

ACID NUMBER AND NAPHTHENIC ACIDS BY COLORIMETRIC TITRATION

UOP Method 587-92

SCOPE

This method is for determining the acid number of petroleum products, petroleum distillates, and other hydrocarbons by colorimetric titration. Inorganic acids, organic acids, mercaptans and thiophenols respond to this analysis, but their respective salts do not. This method is limited to light colored distillates. For dark colored samples, use the potentiometric procedure in UOP Method 565. The typical range for acid number detection is 0.004 to 0.5 mg KOH/g of sample, although higher levels can be accommodated.

The acid number of a sample can be determined on an as-received basis or on a mercaptan and thiophenol-free basis. The method can also be used to determine naphthenic acids including sodium naphthenates (soaps) in caustic washed hydrocarbons. For an estimated relative molecular mass of 130, the range of detection for naphthenic acids is 5 to 250 mass-ppm. The latter two procedures apply almost exclusively to light kerosines and gas oils where it is assumed that the organic acids are entirely naphthenic.

CUTLINE OF METHOD

Procedure A, for the determination of acid number on an as-received basis: A weighed amount of sample is mixed with a titration solvent and is titrated to a colorimetric endpoint with alcoholic KOH using a buret equipped with a CO₂ guard tube. After a blank correction, the acid number is calculated as mg KOH/g of sample.

Procedure B, for the determination of acid number on a mercaptan and thiophenol-free basis: The sample is shaken with a copper sulfate-sodium chloride solution in the presence of air to oxidize (sweeten) the mercaptan and thiophenols to disulfides. After filtration the sample is titrated as described in *Procedure A*.

Procedure C, for the determination of naphthenic acids including sodium naphthenates (soaps) in caustic-washed hydrocarbons: The sample is shaken with a copper sulfate-sodium chloride solution (sweetened) and filtered. The sample is then washed with dilute sulfuric acid, to convert the sodium naphthenates to naphthenic acids, and then with water. The sample is then titrated as described in *Procedure A*.

The mid-boiling point distillation temperature of the sample is determined by ASTM Method D 86 to permit estimation of the relative molecular mass of the naphthenic acids. The naphthenic acid value is calculated in mass-ppm.

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).

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APPARATUS

References to catalog numbers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Balance, readability 0.01-g

Beaker, 250-mL, tall, without spout, borosilicate glass, Fisher Scientific, Cat. No. 02-555B

Buret, Machlett, automatic, 2-mL, Fisher Scientific, Cat. No. 03-847A

Crucible, high form, 10-mL, porcelain, Fisher Scientific, Cat. No. 07-965C

Cylinders, graduated, 10-, 100- and 250-mL, borosilicate glass, Fisher Scientific, Cat. Nos. 08-549-5B, -5E and -5G, respectively

Desiccator, annealed glass, with porcelain plate, Fisher Scientific, Cat. No. 08-615A

Drying tubes, polyethylene, Fisher Scientific, Cat. No. 09-242B

Flask, Erlenmeyer, 500-mL, borosilicate glass, heavy walled, with side arm, Fisher Scientific, Cat. No. 10-180K

Flask, Erlenmeyer, 500-mL, borosilicate glass, iodine, with borosilicate glass stopper, Fisher Scientific, Cat. No. 10-094C

Funnel, filtering, general purpose, borosilicate glass, Fisher Scientific, Cat. No. 10-322E

Funnel, separatory, 500-mL, borosilicate glass, Fisher Scientific, Cat. No. 10-437-5D

Hot plate, Fisher Scientific, Cat. No. 11-498-7H

Mortar, porcelain, 130-mm OD, Fisher Scientific, Cat. No. 12-961C

Oven, drying, capable of operation at 120°C, Fisher Scientific, Cat. No. 13-245-506G

Pestle, porcelain, Fisher Scientific, Cat. No. 12-961-5C

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3104-580

Shaker, wrist action, Fisher Scientific, Cat. No. 14-260

Spatula, micro-, Fisher Scientific, Cat. No. 21-401-15

Stir bar, magnetic, Teflon coated, Fisher Scientific, Cat. No. 14-511-64

Stirrer, magnetic, Fisher Scientific, Cat. No. 14-493-120MR

Stopper, size 7, rubber, Fisher Scientific, Cat. No. 14-130L

Tongs, stainless steel, crucible, Fisher Scientific, Cat. No. 15-186

Tubing, thick walled, rubber for vacuum use, Fisher Scientific, Cat. No. 14-173D

Vacuum pump, Precision Model No. DD-20, Fisher Scientific, Cat. No. 01-182

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 deionized or distilled water.

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

Ascarite II, 20 to 30-mesh, Fisher Scientific, Cat. No. A184

Copper sulfate (cupric sulfate), 98% minimum purity, Fisher Scientific, Cat. No. C493

Desiccant, 8-mesh, indicating, Fisher Scientific, Cat. No. 07-578-3A

Filter paper, acid-free, non acid-washed, Whatman No. 4, available from Fisher Scientific, Cat. No. 09-825A

Isopropyl alcohol (2-propanol), 99% minimum purity, Fisher Scientific, Cat. No. A451

Nitrogen, 99.999% minimum purity

Potassium hydrogen phthalate, primary standard, Fisher Scientific, Cat. No. P243

Potassium hydroxide, 0.1-M, alcoholic (methanol), Fisher Scientific, Cat. No. SP224

Sodium chloride, Fisher Scientific, Cat. No. S671

Sulfuric acid, approximately 0.05-M, Fisher Scientific, Cat. No. SA220

Sweetening reagent. Dissolve 140 ± 1 g of sodium chloride and 150 ± 1 g of copper sulfate in one liter of water.

Thymolphthalein, 1% in ethyl alcohol, Fisher Scientific, Cat. No. EK 112 2688

STANDARDIZATION OF POTASSIUM HYDROXIDE

1. Assemble and operate the buret according to the manufacturer's instructions.
2. Fill the buret with the 0.1-M potassium hydroxide solution.
 - The solution must be protected from atmospheric carbon dioxide by attaching a guard tube containing an absorbent such as ascarite to the buret reservoir.
3. Crush approximately 1 g of potassium hydrogen phthalate using a mortar and pestle.
4. Transfer the potassium hydrogen phthalate to a clean crucible, and dry at 120°C for 2 hours in a drying oven.
5. Remove the crucible from the oven using tongs, place it in a desiccator, and allow the uncovered crucible to cool.
6. Weigh approximately 0.1 g of dried potassium hydrogen phthalate to the nearest 0.1 mg, into each of three 250-mL beakers, and record the mass in each beaker.
 - The standardization is performed in triplicate.

7. Add, by graduated cylinder, 100 mL of water and a stirring bar to each beaker.
 - The water must be carbon dioxide free. Prepare immediately before use by boiling for approximately 10 minutes to expel carbon dioxide and then cooling while purging with nitrogen, or by placing the water under vacuum for sufficient time to degas. For example, 500 mL of water would require approximately 90 minutes under vacuum to fully degas.
8. Add about 10 drops of thymolphthalein indicator.
9. Place one of the beakers on the magnetic stirrer, lower the buret tip and stir.
10. Titrate the potassium hydrogen phthalate solution with the 0.1-*M* potassium hydroxide to the light-blue thymolphthalein endpoint.
 - The endpoint color should remain unchanged for 10 seconds.
11. Record, to the nearest 0.01 mL, the volume of titrant used to reach the endpoint of the titration.
12. Calculate the molarity of the potassium hydroxide, to three significant figures, as follows:

$$M = \frac{10^3 A}{204.2 B} \quad (1)$$

where:

- A** = mass of potassium hydrogen phthalate weighed into beaker, g
- B** = volume of potassium hydroxide solution used to reach the endpoint, mL
- M** = molarity of the potassium hydroxide
- 204.2** = relative molecular mass of potassium hydrogen phthalate, g/mol
- 10³** = factor to convert moles per milliliter to moles per liter

13. Average the results of the three determinations to four significant figures.
 - The potassium hydroxide is standardized at least weekly to detect changes in molarity. A quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

PROCEDURE

Procedure A

Acid Number, As-Received Basis

1. Determine a blank by performing the following Steps 3 through 8 using only the isopropyl alcohol and water solvent, omitting the sample.
2. Weigh approximately 100 g of sample, to the nearest 0.01 g, into a 500-mL Erlenmeyer flask having a side-arm.
3. Add, by graduated cylinder, 200 mL of isopropyl alcohol and 5 mL of water.
4. Add about 10 drops of the thymolphthalein indicator.
5. Purge the flask with nitrogen to expel air and connect a nitrogen line to the side-arm of the flask.
 - Continue purging throughout the titration.

6. Add a stirring bar and stir.
7. Lower the buret tip into the flask and titrate the solution with the 0.1-*M* potassium hydroxide to the light-blue thymolphthalein endpoint.
 - The endpoint color should remain unchanged for 10 seconds.
8. Record, to the nearest 0.01 mL, the volume of titrant needed to reach the endpoint of the titration.

Procedure B

Mercaptan and Thiophenol-free Acid Number

1. Measure, by graduated cylinder, approximately 150 mL of the hydrocarbon sample into a 500-mL Erlenmeyer, iodine flask.
2. Add, by graduated cylinder, 100 mL of the sweetening reagent.
 - The sweetening reagent, in the presence of air, oxidizes mercaptans and thiophenols to disulfides, which do not respond during titration.
3. Secure the ground glass stopper to the flask and shake for 30 minutes with a wrist action shaker.
4. Transfer the mixture to a 500-mL separatory funnel and allow the layers to separate.
5. Separate and discard the lower aqueous layer.
 - Occasionally droplets of sweetening reagent adhere to the side of the separatory funnel. Take care to exclude these droplets from the sample by agitating the funnel a second time to allow them to separate and be removed.
6. Filter the hydrocarbon through acid-free filter paper and collect the filtrate.
7. Proceed as described under *Procedure A, Acid Number, As-Received Basis*, using the sweetened, filtered sample, beginning with Step 2.

Procedure C

Naphthenic Acids Including Sodium Naphthenates in Caustic-Washed Hydrocarbons

1. Determine the boiling range of the sample by ASTM Method D 86. Obtain the mid-boiling point distillation temperature and determine the mid-boiling relative molecular mass using the Figure.
 - The mid-boiling point distillation temperature is the temperature at which 50 volume-% of the sample has distilled over.
2. Sweeten approximately 150 mL of sample, following Steps 1 through 6 as described under *Procedure B, Mercaptan and Thiophenol-free Acid Number*.
3. Measure, by graduated cylinder, approximately 135 mL of the sweetened, filtered sample into a second 500-mL separatory funnel.

4. Add, by graduated cylinder, approximately 50 mL of 0.05-*M* sulfuric acid solution and shake the solution with intermittent venting for approximately one minute.
5. Allow the layers to separate. Draw off and discard the lower acid layer.
6. Wash the hydrocarbon three times by shaking with venting for approximately one minute with 100-mL portions of water and discarding the water each time.
7. Filter the hydrocarbon through acid-free filter paper, discarding the first 10 mL of filtrate and collecting the remainder.
8. Proceed as described under *Procedure A, Acid Number, As-Received Basis*, using the sweetened, acid washed, filtered sample, beginning with Step 2.

CALCULATIONS

Calculate the acid number for the as-received or mercaptan and thiophenol-free sample, in milligrams of potassium hydroxide per gram of sample, to 3 decimal places, as follows:

$$\text{Acid Number, mg KOH/g} = \frac{56.1 (E - D) M}{W} \quad (2)$$

where:

- D** = volume of titrant required to titrate the solvent blank, mL
- E** = volume of titrant required to titrate the sample, mL
- M** = molarity of the potassium hydroxide, Eq. 1
- W** = mass of sample, g
- 56.1** = molecular weight of potassium hydroxide, g/mole

Calculate the naphthenic acids to the nearest mass-ppm as follows:

$$\text{Naphthenic Acids, mass-ppm} = \frac{10^3 (E - D) M C}{W} \quad (3)$$

where:

- C** = relative molecular mass of naphthenic acids obtained from the Figure, g/mol
- D** = previously defined, Eq. 2
- E** = previously defined, Eq. 2
- M** = molarity of the potassium hydroxide, Eq. 1
- W** = mass of sample, g
- 10³** = factor to convert mg/g to mass-ppm

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated for acid numbers at three levels using *Procedure A* and are listed in the Table. Two tests performed in the one laboratory by different analysts on two different days should not differ by more than the allowable difference values listed in the Table at the concentrations listed (95% probability).

Table

Sample Type	Acid Number, mg KOH/g Sample	Within-Lab esd, mg KOH/g Sample	Allowable Difference, mg KOH/g Sample
Lt. Cycle Oil	0.016	0.0010	0.003
Kerosine	0.026	0.0014	0.006
Range Oil	0.017	0.0007	0.003

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for the standardization is 4 hours and the labor requirement is 0.5 hour. The elapsed time for *Procedure A* is 1 hour and the labor requirement is 0.5 hour. The elapsed time for *Procedure B* is 2.3 hours and the labor requirement is 1 hour. The elapsed time for *Procedure C* is 4 hours and the labor requirement is 1.8 hours.

REFERENCES

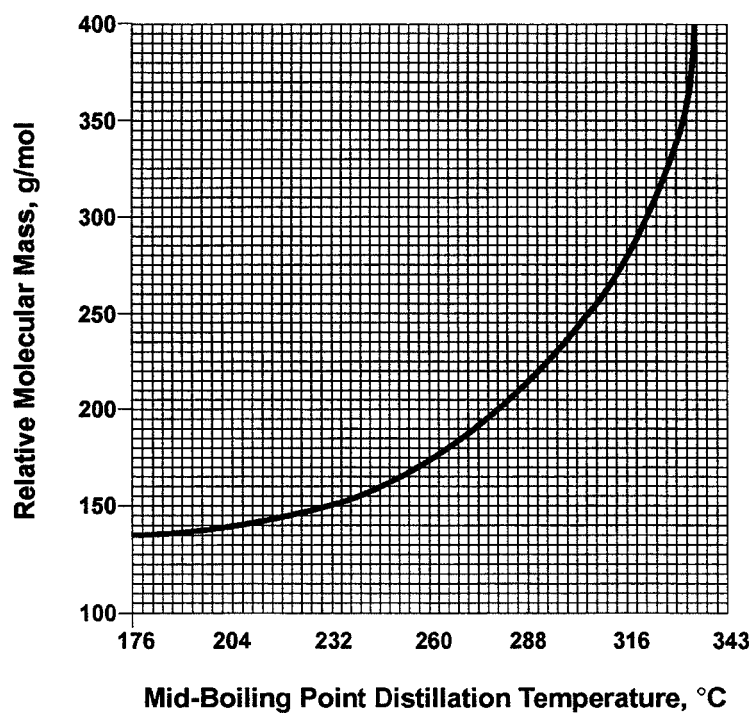
ASTM Method D 86, www.astm.org

UOP Method 565, "Acid Number and Naphthenic Acids by Potentiometric Titration"

SUGGESTED SUPPLIERS

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

Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)



Figure

Mid-Boiling Point Distillation Temperatures Relative and Molecular Mass of Naphthenic Acids
($C_nH_{2n}O_2$)