mixture for two days at ambient conditions. Shake the flask at least twice during this aging period.

Filter to separate solid asphaltenes from oil/precipitant mixture

After aging for two days, a funnel filter assembly (e.g. Kontes Glass Cat.# 953805) can be used to separate precipitated asphaltenes from the oil/precipitant mixture:

- 4) Select and pre-weigh a weighing vessel and filter paper (MF-Millipore Mixed Cellulose Ester Membrane Filter). Start with an 0.22 μm filter. See additional instructions below (Steps 12-17) if mixture does not pass through the 0.22 μm filter.
- 5) Install filter paper into the funnel filter assembly. Use a prefilter immediately beneath it to prevent direct contact of the filter paper with metal supporting net. Direct contact can lead

to development of cracks in the brittle membrane filter and thus cause leakage. Use a strong spring clamp to tightly hold the assembly together.

- 6) Pour about 100 ml of the oil/precipitant mixture into the funnel cup and seal the cup with aluminum foil to reduce evaporation during filtration.
- 7) Connect a vacuum pump to the side arm of the filtration flask to begin filtration. Shake the funnel cup slightly from time to time to prevent deposition of asphaltene on the cup wall, especially when the liquid level reaches the lower part of cup where diameter of cup decreases.
- 8) As long as the mixture passes through the filter rapidly, continue add mixture to the funnel cup. Repeat until the filtration rate becomes very slow. It will be easier to recover asphaltenes if you allow them to accumulate on a single filter. (If the deposited layer is too thin, the asphaltenes may be difficult to remove from the filter after drying due to adhesion or from the weighing boat due to electrostatic forces.)
- 9) Before removing the filtered asphaltenes, rinse the funnel cup with several aliquots of the n-alkane precipitant. Rinsing should be done just as the last of the mixture passes through the filter, before the deposited asphaltene layer begins to dry and crack. After the final rinse, continue to pull a vacuum until the deposited asphaltene dries enough to form cracks.
- 10) Turn off the vacuum pump. Loosen the clamp with one hand while holding the funnel assembly together with the other hand. Carefully peel off the entire filter paper and asphaltenes, placing them in the weighing boat. If any asphaltene remains on the bottom rim of funnel cup, use a spatula to transfer them to the weighing boat.
- 11) Pre-weigh another piece of filter paper and repeat Steps 5 through 10 until all of the mixture has been filtered. Upon successful filtration of the whole mixture through an 0.22 μm filter, proceed to Step 18 for routine determinations or Step 15 for more precise measurements.

Additional measures that may be required if filtration is extremely slow

If the filtration rate is unacceptably low through the 0.22 μm filter, larger pore size(s) can be used to pre-filter the mixture, followed by filtration through the 0.22 μm filter as the final step.

- 12) Select the smallest pore size through which a reasonable filtration rate can be obtained. Filter as outlined in Steps 4-11 above.
- 13) After completion of each pre-filtration step, check the filtrate mixture volume. If the volume has decreased significantly due to evaporation of precipitant, add enough n-alkane precipitant to restore the mixture to the original volume and allow the mixture to re-equilibrate for one day.
- 14) Filter through the next-smallest pore size filter.

Redissolve and reprecipitate the asphaltenes

These steps are often skipped for routine determinations, but for exact measurements toluene insolubles should be removed from the filtered material. Asphaltenes that have been separated using a series of different sizes of filters may be fractionated. They can be recombined using this procedure.

- 15) Carefully dissolve all of the asphaltenes including material adhering to filters and surfaces in toluene. Add more toluene and shake the solution vigorously to dilute the solution to a concentration low enough where asphaltene is not visible under 400x microscope. As a rule of thumb, a concentration of about 0.5-1.0 g asphaltene in 100 ml toluene should be adequate.
- 16) Filter the toluene solution through an 0.22 μm filter.
- 17) Concentrate the filtrate with a rotary evaporator to a minimal volume.
- 18) Estimate the volume of the toluene solution and reprecipitate asphaltenes with 40 times that volume of the original n-alkane. (An alkane of lower molecular weight and higher volatility can sometimes be used if the original precipitant is non-volatile.) Filter as described in Steps 4-11.

Dry and weigh the asphaltenes

- 19) Dry the filtered asphaltenes and filter papers in the hood for several days. To avoid oxidization, the asphaltenes can be dried in a slow stream of nitrogen, although this is not part of the standard procedure. If drying is slow (as would be the case if the precipitant is not very volatile) the asphaltenes, including those adhering to filters and containers, can be redissolved in a minimal amount of toluene, then reprecipitated with an alkane of lower molecular weight and higher volatility. Check the total weight of the weighing boat, filter papers, and asphaltenes every few hours. If the weight change is less than 0.0001g over a 12 hour period, the asphaltenes are dry.

Determine the amount of asphaltene in the oil

- 20) The weight of the asphaltenes can be determined by subtracting the weight of the weighing boat and all filter papers from total weight. The asphaltene content is calculated by:

$$\text{asphaltene content (g/100ml)} = \frac{\text{weight of dried asphaltene (g)}}{\text{crude oil volume (ml)}} \times 100$$

- 21) Use a spatula to transfer the dried asphaltenes to a glass vial and seal it with a Teflon-lined cap. In most cases, only about 80-90% of the separated asphaltene can be collected in the vial. The powdery remainder often cannot be removed from the filters and weighing vessel.