

KTMR-20 CHEMICAL ANALYSIS OF ASPHALT REJUVENATING AGENTS
(Kansas Central Lab Test KT-MR-20)

a. SCOPE

This method is used to determine the composition of petroleum oils and asphalts in terms of: Asphaltenes Content, Polar Compounds Content, First Acidaffins Content, and Saturated Compounds Content. In addition, Second Acidaffins Content and the Maltene Ratio are calculated.

b. DEFINITIONS

b.1. Asphaltenes Content: That portion of the material not soluble in pentane.

b.2. Polar Compounds Content: That portion of the material soluble in pentane and that reacts with cold 85% (of concentrated) sulfuric acid.

b.3. First Acidiffins Content: That portion of the material that is soluble in pentane and that reacts with cold concentrated sulfuric acid.

b.4. Second Acidiffins Content: That portion of the material that is soluble in pentane and reacts with cold fuming sulfuric acid. (This is a calculated quantity)

b.5. Saturated Compounds Content: That portion of the material that is soluble in pentane and does not react with cold fuming sulfuric acid.

b.6. Maltene Ratio: Strictly a calculated quantity.

c. REFERENCED DOCUMENTS

c.1. AASHTO M 231: Weighing Devices Used in the Testing of Materials

PROCEDURE 1: ASPHALTENE CONTENT

a. APPARATUS

- a.1.** (2) 125 Erlenmeyer flask with ground glass stopper fitting and stopper
- a.2.** Pentane, technical grade
- a.3.** Toluene, analytical reagent grade
- a.4.** 50 mL graduated cylinder
- a.5.** (2) 15 mL Gooch crucible with filter
- a.6.** (2) Walter crucible holder
- a.7.** (2) 250 mL side arm vacuum flask
- a.8.** Regulated vacuum source with gauge and hoses
- a.9.** (2) Wash bottles for solvents
- a.10.** (2) Crystallizing dish
- a.11.** 60 mL separatory funnel
- a.12.** Lab stand with ring
- a.13.** Hot plate with adjustable temperature control
- a.14.** Laboratory vent hood
- a.15.** Weighing device in accordance with AASHTO M 231 Class A
- a.16.** Oven capable of maintaining $221 \pm 9^{\circ}\text{F}$ ($105 \pm 5^{\circ}\text{C}$)

b. SAMPLE PREPARATION

b.1. This determination is made on as received material from the asphalt subsection, where the material is reduced.

c. PROCEDURE

- c.1.** Duplicate determinations of this procedure are required.
- c.2.** Place a clean and dry 125 mL Erlenmeyer flask with ground glass stopper fitting onto a tared analytical balance. Record the mass of the flask to the nearest 0.1 mg. Dispense into the flask 1.0 ± 0.1 g of the as received ARA material. Record the mass of the flask plus sample to the nearest 0.1 mg.
- c.2.a.** Calculate the mass of the sample by subtracting the mass of the flask from the mass of the flask plus sample.
- c.3.** Using a 50 mL graduated cylinder add 50 ± 5 mL of tech grade pentane. Stopper the flask and swirl until the sample appears to be completely dissolved.
- c.3.a.** Allow the flask to stand undisturbed for a minimum of 15 hours.
- c.4.** Place a 21 mm fiber glass filter into the bottom of a 15 mL Gooch crucible.
- c.4.a.** Take a 30 mm fiberglass filter and evenly tuck it into the same crucible to form a bowl shaped reservoir in the bottom of the crucible.
- c.4.b.** Place the crucible into a Walter crucible holder that is set into a 250 mL vacuum flask connected to a regulated vacuum source with a gauge. Turn the vacuum on, and run 20 ± 5 mL of pentane through the crucible filter.
- c.4.c.** Turn off the vacuum and place crucible into a drying oven set at $105 \pm 5^\circ\text{C}$ for 30 ± 5 minutes. Remove crucible from oven and allow to cool to room temperature in a dessicator. When cooled weigh and record the mass of the crucible to the nearest 0.1 mg.
- c.5** Transfer the contents of one of the flasks into a 60 mL separatory funnel. Rinse the sample flask into the funnel using pentane dispensed from a wash bottle.
- c.5.a.** Save the sample flask for use in step **c.12** of this procedure.
- c.6.** Set up the apparatus as shown in Figure 1. Adjust the vacuum source so it will deliver a maximum vacuum of 10 inches of mercury.

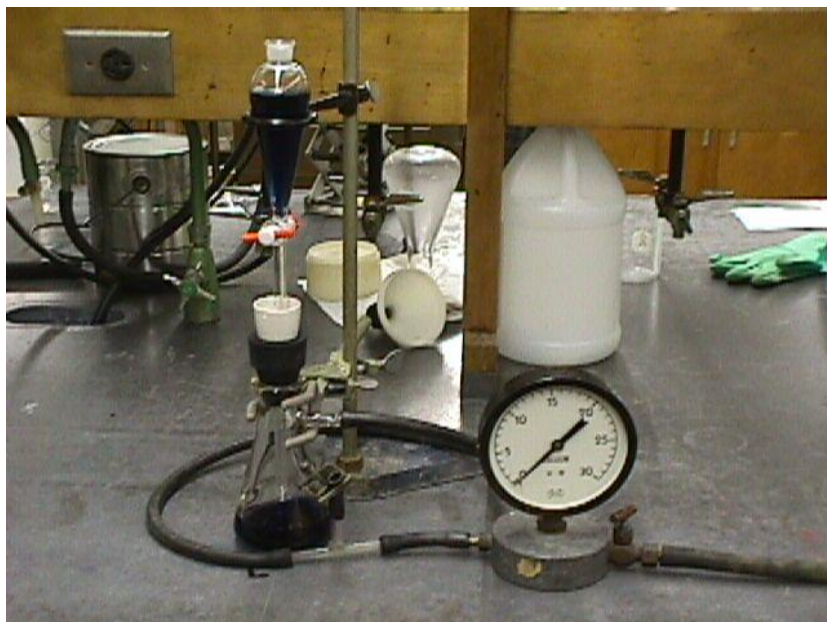


Figure 1

c.7. Place the Gooch crucible in the holder, turn on the vacuum and slightly open the valve on the separatory funnel allowing the solution to drip onto the filter in the crucible. Adjust the flow rate so that the solution level does not exceed the top edge of the filter in the crucible. Adjust flow as needed as asphaltene builds up on the filter.

c.8. Once the separatory funnel is empty, rinse it into the crucible twice using 10 ± 2 mL of pentane. Rinse the inside of the crucible with 15 ± 2 mL of pentane, being sure not to disturb the asphaltene residue held up on the filter.^{a+b}

NOTE a: Save the separatory funnel to be used later in section **c.12.** of the method.

NOTE b: Save the filtrate in the vacuum flask for use in another section of KTMR-20. One of the duplicates will be used in Polar Compounds Content and the other in Saturates Content.

c.9 Shut the vacuum off and remove the crucible from the holder and place it in a 105°C drying oven for 15 ± 2 minutes. Remove the crucible from the oven and allow it to cool to room temperature in a desiccator.

c.10 When the crucible has cooled to room temperature, weigh back and record the mass of the crucible and its contents to 0.1 mg.

c.11 Tare, weigh and record the mass of a clean, dry 60 mL crystallizing dish to 0.1 mg.

c.12 Retrieve the separatory funnel, the sample flask, and any other items such as stir rods, that may have come into contact with the sample solution before filtering. Rinse each item twice using 10 ± 2 mL of toluene capturing the rinse solvent in the crystallizing dish.

c.13 Place the dish on a hot plate inside a vent hood and allow the solvent to evaporate without ever coming to a boil. When it is apparent that the solvent has been driven off, place the dish into a drying oven at 105°C for 15 ± 2 minutes. Remove and allow to cool in a desiccator.

c.14 Once cooled to room temperature, weigh back and record the mass of the dish and its contained residue to 0.1 mg.

d. CALCULATIONS

d.1 Asphaltene Content, $wt/wt\% = \frac{C+D}{M} \times 100\%$

Where: C = (crucible + residue) - (tare mass of crucible), in grams

D = (dish + residue) - (tare mass of dish), in grams

M = sample mass, in grams

PROCEDURE 2: POLAR COMPOUNDS CONTENT

a. APPARATUS

a.1. Pentane, technical grade

a.2. 85% of concentrated sulfuric acid, analytical reagent grade

a.3. 5 mL graduated pipette

a.4. (2) 125 mL Erlenmeyer flask with ground glass stopper fitting

a.5. PTFE boiling chips

a.6. Sodium Hydroxide, pellet form, analytical reagent grade

a.7. Short stemmed filter funnel fitted with 11 cm medium filter paper

a.8. Simple distillation apparatus, including a Condenser, Receiver, and a controllable heat source water bath

a.9. Regulated and gauged vacuum source

a.10. Desiccator

- a.11. Laboratory vent hood
- a.12. Hot Plate with adjustable temperature control
- a.13. Weighing device in accordance with AASHTO M 231 Class A

b. SAMPLE PREPARATION

b.1. The sample is one of the filtrates from the Asphaltenes Content (procedure 1), and is contained in a 250 mL vacuum flask.

c. PROCEDURE

c.1. Transfer the entire sample in the vacuum flask into a 125 mL Erlenmeyer flask with a ground glass stopper fitting using pentane to rinse the vacuum flask into the Erlenmeyer flask. Place two or three PTFE boiling chips into the Erlenmeyer flask taking care not to fill the flask over two thirds full.

c.2. Place the flask on a hot plate located under a vent hood. Using a low heat setting bring the solution to a **slight** boil. Continue to boil until it appears that the solvent has been driven off. Stopper the flask and allow it to cool to room temperature.^a

NOTE a: Care must be used in heating the flask as rapid heating of the solution in the flask can cause the solution to bump (violent reaction) and a good part of the sample would be lost. Also, as the volume in the flask decreases it may be necessary to adjust the heat to prevent over boiling.

c.3. Add to the flask 5 - 10 mL of technical grade pentane and two or three PTFE boiling chips. Swirl the flask to dissolve the sample, then stopper the flask and allow it to set undisturbed for 30 ± 5 minutes.

c.4. Once the sample is dissolved, add 2.5 ± 0.1 mL of 85% sulfuric acid using a graduated 5 mL pipette. Stopper the flask and mix the contents by swirling the flask for 3 ± 0.25 minutes. Occasionally stop to relieve the gas pressure that will build up in the flask.

c.5. Stopper the flask and leave undisturbed for at least two hours.

c.6. Decant the top layer of nearly colorless liquid from the flask into another 125 mL Erlenmeyer with ground glass stopper fitting. Avoid carrying over any of the black tarry substance on the bottom of the first flask. Rinse the first flask into the second flask using pentane, and then carefully dispose of the acid sludge.

c.7. Add to the flask 20 ± 2 g of pelletized sodium hydroxide. Swirl the flask for 1 ± 0.1 minute, then stopper the flask and allow it to sit undisturbed for 20 ± 2 minutes.

c.8. Tare, weigh and record the mass of a clean and dry 100 mL round bottom distillation flask to 0.1 mg.

c.9. Filter the solution in the flask through medium filter paper fitted into a short stemmed filter funnel, catching the filtrate in the distillation flask. Rinse the Erlenmeyer flask and the filter with pentane until the distillation flask is two thirds full.

c.10. Assemble a simple distillation apparatus using a hot water bath as a heat source. Place the distillation flask into the apparatus and distill off the solvent.

c.11. Once it appears that no more solvent is being distilled, remove the flask from the apparatus and connect it to a regulated and gauged vacuum source. Starting at a low magnitude vacuum, increase the heat on the water bath until the water boils, then slowly increase the vacuum until a maximum is reached. Once it appears that all the solvent is gone (no bubbles can be seen coming from the sample in the flask), remove the heat and discontinue the vacuum. Place the flask in a dessicator to cool to room temperature.

c.12. When cooled, weigh back and record the mass of the flask and its contained residue to 0.1 mg.^b

NOTE b: Save the residue for use in procedure 3 First Acidaffins Content.

d. CALCULATIONS

d.1. % Polar Compounds, $wt/wt\% = 100\% - \%A - \frac{Difference}{M} \times 100\%$

Where:

%A = percent asphaltenes (determined previously), wt/wt%

Difference = distillation flask plus residue minus the tare mass of the flask, gram

M = sample mass (determined previously in asphaltenes determination), gram

PROCEDURE 3: FIRST ACIDAFFINS CONTENT

a. APPARATUS

- a.1.** Pentane, technical grade
- a.2.** Sulfuric acid concentrated, analytical reagent grade
- a.3.** 5 mL graduated pipette
- a.4.** 125 mL Erlenmeyer flask with ground glass stopper fitting
- a.5.** 25 mL mixing cylinder with ground glass stopper fitting and stopper
- a.6.** Sodium Hydroxide, pellet form, analytical reagent grade
- a.7.** Short stemmed filter funnel fitted with 11 cm medium filter paper
- a.8.** Simple distillation apparatus, including a Condenser, Receiver, and a controllable heat source water bath
- a.9.** Regulated and gauged vacuum source
- a.10.** Desiccator
- a.11.** Laboratory vent hood
- a.12.** 100 mL round bottomed distillation flask
- a.13.** Weighing device in accordance with AASHTO M 231 Class A

b. SAMPLE PREPARATION

- b.1.** The sample for this determination is the residue saved over from the Polar compounds determination (procedure 2) and is contained in a 100 mL distillation flask.

c. PROCEDURE

- c.1.** Add to the flask 5-10 mL of technical grade pentane then swirl the flask until the sample appears to be dissolved in the solvent. Stopper the flask and allow it to sit undisturbed for 30 ± 2 minutes.

c.2. Transfer the entire contents of the distillation flask to a 25 mL mixing cylinder with a ground glass stopper fitting. Rinse the distillation flask into the cylinder with pentane, do not exceed 25 mL of total volume in the cylinder.

c.3. To the mixing cylinder add 2.5 ± 0.1 mL of concentrated sulfuric acid using a 5 mL pipette. Stopper the cylinder and mix contents by stroking the cylinder up and down for 3.0 ± 0.1 minutes, stopping occasionally to relieve the gas pressure that will build up in the cylinder.

c.4. Let the stoppered cylinder sit for at least two hours.

c.5. Decant the nearly colorless top liquid from the cylinder into a 125 mL Erlenmeyer flask. Use care to avoid carrying over any of the tarry black substance on the bottom of the cylinder into the flask. Rinse the cylinder into the flask with pentane. Dispose of the acid sludge.

c.6. Add 20 ± 2 g of pelletized sodium hydroxide to the solution. Swirl the flask for one minute, then stopper the flask and allow it to sit undisturbed for 20 ± 2 minutes.

c.7. Weigh and record the mass of a clean and dry 100 mL distillation flask to 0.1 mg.

c.8. Filter the solution in the Erlenmeyer flask through 11 cm medium filter paper fitted inside of a short stemmed filter funnel catching the filtrate in the distillation flask. Rinse the Erlenmeyer flask into the filter funnel with pentane, rinse the filter with pentane until the distillation flask is two thirds full.

c.9. Assemble a simple distillation apparatus with a hot water bath as a heat source. Place the distillation flask into the apparatus and distill off the solvent.

c.10. Once it appears that no more solvent is being distilled, remove the flask from the apparatus and connect it to a regulated and gauged vacuum source. Starting at a low magnitude vacuum increase the heat on the water bath until the water boils, then slowly increase the vacuum until a maximum is reached. Once it appears that all the solvent is gone (no bubbles can be seen coming from the sample in the flask), remove the heat and discontinue the vacuum. Place the flask in a desiccator to cool to room temperature.

c.11. When cooled weigh back and record the mass of the flask and its contained residue to 0.1 mg.

d. CALCULATIONS

d.1. % First Acidaffins, $wt/wt\% = 100\% - \%A - \%PC - \frac{\text{Difference}}{M} \times 100\%$

Where:

- %A = percent asphaltenes (determined previously), wt/wt%
- %PC = percent polar compounds (determined previously), wt/wt%
- Difference = Flask plus residue minus tare mass of flask, gram
- M = sample mass (determined previously in asphaltenes determination), gram

PROCEDURE 4: SATURATES CONTENT

a. APPARATUS

- a.1.** Petroleum ether, technical grade
- a.2.** Fuming sulfuric acid, analytical reagent grade
- a.3.** Ice bath
- a.4.** (3) 125 mL Erlenmeyer flask with ground glass stopper fitting
- a.5.** PTFE boiling chips
- a.6.** Sodium Hydroxide, analytical reagent grade
- a.7.** Short stemmed filter funnel fitted with 11 cm medium filter paper
- a.8.** 15 mL graduated cylinder
- a.9.** Regulated and gauged vacuum source
- a.10.** Desiccator
- a.11.** Laboratory vent hood
- a.12.** Hot Plate with controllable heat setting
- a.13.** Weighing device in accordance with AASHTO M 231 Class A
- a.14.** Pasteur pipette with bulb
- a.15.** 100 mL boiling flask
- a.16.** Fullers earth, purified

a.17. 80 mm Buchner filter funnel with glass fiber filter

a.18. 250 mL vacuum flask

a.19. Drying oven capable of maintaining $105 \pm 5^\circ\text{C}$

a.20. Pentane, technical grade

b. SAMPLE PREPARATION

b.1. This sample is one of the filtrates from the asphaltenes content (procedure 1), and is contained in a 250 mL vacuum flask.

c. PROCEDURE

c.1. Transfer the entire sample from the vacuum flask into a 125 mL Erlenmeyer flask with a ground glass stopper fitting using pentane to rinse the vacuum flask into the Erlenmeyer flask. Place two or three PTFE boiling chips into the Erlenmeyer flask taking care not to fill the flask over two thirds full.

c.2. Place the flask on a hot plate located under a vent hood. Using a low heat setting, bring the solution to a slight boil. Continue to boil until it appears that the solvent has been driven off. Stopper the flask and allow it to cool to room temperature.^a

NOTE a: Care must be used in heating the flask as rapidly heating the solution in the flask can cause the solution to bump (violent reaction) and a good part of the sample would be lost. Also, as the volume in the flask decreases it may be necessary to adjust the heat to prevent over boiling.

c.3. Add to the flask 5 - 10 mL of technical grade petroleum ether. Swirl the flask to dissolve the sample, then stopper the flask and allow it to sit undisturbed for 30 ± 2 minutes.

c.4. Place the flask into an ice bath located inside a vent hood, allowing the flask and its contents to sit for 10 ± 1 minute.

c.5. Dispense 10 mL of fuming sulfuric acid into a 15 mL graduated cylinder. Using a Pastuer pipette, slowly and carefully transfer the acid from the cylinder to the Erlenmeyer flask in the ice bath a drop at a time. Stopper the flask and let it sit for 30 ± 2 minutes.^b

NOTE b: When using the fuming sulfuric acid the analyst should be aware of appropriate safety measures.

c.6. With stopper in place, swirl the flask for at least one minute. Carefully crack open the stopper on the flask to allow any built up gas to escape. Repeat this step one more time.

c.7. With the flask stoppered, let the flask sit outside the ice bath for at least 12 hours undisturbed.

c.8. Carefully remove the stopper from the flask and decant the nearly clear layer of liquid into another 125 mL Erlenmeyer flask, with a ground glass stopper fitting. Avoid allowing the black tarry layer on the bottom of the flask to carry over into the new flask. Rinse the first flask into the second flask using petroleum ether.

c.9. To the flask add 20 ± 2 g of pelletized sodium hydroxide, stopper the flask and swirl for one full minute. Let the flask sit undisturbed for 20 ± 2 minutes.

c.10. Using medium filter paper fitted into a short stemmed filter funnel, filter the solution from the sodium hydroxide pellets catching the filtrate into another 125 mL Erlenmeyer flask with a ground glass stopper fitting. Rinse the flask, pellets, and filter into the filtrate flask with petroleum ether.

c.11 To the flask add 6 ± 1 g of purified Fuller's Earth. Stopper the flask and swirl for one full minute. Let the flask sit undisturbed for at least 10 minutes. If, after sitting, the solution in the flask still appears cloudy add some more Fuller's Earth and repeat swirling and sitting.

c.12. Vacuum filter the solution, using an 80 mm Buchner filter funnel fitted with a glass fiber filter, into a 250 mL vacuum flask. Rinse the Erlenmeyer flask a few times into the filter funnel using petroleum ether, also rinse the filter and residue a few times with petroleum ether.

c.13. Place 2-3 PTFE boiling chips into a clean and dry 150 mL boiling flask. Weigh and record the mass of the flask plus chips to 0.1 mg using an analytical balance.

c.14. Transfer the solution in the vacuum flask to the boiling flask. Rinse the vacuum flask into the boiling flask, with petroleum ether. Do not fill boiling flask over two thirds full.

c.15. Place boiling flask on a hot plate located in a vent hood. Allow the solution to come to a slight boil.^c Allow the solvent to boil off completely.

NOTE c: Care must be used in heating the flask as rapidly heating the solution in the flask can cause the solution to bump (violent reaction) and a good part of the sample would be lost. Also, as the volume in the flask decreases it may be necessary to adjust the heat to prevent over boiling.

c.16. Once it appears that the solvent has been driven off, place the flask in a drying oven set at $105 \pm 5^{\circ}\text{C}$ for 30 ± 2 minutes.

c.17. Remove the flask from the oven, place it in a dessicator and allow it to cool to room temperature.

c.18. Weigh back and record the mass of the cooled boiling flask and its contained residue to 0.1 mg.

c.19. The residue may be disposed of after calculations are completed.

d. CALCULATIONS

d.1. % Saturates, $wt/wt\% = \frac{Difference}{M} \times 100\%$

Where:

Difference = flask plus residue minus tare mass of flask, gram

M = sample mass (determined previously in asphaltene determination), gram

PROCEDURE 5: SECOND ACIDAFFINS CONTENT

a. CALCULATIONS

a.1. This procedure can only be calculated after the % asphaltene, % polar compounds, % first acidaffins, and % saturates have been determined.

a.2. % Second Acidaffins = 100% - %A - %PC - %1stA - %Sat

Where:

%A = percent asphaltene, wt/wt%

%PC = percent polar compounds, wt/wt%

%1stA = percent first acidaffins, wt/wt%

%Sat = percent saturates, wt/wt%

PROCEDURE 6: MALTENES RATIO

a. CALCULATIONS

a.1. This procedure can only be calculated after the % polar compounds, % first acidaffins, % second acidaffins, and % saturates have been determined.

a.2. Maltene Ratio = $\frac{\%PC + \%1stA}{\%2ndA + \%Sat}$

Where:

%PC = percent polar compounds, wt/wt%

%1stA = percent first acidaffins, wt/wt%

%2ndA = percent second acidaffins, wt/wt%

%Sat = percent saturates, wt/wt%