ACID NUMBER AND NAPHTHENIC ACIDS BY TITRATION

UOP Method 565-05

SCOPE

This method is for determining the acid number of petroleum products, petroleum distillates, and similar materials by potentiometric titration. Inorganic acids, organic acids, mercaptans and thiophenols respond to this analysis, but their respective salts do not. For naphthenic acids, it is frequently desired to include the salts in the measurement. Therefore, a procedure is also included for the determination of sodium naphthenate salts. The typical range for acid number determination is 0.002 to 5 mg KOH/g of sample, although higher concentrations can be accommodated.

There are three procedures included in the method. 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 quantitation for naphthenic acids is 5 to 500 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.

If no potentiometric titrator is available, and the sample is light in color, the titration may be performed colorimetrically; see the *APPENDIX*.

REFERENCES

ASTM Method D 86, "Distillation of Petroleum Products at Atmospheric Pressure," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

OUTLINE OF METHOD

PROCEDURE A, determination of acid number on an as-received basis:

A weighed amount of sample is mixed with a titration solvent and titrated to a potentiometric endpoint with alcoholic KOH using a titrator equipped with a CO_2 guard tube. The titration is performed using a combination glass electrode. After a blank correction, the acid number is calculated as mg KOH/g of sample.

PROCEDURE B, determination of acid number on a mercaptan- and thiophenol-free basis:

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).

The sample is shaken with a copper sulfate-sodium chloride solution in the presence of air in order to oxidize (sweeten) the mercaptan and thiophenols to disulfides. After filtration, the sample is titrated as described in *PROCEDURE A*.

PROCEDURE C, 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 in order to convert the sodium naphthenates to naphthenic acids. The sample is then washed with water and filtered. The treated 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, "Distillation of Petroleum Products at Atmospheric Pressure," from which the molecular mass of the naphthenic acids is estimated. The naphthenic acid value is calculated in mass-ppm.

APPARATUS

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

Balance, readability 0.01-g

Balance, readability 0.1-mg

Beaker, 250-mL, tall, without spout, borosilicate glass, Reliance Glass, Cat. No. G-9906-002

Bottles, wash, for 2-propanol and water, Fisher Scientific, Cat. Nos. 02-897-6 and -11, respectively

Crucible, high form, 10-mL, porcelain, Fisher Scientific, Cat. No. 07-965C, with cover, Fisher Scientific, Cat. No. 07-970D

Cylinders, graduated, 10-, 100-, 250-, and 1000-mL, borosilicate glass, Fisher Scientific, Cat. Nos. 08-549-5B, -5E, -5G, and -5J, respectively

Desiccator, 160-mm ID, and porcelain plate, Fisher Scientific, Cat. Nos. 08-632 and 08-641A, respectively

Electrode, combination glass, with sleeve diaphragm, double junction, Brinkmann Instruments, Cat. No. 20 91 050-0. Store in water when not in use.

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

Flasks, volumetric, Class A, 100-, 1000-, and 2000-mL, borosilicate glass, Fisher Scientific, Cat. Nos. 10-210-5C, -5G, and -5H, respectively

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

Funnel, separatory, 500-mL and 1-L, borosilicate glass, Fisher Scientific, Cat. Nos. 10-437-5D and -5E, respectively

Hot plate, Fisher Scientific, Cat. No. 11-600-49H, if needed to heat heavy or viscous samples

Magnetic stir bar, Fisher Scientific, Cat. No. 14-511-64, three required

Mortar, porcelain, 130-mm OD, Fisher Scientific, Cat. No. 12-961-C, with pestle, porcelain, Fisher Scientific, Cat. No. 12-961-5C

Oven, drying, capable of operation at 120ºC, Fisher Scientific, Cat. No. 13-246-506G

Pipet, volumetric transfer, Class A, 100-mL, Fisher Scientific, Cat. No. 13-650-2U

Regulator, nitrogen, two-stage, high purity, delivery pressure range 15-200 kPa (2-30psig), Matheson Gas Products, Model 3121-580

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

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

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

Thermometer or thermocouple, if needed for heating heavy or viscous samples

Titrator, potentiometric, recording, ±2000-mV range, 1-mV resolution, capable of reducing the titration rate to a minimum in the vicinity of the endpoint, with dispenser having a volume readout of 0.00 - 99.99 mL, 0.0001 of the buret volume resolution, Metrohm Model 836 Titrando system with optional sample changer, and 20-mL buret with a reservoir guard tube, Brinkmann Instruments

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

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean double deionized or distilled, unless otherwise specified.

Absorbent, carbon dioxide, Ascarite II, 20 to 30-mesh, Fisher Scientific, Cat. No. A184-500

Chloroform, 99% minimum purity, Fisher Scientific, Cat. No. C606

Copper sulfate pentahydrate (cupric sulfate), 98% minimum purity, Fisher Scientific, Cat. No. C493-500

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

Electrolyte, ethanol saturated with lithium chloride, for filling reference electrode, Brinkmann Instruments, Cat. No. 20 09 444-3

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

Methanol, 99.8% minimum purity, Fisher Scientific, Cat. No. A-412

Nitrogen, 99.999% minimum purity

Phenolphthalein solution, 1% in 2-propanol, Fisher Scientific, Cat. No. LC18210-7

Potassium hydrogen phthalate, primary standard, Fisher Scientific, Cat. No. P243-100

Potassium hydroxide, 0.5-*N* (0.5-*M*), alcoholic (methanol), Fisher Scientific, Cat. No. SP222-1

Potassium hydroxide, 0.05-*N* (0.05-*M*), alcoholic (methanol). Pipet 100 mL of 0.5-*N* alcoholic (methanol) KOH into a 1-L volumetric flask, and dilute to the mark with methanol. Mix thoroughly by repeated inversions.

2-propanol, 99% minimum purity, Fisher Scientific, Cat. No. A451-4

Sodium chloride, Fisher Scientific, Cat. No. S671-500

Sulfuric acid, approximately 0.1-*N* (0.05-*M*), Fisher Scientific, Cat. No. SA220-1

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

Tape, electrical, Fisher Scientific, Cat. No. 09-356

Titration solvent 1. Add, by graduated cylinder, 1000 mL of toluene, 990 mL of 2-propanol, and 10 mL of water to a 2000-mL volumetric flask. Mix thoroughly by repeated inversions.

Titration solvent 2. Add, by graduated cylinder, 500 mL of toluene, 500 mL of chloroform and 500 mL of 2-propanol to a 2000-mL volumetric flask. Mix thoroughly by repeated inversions.

Toluene, 99.8% minimum purity, Fisher Scientific, Cat. No. T290-4

STANDARDIZATION OF POTASSIUM HYDROXIDE

The analyst is expected to be familiar with general laboratory practices, the technique of titration, and with the equipment being used.

1. Assemble and operate the titrator and electrodes according to the manufacturer's instructions.
2. Fill the dispenser reservoir of the titrator with the 0.05-*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 dispenser 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 120ºC for 2 hours in a drying oven.
5. Remove the crucible from the oven using tongs, place it in a desiccator, cover it, and allow it to cool to ambient temperature.
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 masses in each beaker.
    - The standardization is performed in triplicate.