



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 CO₂ 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:

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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 120°C, 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

Titration, 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 Titration 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 120°C 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.

7. Add, by graduated cylinder, 100 mL of carbon dioxide free 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 requires approximately 90 minutes under vacuum to fully degas.
8. Place one of the beakers on the titration stand, immerse the electrodes and buret tip, and stir.
 - Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center.
 - Obtain a stable reading before proceeding to Step 9.
9. Adjust the titration parameters so that the initial titration rate in the plateau region is 0.3 mL/min and the titration rate in the region of the endpoint is reduced to 0.1 mL/min. Titrate the potassium hydrogen phthalate solution with the 0.05-*M* potassium hydroxide. Record the volume of titrant used to reach the endpoint of the titration.
 - The endpoint is the midpoint of the inflection; the point at which the curve changes from concave to convex, see Figure 1.
10. Titrate the contents of the other two beakers in the same manner.
11. For each titration, calculate the molarity of the potassium hydroxide, to four significant figures, using Equation 1:

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

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 0.05-*M* potassium hydroxide, moles/L
- 204.2** = molecular mass of potassium hydrogen phthalate, g/mole
- 10³** = factor to convert moles/mL to moles/L

12. Average the results of the three determinations to four significant figures.
 - Results from each of the triplicate runs should not deviate by more than 0.001*M*. If greater deviations occur, make certain that there are no problems with the equipment or the procedure; then repeat the procedure until the required repeatability is obtained on three consecutive runs.
 - The potassium hydroxide solution must be standardized at least weekly to detect changes in molarity. A reference quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

PROCEDURE

Part A: Acid Number, As-Received Basis

1. Select the appropriate titration solvent (see *REAGENTS AND MATERIALS*) and sample size for the sample being analyzed; use Table 1 as a guide.
2. Determine a blank by performing the following Steps 6 through 10, using only the titration solvent, omitting the sample.

3. Heat heavy or viscous samples containing suspended materials to $60 \pm 5^\circ\text{C}$ until the sample is completely fluid.
 - The heating may be accomplished by using an oven, a heated bath, a hot plate, or other convenient means. Do not use the oven used to dry the potassium hydrogen phthalate to warm the samples. Subsequent batches of potassium hydrogen phthalate could be contaminated by sample residue.
4. Shake vigorously to obtain a representative sample.

Table 1
Titration Solvent and Sample Size

<u>Sample Type</u>	<u>Titration Solvent</u>	<u>Approximate Sample Size, g</u>
Light petroleum distillates such as kerosines, diesel fuels, jet fuels, gas oils, both sweetened and unsweetened	1	100^a
Vacuum gas oil, resid, coal oil, shale oils and crude oils	2	50

^a Do not exceed 120-mL sample volume.

5. Weigh the sample, to the nearest 0.01 g, into a 250-mL titration beaker.
6. Add, by graduated cylinder, 100 mL of the titration solvent selected in Step 1.
7. Add a stirring bar, position the beaker on the titration stand, start a slow flow of nitrogen to the headspace of the beaker to expel air, and stir.
 - Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center.
 - Continue applying a nitrogen blanket throughout the titration.
8. Immerse the electrodes into the solution and wait for a stable reading.
9. Titrate the solution with the 0.05-M potassium hydroxide using the following conditions. Adjust the titration parameters so that the initial titration rate in the plateau region is 0.3 mL/min, and the titration rate in the region of the endpoint is reduced to 0.1 mL/min.
 - One drop of phenolphthalein indicator may be used to help determine whether the potentiometric titration is complete, as indicated by the phenolphthalein color change from colorless to pink. This is especially helpful where the titration proceeds through two inflections. Note, however, that the potentiometric endpoint may occur slightly after the phenolphthalein color change is observed. Also, care must be taken that the amount of phenolphthalein added is minimal. If more than one drop is added, a false high endpoint may result.
10. Record, to the nearest 0.001 mL, the volume of titrant needed to reach the endpoint of the titration.
 - The endpoint is the midpoint of the inflection; the point at which the curve changes from concave to convex, see Figure 1.
 - If the titration curve has two inflections, the total volume of titrant needed to reach the second inflection is recorded for use in the calculations.
 - After each titration, rinse the electrodes and the dispenser tip with 2-propanol and then with water.
 - Immerse the electrodes in water for 2 minutes between titrations to restore the aqueous gel layer of the glass electrode.

Part B: Acid Number, Mercaptan- and Thiophenol-Free Basis

1. Measure, by graduated cylinder, approximately 150 mL of the hydrocarbon sample into a 500-mL Erlenmeyer flask.
 - If both Parts B and C are needed, perform Steps 1-3 in duplicate.
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 with electrical tape and shake for 30 minutes with a wrist action shaker.

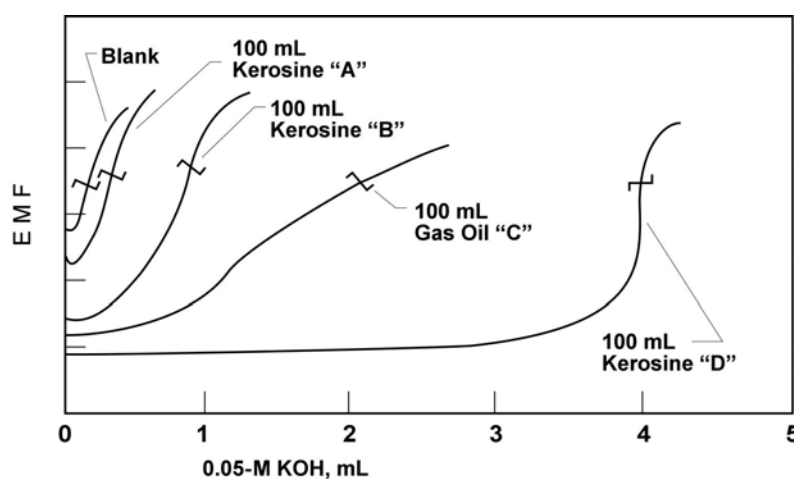


Figure 1
Acid Number Titration, Typical Curves

4. Transfer the mixture to a 500-mL separatory funnel and allow the layers to separate.
 - If both Parts B and C are needed, combine the mixtures from the duplicate flasks into a 1-L 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 hydrocarbon 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 *Part A: Acid Number, As-Received Basis*, using the sweetened, filtered sample and Titration Solvent 1.

Part 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 Figure 2.

- The mid-boiling point distillation temperature is the temperature at which 50 volume-% of the sample has distilled over.

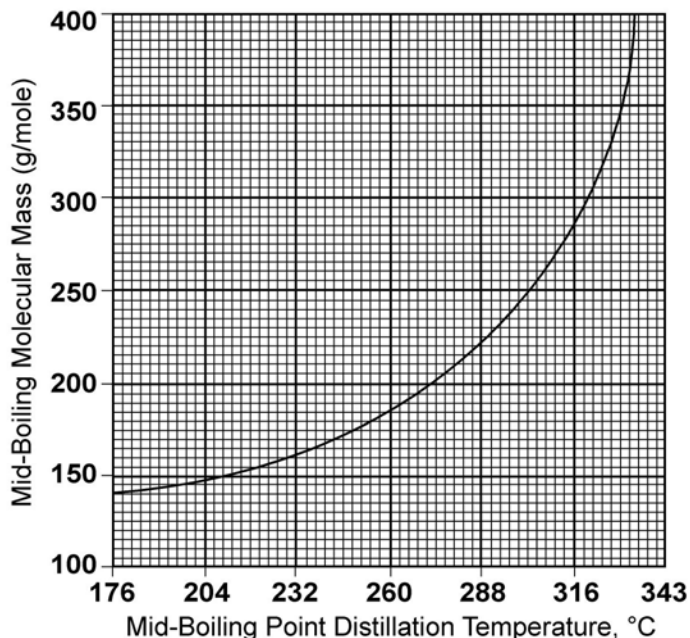


Figure 2
Mid-Boiling Point Distillation Temperatures and
Relative Molecular Mass of Naphthenic Acids ($C_nH_{2n}O_2$)

- Sweeten approximately 150 mL of sample, following Steps 1 through 6 as described under *Part B: Acid Number, Mercaptan- and Thiophenol-Free Basis*.
 - If both Parts B and C were requested, the remaining sweetened sample from Part B, Step 7, should be used as the aliquot for Part C, and does not need further sweetening.
- Measure, by graduated cylinder, approximately 135 mL of the sweetened, filtered sample into a second 500-mL separatory funnel.
- Add, by graduated cylinder, approximately 50 mL of 0.05-M sulfuric acid solution and shake the solution with venting for approximately one minute.
- Allow the layers to separate. Draw off and discard the lower acid layer.
- 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.
- Filter the hydrocarbon through acid-free filter paper, discarding the first 10 mL of filtrate and collecting the remainder.
- Proceed as described under *Part A: Acid Number, As-Received Basis*, using the sweetened, acid washed, filtered sample and Titration Solvent 1.

CALCULATIONS

Calculate the acid number, in milligrams of potassium hydroxide per gram of sample, to three decimal places, using Equation 2:

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

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, moles/L, Equation 1
- W** = mass of sample, g
- 56.1** = molecular mass of potassium hydroxide, g/mole

Report the acid number and whether it is on an as-received basis or on a mercaptan- and thiophenol-free basis.

Calculate the naphthenic acids to the nearest mass-ppm using Equation 3:

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

where:

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

PRECISION

Precision statements were determined using UOP Method 999, from precision data obtained using a Brinkmann Metrohm 751GPD Titrino titrator with an automatic sample changer.

Repeatability and Intermediate Precision

A nested design was carried out for determining acid number with two analysts in one laboratory using Procedure A. Each analyst carried out two tests on each of four samples on two separate days. The total number of tests for each sample was eight. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for each concentration and is listed in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table 3 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable difference shown in Table 3 with 95% confidence.

The data in Table 3 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table 3
Repeatability and Intermediate Precision, mg KOH/g sample

<u>Acid Number</u>	<u>Solvent</u>	<u>Repeatability</u>		<u>Intermediate Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
0.009	1	0.0005	0.002	0.0006	0.002
0.014	1	0.0008	0.003	0.0009	0.003
0.022	1	0.0007	0.003	0.0011	0.004
0.624	2	0.0038	0.015	0.0052	0.021

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

SUGGESTED SUPPLIERS

Brinkmann Instruments Co., One Cantiague Rd., Westbury, NY 11590 (516-334-7500)
www.brinkmann.com

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300)
www.fishersci.com

Matheson Gas Products Inc., 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Reliance Glass Division, Wilmad/LabGlass, 1002 Harding Highway, Buena, NJ 08310-0688
 (856-697-3000) www.wilmad-labglass.com

APPENDIX

Analysis Using Colorimetric Titration

If a potentiometric titrator is not available, the procedure can be performed colorimetrically by substituting the procedure below for Part A of the *PROCEDURE* in the body of the method. This procedure is limited to light colored distillates, soluble in alcohol, only. For dark colored samples, the potentiometric procedure must be used. The typical range for acid number detection by the colorimetric procedure is 0.004 to 0.5 mg KOH/g of sample, although higher levels can be accommodated. *PROCEDURE* Parts B and C remain unchanged except for the titration. The calculations also remain unchanged.

APPARATUS

The following items are required in addition to, or as an alternative to, those listed in the body of the method.

Buret, Machlett, automatic, 2-mL, Fisher Scientific, Cat. No. 03-847-1A

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

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

REAGENTS

The following items are required in addition to, or as an alternative to, those listed in the body of the method.

Thymolphthalein, 1% in ethyl alcohol, Spectrum Chemicals and Laboratory Products, Cat. No. T-141

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. Crush approximately 1 g of potassium hydrogen phthalate using a mortar and pestle.
2. Transfer the potassium hydrogen phthalate to a clean crucible, and dry at 120°C for 2 hours in a drying oven.
3. Remove the crucible from the oven using tongs, place it in a desiccator, cover it, and allow it to cool to ambient temperature.
4. 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.
5. Add, by graduated cylinder, 100 mL of carbon dioxide free 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 requires approximately 90 minutes under vacuum to fully degas.
6. Add about 10 drops of thymolphthalein indicator.
 7. Purge the headspace of the flask with nitrogen to expel air and connect a nitrogen line to the side-arm of the flask.
 - Continue applying a nitrogen blanket throughout the titration.
 8. Add a stirring bar, position the beaker on the titration stand, and stir.
 - Stir at a rate sufficient to form a vortex, but not to create bubbles.
 9. Lower the buret tip into the flask and titrate the solution with the 0.05-*M* potassium hydroxide to the light-blue thymolphthalein endpoint.
 - The endpoint color should remain unchanged for 10 seconds.
 10. Record, to the nearest 0.01 mL, the volume of titrant needed to reach the endpoint of the titration.
 11. Calculate the molarity of the potassium hydroxide, to three significant figures, using Equation 1 in the body of the method.

PROCEDURE

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

1. Standardize the potassium hydroxide solution as described in the body of the method.
2. Determine a blank by performing the following Steps 5 through 10, using only the titration solvent (Step 5), omitting the sample.
3. Shake the sample vigorously to obtain a representative aliquot.
4. Weigh approximately 100 g of sample, to the nearest 0.01 g, into a 500-mL Erlenmeyer flask with a side-arm.
5. Add, by graduated cylinder, 200 mL of 2-propanol and 5 mL of water.
6. Add about 10 drops of thymolphthalein indicator.
7. Purge the headspace of the flask with nitrogen to expel air and connect a nitrogen line to the side-arm of the flask.
 - Continue applying a nitrogen blanket throughout the titration.
8. Add a stirring bar, position the beaker on the titration stand, and stir.
 - Stir at a rate sufficient to form a vortex, but not to create bubbles.
9. Lower the buret tip into the flask and titrate the solution with the 0.05-*M* potassium hydroxide to the light-blue thymolphthalein endpoint.
 - The endpoint color should remain unchanged for 10 seconds.

10. Record, to the nearest 0.01 mL, the volume of titrant needed to reach the endpoint of the titration.
11. Calculate the acid number to two decimal places as described in the body of the method.

PRECISION

The precision statements were determined using UOP Method 999.

Repeatability and Intermediate Precision

A nested design was carried out for determining acid number with two analysts in one laboratory. Each analyst carried out two tests on each of three samples on two separate days. The total number of tests for each sample was eight. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for each concentration and is listed in Table A1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table A1 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable difference shown in Table A1 with 95% confidence.

The data in Table A1 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

Table A1

Repeatability and Intermediate Precision, mg KOH/g sample

<u>Sample</u>	<u>Acid Number</u>	<u>Repeatability</u>		<u>Intermediate Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Light Cycle Oil	0.016	0.0007	0.003	0.0009	0.003
Kerosine	0.026	0.0009	0.004	0.0014	0.006
Range Oil	0.017	0.0003	0.001	0.0008	0.004

SUGGESTED SUPPLIER

Spectrum Chemicals and Laboratory Products, 14422 South San Pedro Street, Gardena, CA 90248
(310-516-8000) www.spectrumchemical.com