

NITROGEN BASES IN PETROLEUM DISTILLATES BY COLOR INDICATOR TITRATION

UOP Method 313-89

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 0.1 to 100 mass-ppm as nitrogen, but is especially useful from 0.1 to 1.0 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 UOP Method 269.

OUTLINE OF METHOD

The distillate sample is dissolved in glacial acetic acid and manually titrated with 0.01-M perchloric acid in glacial acetic acid, using crystal violet as a visual indicator.

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

Beakers, 250- and 400-mL, tall, without spout, borosilicate glass, Fisher Scientific, Cat. No. 02-555B and 02-555D, respectively

Bottle, dropping, with ground glass stopper/pipet, 125-mL, Fisher Scientific, Cat. Nos. 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

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

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

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

Oven, drying

Pipets, volumetric, 10-, 25- and 100-mL, Class A, Fisher Scientific, Cat. Nos. 13-650-2L, -2P and -2V, respectively

REAGENTS

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.

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

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

Crystal violet, Fisher Scientific, Cat. No. C581

Crystal violet indicator solution. Dissolve approximately 0.1 g of crystal violet in 100 mL of glacial acetic acid.

Perchloric acid, 70-72%, Fisher Scientific, Cat. No. A2296

Perchloric acid, approximately 1-*M* stock solution. Pipet 25 mL of 70% perchloric acid into a 250-mL volumetric flask containing 100 mL of glacial acetic acid and mix well. Fill to the mark with glacial acetic acid and again mix.

Perchloric acid, approximately 0.01-*M*. Pipet 10 mL of 1-*M* perchloric acid stock 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*.

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

THAM solution. Weigh, to the nearest 0.1 mg, between 0.5 and 0.6 g of THAM, previously oven dried at 110 C for 2 hours, into a 100-mL volumetric flask. Dilute to the mark with glacial acetic acid and mix well.

STANDARDIZATION

Standardize the 0.01-*M* perchloric acid solution as follows: Pipet 10 mL of the THAM solution into a clean, dry 250-mL beaker. Add 90 mL of glacial acetic acid, a stirring bar and 4 to 5 drops of crystal violet indicator solution to the beaker. Set the beaker on a magnetic stirrer and adjust the stirring rate so there is rapid stirring but no splashing. Titrate with the 0.01-*M* perchloric acid solution by adding the titrant dropwise from the 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. Record the volume of 0.01-*M* perchloric acid titrant used, estimated to the nearest 0.01 mL.

With a graduated cylinder, add 100 mL of glacial acetic acid to a 250-mL beaker and obtain a blank by titrating in the same manner as previously described (see *NOTE*). Calculate the molarity of the perchloric acid to the fourth decimal place as follows:

$$M = \frac{1000 A \left(\frac{W}{F} \right)}{121.14 (B - G)}$$

where:

A = volume of THAM solution used for titration, mL

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

F = volume to which THAM solution was diluted, mL

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

M = molarity of perchloric acid solution

W = mass of THAM, weighed into flask, g

121.14 = molecular weight of THAM, g/mole

1000 = factor to convert liters to milliliters

PROCEDURE

Prepare and fill the 10- or 50-mL buret, for low or high nitrogen concentrations, respectively, with the 0.01-*M* perchloric acid in glacial acetic acid. Record the initial buret reading. Pipet the appropriate amount of sample (see Table 1) into a 400-mL tall-form titration beaker. Take care to exclude any water that might be entrained in the sample. Add the appropriate volume of glacial acetic acid (see Table 1), if required. Add a stirring bar, 4 to 5 drops of crystal violet indicator solution and set the beaker on a magnetic stirrer. Adjust the stirring rate so there is rapid stirring but no splashing. Titrate with 0.01-*M* 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 relative density of the sample by ASTM Method D 4052 or other acceptable technique.

Table 1

Basic N Expected, ppm	Sample, mL	Glacial Acetic Acid, mL
0.1-10	200	0
11-35	100	100
36-100	25	75

CALCULATION

Calculate the concentration of nitrogen in the sample to two significant figures as follows:

$$\text{Nitrogen, mass-ppm} = \frac{14,000(C - D)M}{ER}$$

where:

C = volume of perchloric acid to titrate sample, mL

D = volume of perchloric acid to titrate blank, mL

E = volume of sample, mL

M = molarity of perchloric acid, previously calculated

R = relative density of sample

14,000 = molecular weight of nitrogen times 1000 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-*M* 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

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 nitrogen bases in toluene at two concentrations and are listed in Table 2. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable difference values listed in Table 2 at the concentrations listed (95% probability).

Table 2

Nitrogen Bases Concentration, mass-ppm	Within-Lab esd, mass-ppm	Allowable Difference, mass-ppm
0.1	0.015	0.06
100.0	0.97	3.2

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time and labor requirement are equivalent, 0.5 hour.

REFERENCES

ASTM Method D 4052, www.astm.org

UOP Method 269

SUGGESTED SUPPLIER

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60413