

PARAFFIN WAX CONTENT OF PETROLEUM OILS AND ASPHALTS

UOP Method 46-85

SCOPE

This method is for estimating the paraffin wax content of petroleum oils and asphalts. Wax content is an empirical value dependent upon the conditions under which the wax is separated from the original material. In this method paraffin wax content is defined as the mass-percent of material precipitated when a solution of asphalt-free sample in methylene chloride is cooled to -30°C . The lower limit of detection is 5 mass-percent.

OUTLINE OF METHOD

Light, clear oils are analyzed as received. Heavily colored oils and asphalts are clarified by treatment with sulfuric acid. The asphalt-free sample is dissolved in warm methylene chloride. This solution is chilled to -30°C and filtered through a cold fritted glass filter. The wax collected on the filter is removed with hot hexane. The hexane is evaporated and the wax weighed.

APPARATUS

Balance, readability, 0.1-mg

Bath, water, Sargent-Welch Scientific Co., Cat. No. S-84215, or equivalent

Colorimeter, ASTM, Precision, Sargent-Welch Scientific Co., Cat. No. S-66280, or equivalent

Cylinder, graduated, 10- and 50-mL

Desiccator, Scheibler, knob top cover, 250-mm ID, Sargent-Welch Scientific Co., Cat. No. S-25005E, or equivalent

Desiccator plate, Scheibler form, Coors porcelain, 230-mm diameter, Sargent-Welch Scientific Co., Cat. No. S-25185F, or equivalent

Flask, filtering, one-liter

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Flask, polyethylene, foam insulated, 2-L, Sargent-Welch Scientific Co., Cat. No. S-34755-B, or equivalent

Funnel, Büchner, fritted glass, fine porosity, 60-mL capacity, Sargent-Welch Scientific Co., Cat. No. S-35590-E, or equivalent

Funnel, separatory, 250-mL

Hot plate, electric, Sargent-Welch Scientific Co., Cat. No. S-41043-50, or equivalent

Oven, gravity convection, 225 C maximum temperature, Sargent-Welch Scientific Co., Cat. No. S-64090-C, or equivalent

Pump, vacuum, heavy duty, Sargent-Welch Scientific Co., S-71380, or equivalent

Regulator, nitrogen, Matheson, 8-BF, CGA No. 580, or equivalent

Sample bottles, for colorimeter, Sargent-Welch Scientific Co., Cat. No. S-8975, or equivalent

Stopper, rubber, No. 9

Tubing, glass, 122-cm, 6-mm OD, standard wall

Tubing, rubber, 3-m, 6.4-mm ID, 1.6-mm wall

Watch glass, plain, 65-mm diameter

Wax content apparatus consisting of: (see Figure)

Bath, glass, 125-mm OD, 119-mm ID, 110-mm deep, with a 20-mm diameter hole drilled in the center of the bottom, UOP Inc., or equivalent

Column clamp and clamp holder, 121-140-mm adjustable, VWR Scientific, Cat. Nos. 21572-160 and 21572-501, respectively, or equivalent

Flask, Erlenmeyer, 125-mL

Ring stand, 15 × 28-cm base, 91-cm support rod, Sargent-Welch Scientific Co., Cat. No. S-78306D, or equivalent

Stoppers, rubber, Nos. 3 and 5

Support ring, with screw clamp, 114-mm ID, 127-mm OD, Sargent-Welch Scientific Co., Cat. No. S-73045D, or equivalent

Support shelf, with screw clamp, 127-mm diameter, VWR Scientific, Cat. No. 60125-004, or equivalent

Thermometer, ASTM 6C, Cloud and Pour, low, Sargent-Welch Scientific Co., Cat. No. S-80585, or equivalent

Thermometer clamp and clamp holder, Fisher Scientific, Cat. Nos. 05-809-10 and 05-754, respectively, or equivalent

Tubing, glass, 6-mm OD, standard wall

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean distilled water.

Ammonium hydroxide solution, 0.1-M

Carbon dioxide, solid (dry ice)

Desiccant, activated alumina, Sargent-Welch Scientific Co., Cat. No. SC-10486, or equivalent

Hexane, 95% minimum purity

Methylene chloride, 95% minimum purity

(CAUTION: Avoid prolonged or repeated breathing of vapor. Use only with adequate ventilation.)

Nitrogen, extra dry, 99.9% minimum purity

Phenolphthalein, indicator solution, Sargent-Welch Scientific Co., Cat. No. SC-14007, or equivalent

Sulfuric acid, concentrated, 95% minimum purity

PROCEDURE

Section A

Dry a clean 125-mL Erlenmeyer flask in an oven at 105 C for fifteen minutes, and cool in a desiccator for one hour. Weigh the flask to the nearest 0.1 mg and record the mass. Determine the ASTM color of the sample according to ASTM D 1500. If the sample is above 3 ASTM color or contains asphaltenes (cloudy to opaque in appearance), proceed to *Section B*. If the sample is 3 ASTM color or lighter, and clear, add 1.5 ± 0.25 g to the clean, dried, tared flask. Reweigh and record the mass to the nearest 0.1 mg. Continue the procedure as described in *Section C*.

Section B

Add 2.0 ± 0.25 g of the sample to the clean, dried, tared flask and record the mass to the nearest 0.1 mg. Warm the sample to aid in dissolution. Add 50 mL of hexane and carefully bring to a boil on an electric hot plate located in a hood. Add approximately 4 mL of concentrated sulfuric acid and swirl vigorously to effect intimate contact between the oil and acid. Heat the mixture gently with continued swirling over the hot plate until an acid tar is formed and there are no visible lumps.

Allow the tar to settle for a minimum of 2 hours. Decant the clear asphalt-free solution into a 250-mL separatory funnel. The acid tar formed will normally adhere to the sides of the flask. Wash the tar in the flask five times with 5-mL portions of hexane warmed to 60 C. Add the washings to the contents of the separatory funnel.

Add 50 mL of warm water, about 40 C, to the separatory funnel and wash the hexane solution to dilute the acid. Wash with a swirling motion to avoid the formation of emulsions. Allow the layers to settle. Remove and discard the water. Add 15-mL of 0.1-M ammonium hydroxide solution to the separatory funnel to neutralize the remaining acid and swirl. Remove and discard the ammonium hydroxide layer. Wash the hexane solution several times, with 50-mL quantities of warm water, until the separated water shows no color change when several drops of phenolphthalein are added.

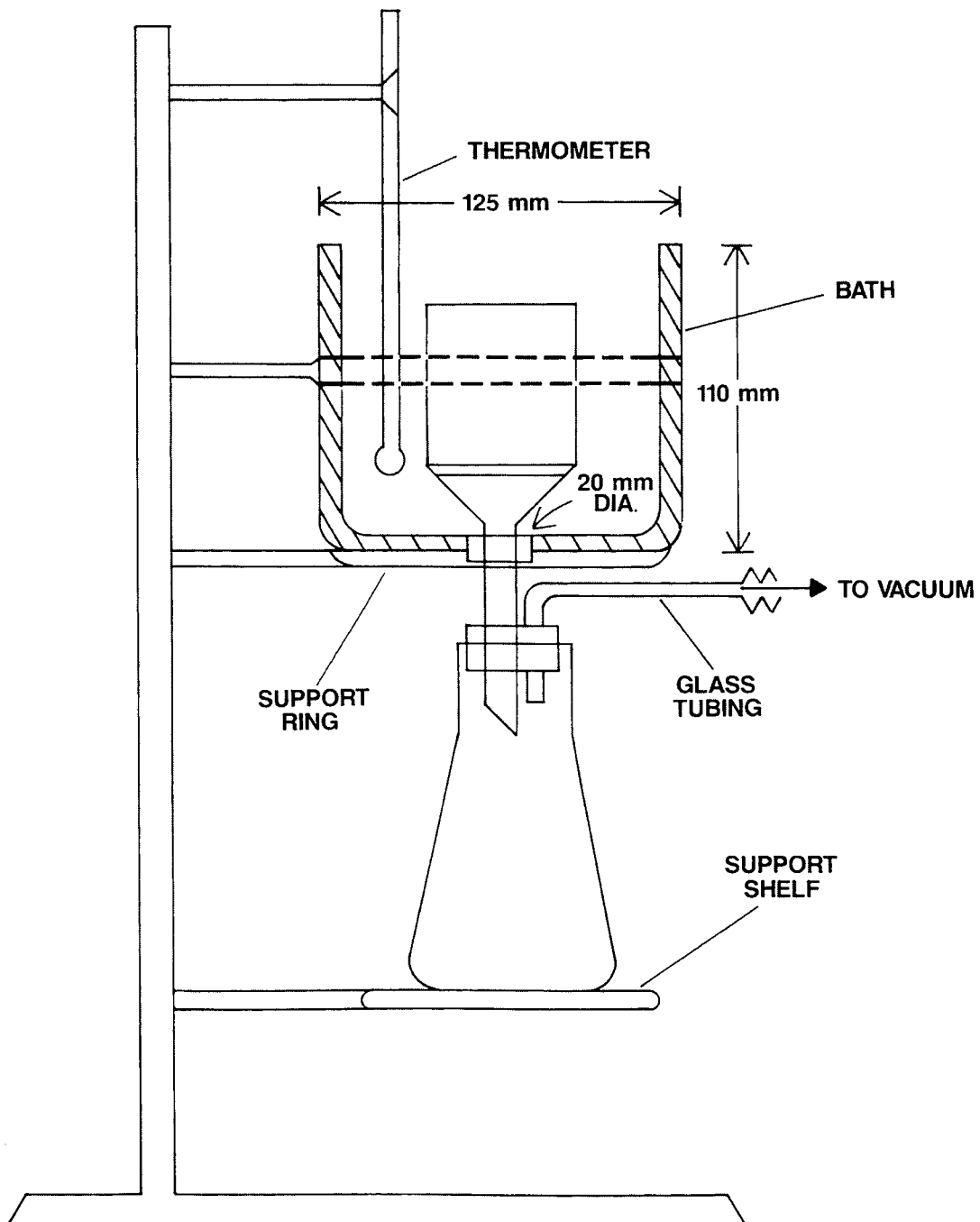


Figure
Wax Contents Apparatus

Transfer the neutral hexane solution to a clean, dried, tared 125-mL Erlenmeyer flask. Wash the separatory funnel three times with 5-mL portions of hexane warmed to 60 C and add the washings to the flask. Place the flask on the water bath heated to 95 C and evaporate off the hexane. Use a nitrogen purge to aid in the removal of the last traces of hexane. Follow the procedure in *Section C*.

Section C

Dissolve the sample obtained in *Section A or B* in 20 mL of methylene chloride warmed to 35 C. If the sample is solid at room temperature, melt it before the addition of methylene chloride.

Set up a methylene chloride cooling bath in the polyethylene flask. Maintain the temperature at – 30 C by the addition of dry ice. (Mechanical cooling may be substituted if dry ice is not available.) Place the sample in the bath with a swirling motion to avoid local freezing and allow it to cool for thirty minutes. Agitate the sample frequently by swirling.

Set up the wax content apparatus according to the figure. Add methylene chloride to the bath and chill it to – 30 C by the addition of dry ice. Cover the top of the funnel with a watch glass during the cooling process to prevent condensation of moisture.

Transfer the contents of the Erlenmeyer flask to the cold fritted glass funnel. Do not allow the level of the mixture in the filter funnel to rise above the level of the liquid in the cooling bath. Use vacuum to aid in filtering. Do not allow the filter to run dry, which would cause the wax to cake.

Rinse the Erlenmeyer flask five times with 5-mL quantities of methylene chloride cooled to –30 C, or until the flask and the small quantity of wax adhering to it are free from oil. Wash the wax on the filter with 30 to 35 mL of cold methylene chloride. The filtrate should be colorless and the wax white, or not darker than slightly yellow (Note 1).

Remove the flask containing the filtrate and replace it with the original flask. Using a one-liter filter flask, remove by suction the methylene chloride from the cooling bath and allow the filter funnel to reach room temperature. Dissolve the wax on the filter with 20 mL of hexane warmed to 60 C. A slight vacuum may be necessary to pull the last of the dissolved wax through the filter. Do not use the vacuum at the beginning as the loss of heat by evaporation may cause the wax to solidify on the filter.

When the wax is completely dissolved from the filter, remove the flask and place it on the water bath heated to 95 C to evaporate the hexane. Purge the flask with a stream of nitrogen to aid in the removal of the last traces of hexane.

Dry the flask and the wax in an oven at 105 C for 15 minutes. Allow to cool for one hour in a desiccator and then weigh it to the nearest 0.1 mg.

CALCULATION

Calculate the wax content of the sample as follows:

$$\text{Wax Content, mass-\%} = 100 \frac{W}{S}$$

where:

S = mass of the sample, g

W = mass of the wax, g

100 = factor to convert to percentage

Report the result to the nearest 0.1 mass-%.

NOTES AND PRECAUTIONS

1. If the wax cake is highly colored, continue the procedure to remove the wax from the filter disk. Instead of evaporating the hexane, repeat the clean-up procedure beginning with the addition of the sulfuric acid.

2. Do not evaporate hexane over an open flame or on a hot plate. Use a hot water bath.

PRECISION

Based on 5 replicate determinations, the estimated standard deviation (esd) for wax content on a non-treated sample at the 12% level was calculated to be 0.46. Duplicate results by the same operator should not differ by more than 1.8% (95% probability).

Based on 6 replicate determinations, the estimated standard deviation (esd) for wax content of acid-treated samples at the 15% level was calculated to be 1.47. Duplicate results by the same operator should not differ by more than 5.8% (95% probability).

TIME FOR ANALYSIS

The elapsed time for one analysis, not requiring pretreatment, is 8 hours. The labor requirement is 6 hours.

The elapsed time for one analysis requiring pretreatment is 12 hours. The labor requirement is 8 hours.

REFERENCES

ASTM D 1500 www.astm.org

BP Method 237/55 "Wax Content of Petroleum Products" British Petroleum Company Ltd., Chertsey Rd., Sunbury-on-Thames, Middlesex, TW16 7LN, United Kingdom

SUGGESTED SUPPLIERS

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143

Matheson, P.O. Box 96, Joliet, IL 60434

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

UOP Inc., Algonquin & Mt. Prospect Rds., Box 5017, Des Plaines, IL 60017-5017

VWR Scientific, P.O. Box 66929, O'Hare AMF, Chicago, IL 60666