



A Honeywell Company

Nitrogen Bases in Hydrocarbons by Titration

UOP Method 269-10

Scope

This method is for determining basic organic nitrogen in petroleum distillates using potentiometric titration. This method may be applied to both clear and colored samples. The range of quantitation for petroleum distillates is from 0.0005 to 1.0 mass-% nitrogen, while for viscous materials, such as heavy oils, the range is 0.001 to 5.00 mass-% nitrogen. This method may give erroneous results for materials containing bases other than nitrogen compounds (e.g., caustic-washed distillates containing sodium soaps, or crude oil containing inorganic bases).

Clear or very lightly colored samples may be analyzed down to a lower limit of quantitation of 0.5 mass-ppm (0.00005 mass-%) using the color indicator titration technique described in the *Appendix*.

Reference

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

Outline of Method

Organic bases are titrated potentiometrically using a pH electrode, a perchloric acid in acetic acid titrant, and an acetic acid titration solvent.

Apparatus

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

Balance, readability 0.1-mg

Beaker, 250-mL, tall, without spout, borosilicate glass, Brinkmann Instruments, Cat. No. 020212209, Metrohm USA

Cylinder, graduated, 100-mL, Fisher Scientific, Cat. No. 08-548D

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

Electrode, Ecotrode™ combination Long Life pH, Metrohm USA, Cat. No. 020.912.146

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Flasks, Class A, volumetric, 100-, 250-, and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5C, -5E, and -5G, respectively

Hot plate, Fisher Scientific, Cat. No. 11-100-16H

Oven, drying, capable of operation at 110°C

Pipets, 10-, 20-, 25-, and 50-mL, Class A, Fisher Scientific, Cat. Nos. 13-650-2L, -2N, -2P, and -2S, respectively

Rubber bulb-type pipet filler, Fisher Scientific, Cat. No. 13-681-51

Titration, potentiometric, recording, 2000-mV range, 1-mV resolution, capable of following a maximum allowable drift throughout a titration and/or reducing the titration rate to a minimum in the vicinity of the equivalence point, with dispenser having a volume readout of 0.001-99.999 mL with a resolution of 0.0001 of the buret volume, Metrohm Model 835 Titrando™ system with optional Model 814 sample changer, and 20-mL buret

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 deionized or distilled.

Acetic acid, glacial, less than 0.10% water, Fisher Scientific, Cat. No. A38

Acetone, 99.5% minimum purity, Fisher Scientific, Cat. No. A18

Dessicant, indicating, Fisher Scientific, Cat. No. 07-578-3B

Perchloric acid, approximately 1-N, Fisher Scientific, Cat. No. SP339-500

Perchloric acid, approximately 0.02-N. Pipet 20 mL of the 1-N perchloric acid solution into a one-liter volumetric flask. Dilute to the mark with glacial acetic acid and mix well. Standardize this solution against THAM solution as described under *Standardization*. This solution is stable for two months, after which a new solution is prepared.

Potassium chloride solution, 3 mol/L, Metrohm USA, Cat. No. 6.2308.020

THAM, tris(hydroxymethyl)aminomethane, primary standard, Fisher Scientific, Cat. No. T395

THAM solution. Dry THAM in an oven at 110°C for 2 hours; cool in a desiccator. Weigh, to the nearest 0.1 mg, between 0.5 and 0.6 g of dried THAM into a 100-mL volumetric flask. Dilute to the mark with glacial acetic acid and mix well. The prepared solution is stable for 2 weeks.

Toluene, 99.5% minimum purity, Fisher Scientific, Cat. No. T324

Water, deionized or distilled

Procedure

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

Standardization

1. Assemble and operate the titrator and electrode according to the manufacturer's instructions.
2. Fill the dispenser reservoir of the titrator with the 0.02-N perchloric acid solution.
3. Pipet 10 mL of THAM solution into a clean, dry 250-mL beaker.

4. Add, by graduated cylinder, 100 mL of glacial acetic acid to the beaker.
5. Place the beaker containing the diluted standard on the titration stand, stir and titrate the standard with the 0.02-N perchloric acid under the following conditions: Adjust the titrator parameters so that the initial titration rate in the plateau region is 0.5 mL/min while the titration rate in the region of the endpoint is reduced to 0.1 mL/min.
 - The standardization is performed in triplicate.
6. Record the volume of titrant required to reach the endpoint of the titration.
 - The end point is the midpoint of the inflection, that point at which the curve changes from concave to convex, see Figure.
7. Add, by graduated cylinder, 100 mL of glacial acetic acid to another 250-mL beaker, for use as a blank.
8. Titrate the blank using the 0.02-N perchloric acid in duplicate as described above. If the blanks do not repeat within 0.02 mL, check the equipment and procedures, and repeat the blank titrations.
9. Calculate the normality of the perchloric acid to the fourth decimal place using Equation 1:

$$\text{Normality of perchloric acid} = \frac{8.2549 A \left(\frac{W}{F} \right)}{B - G} \quad (1)$$

where:

A = volume of dilute THAM solution titrated, mL

B = volume of perchloric acid solution used to reach the endpoint of the dilute THAM solution, mL

F = volume to which THAM solution was diluted, mL

G = volume of perchloric acid used to reach the endpoint of the acetic acid blank, mL

W = mass of THAM, weighed into flask, g

$$8.2549 = \frac{1000}{121.14} \quad (1a)$$

where:

121.14 = molecular weight of THAM, g/mole

1000 = factor to convert liters to milliliters

10. Average the results of the three determinations.
 - Results from each of the triplicate runs should not deviate by more than 0.001-N. 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 perchloric acid solution must be standardized at least weekly to detect changes in normality. A reference quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

Part A Samples Soluble in Glacial Acetic Acid

1. Add, by graduated cylinder, 100 mL of glacial acetic acid into a clean dry 250-mL beaker.

2. Add the sample, weighed to the nearest 0.1 mg, to the glacial acetic acid. The sample amount depends on the concentration of basic nitrogen present. Use Table 1 as a guide to choose the appropriate sample mass.

Table 1
Guide to Choose the Appropriate Sample Mass

<u>Estimated Basic N, mass-%</u>	<u>Approximate Sample Mass, g</u>
<0.0015	100
0.0015 to 0.025	25
0.025 to 0.070	15
0.070 to 0.15	5
0.15 to 1.0	1

3. Place the beaker containing the weighed sample in position for titration, stir and titrate the sample with the 0.02-N perchloric acid using the parameters established in the section on Standardization, Step 5.
4. Record the volume of titrant required to reach the endpoint of the titration, see *Standardization*, Step 6.
 - The Figure shows several typical titration curves.

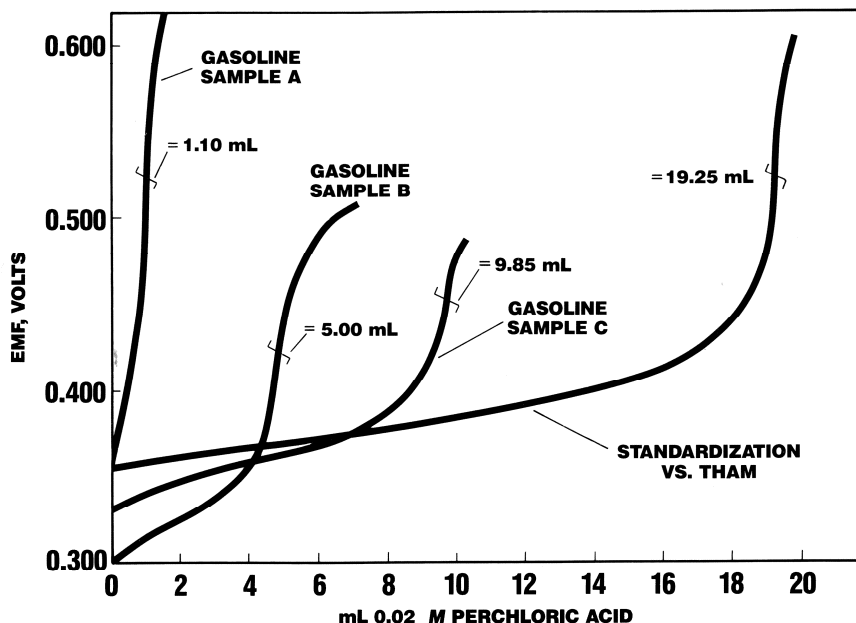


Figure
Nitrogen Base Determination, Typical Titration Curves

5. Prepare a blank containing 100 mL of glacial acetic acid and analyze it in the same manner as the sample.

Part B

Samples Insoluble in Glacial Acetic Acid (Heavy Oils)

1. Warm the sample on a hot plate and shake it to make sure it is homogeneous.

2. Weigh, to the nearest 0.1 mg, a representative aliquot of the sample into a 250-mL beaker. See Table 2 for the amount to weigh, based upon the expected concentration of nitrogen in the sample.
3. Dissolve a weighed sample in toluene; the amount of sample and toluene will vary. Use Table 2 as a guide.
 - If the sample does not dissolve readily in toluene, warm again.

Table 2
Guide to Choose the Appropriate Amount of Toluene to Use

<u>Estimated Basic N, mass-%</u>	<u>Approximate Sample Mass, g</u>	<u>Toluene, mL</u>
<0.01	25	50
0.010 to 0.035	10	50
0.035 to 1.0	1	25
1.0 to 5.0	0.3	25

4. Using a graduated cylinder, add glacial acetic acid slowly. If no precipitate forms, add a total of 75 mL of glacial acetic acid. If a precipitate forms, add an amount of glacial acetic acid equal to the total amount of sample-plus-toluene used.
 - In some heavy oil samples a precipitate will form as soon as any glacial acetic acid is added. Ignore the precipitate formed.
5. Place the beaker containing the weighed sample in position for titration, stir and titrate the sample with the 0.02-N perchloric acid using the parameters established in the section on *Standardization*, Step 5.
6. Record the volume of titrant required to reach the endpoint of the titration, see *Standardization*, Step 6.
 - The Figure shows several typical titration curves.
7. Prepare a blank containing the same amount of toluene and glacial acetic acid as used for the sample, and analyze it in the same manner as the sample.

Calculations

Calculate the mass-% basic nitrogen in the sample to three significant figures as follows:

$$\text{Basic nitrogen, mass-\%} = \frac{1.4 (C - D) N}{S} \quad (2)$$

where:

C = volume of perchloric acid used to reach the endpoint of the sample titration, mL

D = volume of perchloric acid used to reach the endpoint of the blank titration, mL

N = normality of perchloric acid solution, from Equation 1

S = sample mass, g

$$1.4 = \frac{(14)(100)}{1000} \quad (2a)$$

where:

14 = molecular weight of nitrogen, g/mole

100 = factor to convert g/g to mass-%

1000 = factor to convert liters to milliliters

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining basic nitrogen on three samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on each sample each day. The total number of tests was 24. The precision data are summarized in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table 3
Repeatability and Site Precision, basic nitrogen, mass-%

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Part A, 1	0.0006	0.00004	0.0002	0.00019	0.0012
Part A, 2	0.7673	0.01083	0.0425	0.01104	0.0434
Part B, 3	0.0017	0.00011	0.0005	0.00019	0.0009

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.

Reproducibility

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

Time for Analysis

The elapsed time and labor requirement are identical, 0.5 hour for Part A, and 1.0 hour for Part B.

Suggested Supplier

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

Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL 33578 (813-316-4700)
www.metrohmusa.com

Appendix

Nitrogen Bases in Petroleum Distillates by Color Indicator Titration

Scope

This method is for determining basic organic nitrogen in clear or very light-colored distillates using a visual indicator titration. It is applicable over the range 0.5 to 100 mass-ppm as nitrogen, but is especially useful from 0.5 to 5.0 mass-ppm. Colored samples interfere with the observation of the color indicator and, therefore, cannot be accurately analyzed by this method. Colored samples can be analyzed over a wide concentration range by potentiometric titration as described in the body of the method.

Reference

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter,"
www.astm.org

Outline of Method

Samples are titrated colorimetrically with a perchloric acid in acetic acid titrant, using crystal violet as a visual indicator.

Apparatus

The following apparatus are an addition or substitution to that listed in the body of the method.

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

Beakers, 400-mL, tall, without spout, borosilicate glass, Fisher Scientific, Cat. No. 10-310-9

Bottle, dropping, with ground glass stopper/pipet, 125-mL, Fisher Scientific, Cat. No. 02-9863

Buret, micro, 10-mL, 0.02-mL subdivisions, Class A, with Teflon stopcock, Fisher Scientific, Cat. No. 20-105B

Buret, 50-mL, 0.1-mL subdivisions, Class A, with PTFE stopcock, Fisher Scientific, Cat. No. 03-700-22C

Magnetic stirrer, with stir bar, Fisher Scientific, Cat. Nos. 14-493-120M and 14-511-64, respectively

Pipets, volumetric, 5- and 100-mL, Class A, Fisher Scientific, Cat. Nos. 13-650-2F and -2U, respectively

Reagents and Materials

The following reagents and materials are an addition or substitution to that listed in the body of the method.

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

Crystal violet, Fisher Scientific, Cat. No. C581

Crystal violet indicator solution. In the dropping bottle, dissolve approximately 0.1 g of crystal

violet in 100 mL of glacial acetic acid.

Perchloric acid, approximately 0.01-N. Pipet 10 mL of 1-N perchloric acid solution into a one-liter volumetric flask. Dilute to the mark with glacial acetic acid and mix well. Standardize this solution against THAM solution as described under *Standardization*.

Procedure

Standardization

Standardize the 0.01-N perchloric acid solution as follows:

1. Prepare and fill the 10- or 50-mL buret, for low (0.5 – 5 mass-ppm nitrogen expected) or high (5 – 100 mass-ppm nitrogen expected) nitrogen concentrations, respectively, with the 0.01-N perchloric acid in glacial acetic acid. Record the initial buret reading.
2. Pipet 5 mL of THAM solution into a clean, dry 250-mL beaker.
3. Add, by graduated cylinder, 100 mL of glacial acetic acid a stirring bar and 4 to 5 drops of crystal violet indicator solution to the beaker.
4. Set the beaker on a magnetic stirrer and adjust the stirring rate so there is rapid stirring but no splashing.
5. Titrate with the 0.01-N perchloric acid solution by adding the titrant dropwise from the 10- or 50-mL buret and waiting approximately one minute after each addition until a stable dark sky-blue color is obtained. This occurs after the last trace of purple is gone and before any shade of green appears.
6. Record the volume of 0.01-N perchloric acid titrant used, estimated to the nearest 0.01 mL.
 - The standardization is performed in triplicate.
7. With a graduated cylinder, add 100 mL of glacial acetic acid to a 250-mL beaker containing a stir bar and obtain a blank by titrating in the same manner as previously described (see Note). If the blanks do not repeat within 0.02 mL, check the equipment and procedures, and repeat the blank titrations.
8. Calculate the normality of the perchloric acid to the fourth decimal place using Equation A1.

$$\text{Normality of perchloric acid} = \frac{8.2549 \text{ A} \left(\frac{\text{W}}{\text{F}} \right)}{\text{B} - \text{G}} \quad (\text{A1})$$

where:

A = volume of dilute THAM solution titrated, mL

B = volume of perchloric acid solution used to reach the endpoint of the dilute THAM solution, mL

F = volume to which THAM solution was diluted, mL

G = volume of perchloric acid used to reach the endpoint of the acetic acid blank, mL

W = mass of THAM, weighed into flask, g

$$8.2549 = \frac{1000}{121.14} \quad (\text{A1a})$$

where:

121.14 = molecular weight of THAM, g/mole

1000 = factor to convert liter to milliliters

9. Average the results of the three determinations.

- Results from each of the triplicate runs should not deviate by more than 0.001-N. 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 perchloric acid solution must be standardized at least weekly to detect changes in normality. A reference quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

Sample Analysis

- Prepare and fill the 10- or 50-mL buret, for low or high nitrogen concentrations, respectively, with the 0.01-N perchloric acid in glacial acetic acid. Record the initial buret reading.
- Pipet the appropriate amount of sample (see Table A1) into a 400-mL tall-form titration beaker. Take care to exclude any water that might be entrained in the sample.
- Using a graduated cylinder, add the appropriate volume of glacial acetic acid (see Table A1). Add a stir bar, 4 to 5 drops of crystal violet indicator solution, and set the beaker on a magnetic stirrer.

Table A1
Guide to Choose the Appropriate Sample and Acid Volumes

Estimated Basic N, mass-ppm	Sample Volume, mL	Glacial Acetic Acid, mL
0.1 - 10	200	50
11 - 35	100	100
36 - 100	25	100

- Adjust the stirring rate so there is rapid stirring but no splashing. Titrate with 0.01-N perchloric acid in glacial acetic acid, by adding the titrant dropwise and waiting approximately one minute after each addition until a stable dark sky-blue color is obtained. This occurs after the last trace of purple is gone and before any shade of green appears.
- Record the volume of titrant used, estimated to the nearest 0.01 mL.
- Run a blank on the same volume of glacial acetic acid that was added to the sample, in the same manner as the sample.
- Determine the density of the sample by ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," or other acceptable technique.

Calculation

Calculate the concentration of basic nitrogen in the sample to two significant figures, not to exceed one decimal place, using Equation A2:

$$\text{Basic nitrogen, mass-ppm} = \frac{14000 (C - D) N}{E R} \quad (\text{A2})$$

where:

C = volume of perchloric acid used to titrate the sample, mL

D = volume of perchloric acid used to titrate the blank, mL

E = volume of sample, mL

N = normality of perchloric acid solution, from Equation A1

R = density of sample at ambient laboratory temperature

$$14000 = (14)(1000)$$

(A2a)

where:

14 = molecular weight of nitrogen, g/mole

1000 = factor to convert to mass-ppm

Note

Alternatively, when many samples are to be run, the stock solution of glacial acetic acid can be blanked out as follows: Add a few drops of the crystal violet solution to the acetic acid and titrate with 0.01-N perchloric acid to a stable dark sky-blue color. This eliminates the need to run a blank with each sample. The equations for standardization and calculations are modified accordingly.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining basic nitrogen on one sample with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on the sample each day. The total number of tests was eight. The precision data are summarized in Table A2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table A2
Repeatability and Site Precision, Basic Nitrogen, mass-ppm

<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
	<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
1.2	0.05	0.2	0.06	0.2

The data in Table A2 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 reproducibility of the test at this time.

Time for Analysis

The elapsed time and labor requirement are equivalent, 1.0 hour.