

PYRROLE NITROGEN IN PETROLEUM DISTILLATES BY VISIBLE SPECTROPHOTOMETRY

UOP Method 276-85

SCOPE

This method is for determining the approximate concentration of pyrroles and indoles having at least one hydrogen per carbon atom in the heterocyclic ring by visible spectrophotometry. It is applicable to gasolines, naphthas, kerosines and distillate burner oils, but is not applicable to crude and vacuum gas oils which are not completely soluble in *n*-heptane. Carbazoles and tetra substituted pyrrole, if present, are not determined. Olefins interfere with the determination and must be removed prior to analysis. Aromatic amines or aliphatic mercaptans can interfere with the test. The working range is 1 to 2000 mass-ppm pyrrole nitrogen.

OUTLINE OF METHOD

After removing olefins from the sample by column chromatography, the pyrroles are added to 85% phosphoric acid containing *p*-dimethylaminobenzaldehyde. Acetic acid is added and a deeply-colored red solution is formed. The absorbance of the colored solution is determined spectrophotometrically at 540 nm and the result compared to a previously prepared calibration curve. The calibration curve is prepared using 2-methylindole as a standard since it is believed that 2-methylindole produces an absorbance representative of the array of compounds that are encountered in most samples.

APPARATUS

Balance, readability, 0.1-mg

Beaker, 2-L

Chromatographic column, 19-mm ID by 400-mm long, with 2-mm Teflon plug, Kontes, Cat. No. K-420540, Size Code 0224, or equivalent. Substitute the stopcock provided with Varibor Stopcock, Teflon, Kontes, Cat. No. K-821111, Size 2, or equivalent.

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).

Column, glass tube, 29.5-mm ID by 400-mm length with 500-mL reservoir at top and Teflon stopcock at bottom end, SGA Scientific, Cat. No. JC-1506, or equivalent. The column is used for holding silica gel.

Cuvettes, 10-mm, conventional rectangular, with Teflon covers, Beckman Instrument Co., Cat. Nos. 580012 and 22636, respectively, or equivalent

Flasks, volumetric, 10-, 25-, 50-, 100- and 200-mL

Pipets, 0.5-, 1-, 2-, 5-, 10- and 25-mL

Regulator, nitrogen, two-stage, Matheson, Model 8-580, or equivalent

Spectrophotometer, Bausch & Lomb, Spectronic 70, Cat. No. 33-30-41, or equivalent

Stirring apparatus, magnetic, variable speed, with stirring bar, Sargent-Welch Scientific, Cat. No. S-76506, or equivalent

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 water.

Acetic acid, glacial

Chromic acid cleaning solution. Add a premeasured bottle of Chromerge, (Sargent-Welch Scientific, Cat. No. S19692) to 4 kg of concentrated sulfuric acid.

p-Dimethylaminobenzaldehyde, 99.9% minimum purity, Alpha Products, Cat. No. 12072, or equivalent

Florisil, 60-100 mesh, synthetic magnesium silicate, Aldrich Chemical Co., Cat. No. 22,075-2, or equivalent

n-Heptane, ASTM knock test-grade, Sargent-Welch Scientific, Cat. No. SC 12594, or equivalent. Purify by passing it through the silica gel column to remove pyrrolic nitrogen and olefins.

Hydrochloric acid, concentrated

Isopropyl alcohol

2-Methylindole, 98% minimum purity, Aldrich Chemical Co., Cat. No. M5, 140-7, or equivalent. Use only fresh 2-methylindole since it oxidizes on long standing, showing discoloration of crystals, thereby affecting the solubility of the material in toluene.

Stock Solution A (1000 μg of 2-methylindole nitrogen/mL). Weigh 0.9563 g $\pm$ 0.1 mg of 2-methylindole into a 100-mL volumetric flask. Add purified toluene that has been purged with nitrogen and dilute to volume.

Stock Solution B (10.0 μg of 2-methylindole nitrogen/mL). Pipet 2 mL of Stock Solution A into a 200-mL volumetric flask and dilute to volume with toluene.

Nitrogen, 99.99% minimum purity

Phosphoric acid, 85%

Silica gel, 100-200 mesh, chromatographic grade, Sargent-Welch Scientific, Cat. No. SC-14606, or equivalent

Sodium hydroxide, 0.1-M

Toluene, purify by passing it through the silica gel column

Pyrrole nitrogen reagent solution. Dissolve 400 ± 0.1 mg of *p*-dimethylaminobenzaldehyde in 100 mL of 85% phosphoric acid. This reagent should be colorless when used for analysis. The reagent discolors after being stored for long periods of time and new reagent solution must be prepared.

PROCEDURE

Preparation of Calibration Curve

Clean all glassware with chromic acid cleaning solution. The colored dye formed with the pyrrolic compounds adheres to the glass and is not removed by common solvents.

Pipet 0.5, 1.0 and 1.5 mL of Stock Solution B into three 10-mL volumetric flasks and dilute each to volume with nitrogen-purged toluene. The concentration of 2-methylindole nitrogen/100 mL in each will be 5-, 10- and 15- μ g, respectively. Analyze these 3 standards as described under *Sample Analysis*. Plot the absorbance vs. concentration on rectangular graph paper and construct a calibration curve. An example is shown in the attached figure.

Olefin Removal

Determine the density of the sample by ASTM Method D 4052 or other suitable technique.

All samples are separated by elution chromatography to remove any olefins. Prepare the chromatographic column by packing it to a depth of about 275 mm with florisil. Pipet 10 ± 0.1 mL of sample into the column and, after it is absorbed, add 50 ± 1 mL of the purified *n*-heptane. When all of the *n*-heptane has entered the florisil, add 75 ± 1 mL of purified toluene and, after the toluene is absorbed, add about 75 mL of isopropyl alcohol to displace the toluene. Adjust the flow rate to about 40 drops per minute with the Varibor stopcock.

Discard the first 50 mL eluted from the column (*n*-heptane containing any olefins the sample may have contained). Collect the next 50 mL eluted (toluene containing the pyrrolic compounds) in a 50-mL volumetric flask, stopper and shake well. Discard the remainder of the eluent from the column.

Sample Analysis

Pipet a 10-mL aliquot of the toluene solution from the 50-mL flask into a 100-mL volumetric flask to be used for the pyrrole determination. Then pipet a second 10-mL aliquot of the toluene solution into a second 100-mL volumetric flask to be used as a reference blank.

Pipet 5 mL of the pyrrole nitrogen reagent solution into the flask that will be used for the pyrrole determination. Pipet 5 mL of 85% phosphoric acid into the blank. Shake both flasks vigorously for 5 minutes. Add 50 ± 0.5 mL of glacial acetic acid to both flasks and shake 2 more minutes. Dilute to volume with acetic acid and shake to thoroughly mix.

Determine the absorbance of the colored solution at 540 nm using the blank as a reference solution. Use Teflon stoppered cells in the spectrophotometer, since the acid solution creeps. The absorbance should be measured within 10 minutes of diluting to volume as the blank tends to darken on standing.

If the absorbance is greater than 0.75, take smaller aliquots from the 50-mL volumetric flask for color development and blank. The total aliquot added to the 100-mL flask must be 10 mL. Therefore, add an appropriate amount of toluene to bring the aliquot volume to a total of 10 mL.

CALCULATIONS

Calculate the concentration of pyrrole nitrogen using the following equation:

$$\text{Pyrrole Nitrogen, mass - ppm} = \frac{50 A}{10 BC}$$

where:

A = 2-methylindole nitrogen obtained from calibration curve, $\mu\text{g}/100 \text{ mL}$

B = volume of sample taken from 50-mL volumetric flask for color development, mL

C = relative density of sample

10 = volume of original sample added to the chromatographic column, mL

50 = volume of toluene fraction from chromatographic column

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) was calculated for the concentration ranges listed in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Pyrrole Nitrogen Level, mass-ppm	esd, mass-ppm	Allowable Difference mass-ppm
1.5	0.14	0.5
58	2.5	9
150	6.7	25

ACCURACY

An estimate of the accuracy is $\pm 20\%$ of the actual value.

TIME FOR ANALYSIS

The elapsed time for one analysis is 3.75 hours. The labor requirement is 1.25 hours.

REFERENCE

ASTM Method D 4052, www.astm.org

Muhs, M.A., and Weiss, F.T., *Anal. Chem.*, **30**, 259 (1958)

SUGGESTED SUPPLIERS

Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201

Alfa Products, Thiokol/Dentron Div., 152 Andover St., Danvers, MA 01923

Bausch & Lomb Co., 820 Linden Ave., Rochester, NY 14602

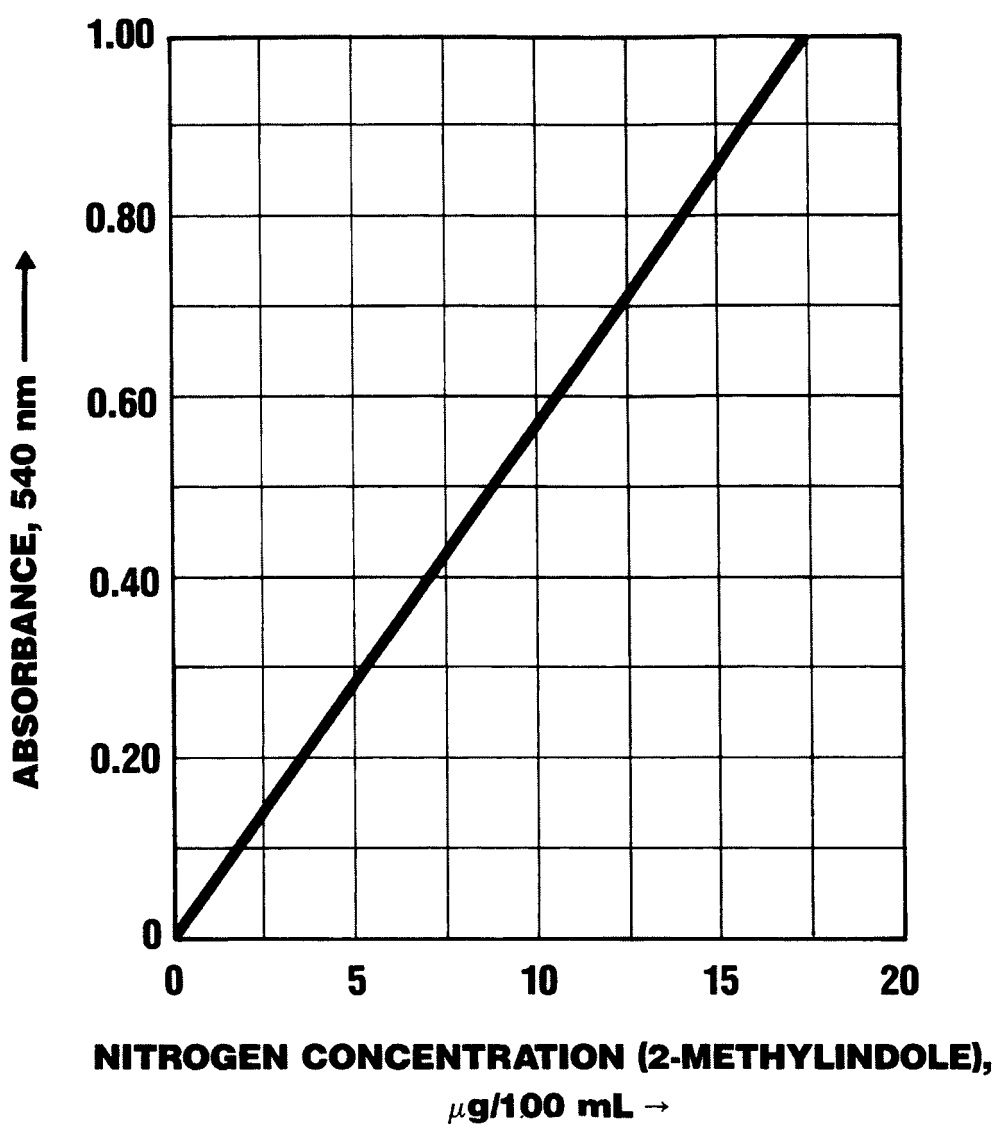
Beckman Instrument Co., 7360 N. Lincoln Ave., Lincolnwood, IL 60646

Kontes, P.O. Box 729, Vineland, NJ 08360

Matheson, P.O. Box 96, Joliet, IL 60434

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

SGA Scientific, Inc., 188 Industrial Dr., Elmhurst, IL 60126



Typical Pyrrole Nitrogen
Calibration Curve