

# BASIC NITROGEN IN LPG BY ION CHROMATOGRAPHY

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## UOP Method 939-96

### SCOPE

This method is for determining basic nitrogen in liquefied petroleum gas (LPG). The method determines basic nitrogen species that are extractable by aqueous acid, including ammonia and alkyl amines, which typically adsorb on the stainless steel surface of a LPG cylinder. This method is limited to ammonia, primary amines containing four or less carbon atoms, secondary amines containing eight or less carbon atoms and tertiary amines with nine or less carbon atoms. All linear aliphatic substituents of the amine analytes must contain less than five carbon atoms. Combined nitrogen can be determined using UOP Method 936. Nitriles are not detected by this method. Amides and/or ionic sodium, if present at a concentration of 10 mass-ppm or greater, will interfere with the quantitation of ammonia. Potassium ions in the acid extract can also interfere with the detection of methylamine and ethylamine. The procedure yields quantitative basic nitrogen results in the range of 0.1 mass-ppm to 3 mass-%.

### OUTLINE OF METHOD

Nitrogen compounds are extracted from an LPG sample using a solution of acetic acid in water according to the procedure specified in UOP Method 936. The sample extract is diluted and injected into an ion chromatograph equipped with a cation exchange column, conductivity suppressor device and conductivity detector. Analytes are separated by cation exchange. Analyte column retention is based primarily on ionic size and charge. The column effluent enters a conductivity suppressor device, where the background conductivity of the column effluent is reduced and the analytes are converted into more conductive forms. The analyte effluent from the conductivity suppressor device flows to a conductivity detector where solution conductance is continuously measured. The solution conductance is proportional to ionic concentration and the inherent mobility of each ion present in the detector flow cell.

An external standard method of quantitation is used. The best quantitation is achieved by matching absolute calibration blends to known sample analyte composition. If the analyte composition of a sample is unknown, representative response factors are determined by analyzing calibration blends that provide a representative mean detector response.

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## APPARATUS

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

In addition to the equipment listed below, all of the acid extraction related apparatus specified in UOP Method 936 is also required for this method.

*Balance*, readability 0.1-mg

*Cation MicroMembrane Suppressor*, conductivity suppressor device, Dionex CMMS-II, Dionex, Cat. No. 43021

*Cation MicroMembrane Suppressor installation kit*, includes one 4-L pressurizable regenerant reservoir, one 0 to 30 psi pressure regulator, and all tubing and fittings required to install the CMMS-II, Dionex, Cat. No. 38018

*Chromatographic column*, IonPac CS3 Analytical, dimensions 250-mm long by 4-mm ID, Dionex, Cat. No. 37024

*Cylinders*, graduated, borosilicate glass, 10-, 50-, 250-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 08-556-A, C, E, F and G, respectively

*Filter apparatus*, all glass filter, 47-mm diameter, 300-mL capacity, one-liter flask, Millipore, Cat. No. XX1504700

*Filters*, Nylon-66, 47-mm diameter, 0.45- $\mu$ m pore size, Rainin Instrument, Cat. No. 38-114

*Flask*, Erlenmeyer, 4-L Pyrex glass, Fisher Scientific, Cat. No. 10-040P

*Flask*, filtering, 4-L Pyrex glass with tubulation, Fisher Scientific, Cat. No. 10-180H

*Flasks*, volumetric, 2000-mL, with caps, Fisher Scientific, Cat. No. 10-210-5H

*Integrator*, electronic, for obtaining peak areas

*Ion chromatograph*, equipped with a Dionex APM-2 analytical pump, a Dionex Universal Sampler with auxiliary sampling pump, a Dionex CDM-2 conductivity detector and a Dionex Advanced Chromatography Module CHA-2 system controller

*Magnetic stir bar*, 0.5-inch diameter x 3-inch length, octagonal shape, covered with Teflon fluorocarbon resin, Fisher Scientific, Cat. No. 14-511-85

*Mobile Phase Reservoir*, 4-L pressurizable mobile phase reservoir and plastic tubing, Dionex, Cat. No. 38018

*Pasteur pipet*, 146-mm length disposable borosilicate glass, Fisher Scientific, Cat. No. 13-678-20A

*Recorder*, 10-mV full scale

*Regulator*, nitrogen, two-stage, Matheson Gas Products, Model 3122-580

*Reservoir*, 4-L, propylene bottle, Dionex, Cat. No. 39164

*Sample vials*, for dilution of acid extract, Kimble Scientific, Cat. No. 60957-1, with Quorpack black phenolic caps and polyseal liners, Cat. No. 02-883-5G, all available from Fisher Scientific

*Stir plate*, magnetic stirrer with 7- x 7-inch ceramic stirring surface, Fisher Scientific, Cat. No. 11-496-79

*Test tubes*, 16- x 100-mm borosilicate glass culture tubes with plain end, Fisher Scientific, Cat. No. 14-961-29

*Tubing*, vacuum, 1/4-inch ID (6.4-mm), Fisher Scientific, Cat. No. 14-173C

*Vacuum pump*, house vacuum can be substituted

*Valve*, needle, Supelco, Cat. No. 2-2116

*Vials*, 6 dram

*Water purification system*, Barnstead NANOpure II, 3 module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, Fisher Scientific

## REAGENTS AND MATERIALS

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 distilled and deionized water that is further treated with a Barnstead NANOpure II or other equivalent water purification system.

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

In addition to the reagents listed below, the reagents specified in UOP Method 936 are also required for this method.

*Acetic acid*, approximately 99.7% purity, Fisher Certified, Fisher Scientific, Cat. No. A38-212

*Acetic acid*, approximately 0.4-N. Prepare two liters by slowly adding 46 mL of concentrated acetic acid from a graduated cylinder to approximately 1500 mL of water in a 2000-mL volumetric flask. After the heat of dilution dissipates, dilute to volume with water and mix thoroughly by capping the flask and inverting at least 10 times.

*Ammonium chloride*, 99.998% pure, Aldrich Chemical, Cat. No. 25,413-4

*Dibutylamine*, 99+% pure, Aldrich Chemical, Cat. No. 24,000-1

*Diethylamine*, redistilled, 99.5% pure, Aldrich Chemical, Cat. No. 38,645-6

*Dimethylamine hydrochloride*, 99% pure, Aldrich Chemical, Cat. No. 12,636-5

*Dipropylamine*, 99+% pure, Aldrich Chemical, Cat. No. 24,008-7

*Hydrochloric acid*, Fisher Reagent ACS HCl, Fisher Scientific, Cat. No. A144-500

*Hydrochloric acid*, approximately 18-mM. Prepare four liters by slowly adding 6 mL of concentrated hydrochloric acid from a graduated cylinder to 4 liters of water contained in a 4-L filtering flask. Mix solution thoroughly with a magnetic stir bar on a stir plate. Filter one liter at a time through the filter apparatus, under vacuum. Combine the filtrate in the 4-L mobile phase reservoir.

*Nitrogen*, zero gas, total hydrocarbons less than 0.5 ppm as methane

*Tetrabutylammonium hydroxide*, 40 mass-% solution in water, Aldrich Chemical, Cat. No. 17,878-0

*Tetrabutylammonium hydroxide*, approximately 100-mM. Prepare four liters by slowly adding 275 mL of 40 mass-% solution of tetrabutylammonium hydroxide (in water) to 3725 mL of water in a 4-liter Erlenmeyer flask. Filter one liter at a time through the Millipore vacuum filter apparatus. Combine filtrate into 4-liter regenerant reservoir.

*Water*, ionically pure, 18 megohm-cm organic-free, prepared with NANOpure II water purification system

## PROCEDURE

### Sample Extraction

1. Obtain an acetic acid extract of the sample according to the procedure specified in UOP Method 936.
2. Decant a portion of the acid extract from the volumetric flask into a 6-dram sample vial and analyze the acid extract by ion chromatography (see *Sample Analysis*).
  - A single extraction will provide enough extract for determining both combined nitrogen (UOP Method 936) and basic nitrogen (this method).

### Chromatographic Technique

1. Assemble and test all chromatographic system components (see Fig. 1) per the manufacturer's specifications.
2. Install the analytical column and suppressor device.
3. Fill the mobile phase reservoir with four liters of 18-mM HCl, and pump mobile phase through the chromatographic system at a flow rate of 1.0 mL/minute.

4. Fill the regenerant reservoir with 100-mM tetrabutylammonium hydroxide, and establish a flow rate of approximately 3 to 4 mL/min of regenerant solution through the cation micromembrane suppressor device. Flow is accomplished by applying 5 to 10 psig pressure of nitrogen gas to the regenerant reservoir.
5. Set the conductivity detector sensitivity at one micro-Siemen ( $\mu\text{S}$ ), full scale. The detector baseline should level off at a steady flat baseline within one hour.
  - When the system is fully equilibrated, the background conductivity should be between 3 and 10  $\mu\text{S}$ .

### Sample Analysis

1. Weigh approximately 2 grams of LPG-acetic acid extract into a 6-dram vial and record the mass to the nearest 0.1 mg.
2. Add 8 grams of water to sample and record the total diluted sample mass (sample plus water) to the nearest 0.1 mg. Cap the solution and mix thoroughly by inverting 10 times.
  - This dilution is generally sufficient to bring the sample into the calibration range of the procedure. However, if further dilution is required, use 0.04-N acetic acid as the diluent to maintain the matrix match, and modify Eq. 4 to reflect the additional dilution.
3. Inject 50  $\mu\text{L}$  of the diluted sample solution into the ion chromatograph and immediately start the recorder and integrator. Collect data on the integrator until the last analyte has fully eluted.
  - If the sample content is unknown, collect data for a maximum of 50 minutes.
4. Identify the components of interest by comparing the chromatogram obtained with chromatograms of standard pures that have been prepared and analyzed according to *Calibration*. When calibrating with Representative Calibration Standard Blends (*Calibration Procedure 2*), determine the following Species Group peak areas: 1) ammonium site, 2) sum of peak areas beyond ammonium site through dimethylamine site, 3) sum of peak areas beyond dimethylamine site through diethylamine site, 4) sum of peak areas beyond diethylamine site through dipropylamine site and 5) sum of any remaining peak areas.

### Calibration

Calibration factors are required, as detector response varies for each analyte. Detector response is measured in micro-Siemens ( $\mu\text{S}$ ) units of conductivity. It is proportional to the ionic concentration and the inherent mobility of each analyte ion type present when measured using the conductivity detector, flow cell electrode. Calibration of the method is performed in one of two ways, dependent upon whether or not the approximate analyte composition of the sample is known.

#### Calibration Procedure 1

Use this procedure when the approximate analyte composition is known and the analytes of interest are chromatographically resolved.

1. Prepare a Stock Calibration Blend by weighing in one sample vial, 0.1 g of each individual analyte standard pure, and record the mass of each analyte (A) to the nearest 0.1 mg.

2. Dissolve the standard pures in approximately 10 g of 0.4-*N* acetic acid, recording the total mass (**B**) of this Stock Calibration Blend to the nearest 0.1 mg. Cap and mix the Stock Calibration Blend thoroughly, to ensure that all components are brought into solution.
3. Determine the mass-ppm nitrogen for each analyte in the Stock Calibration Blend, to three significant figures, using Eq. 1.

$$E = \frac{10^6 AD}{100B} \quad (1)$$

where:

**A** = mass of each analyte, g

**B** = total mass of Stock Calibration Blend, g

**D** = % nitrogen in each analyte (see *NOTE*)

**E** = mass-ppm nitrogen for each analyte in the Stock Calibration Blend

**100** = factor to convert % to mass fraction

**10<sup>6</sup>** = factor to convert g to mass-ppm (μg)

4. Perform serial dilutions by mass (sample diluent: 0.4-*N* acetic acid) of the Stock Calibration Blend, prepared in Step 2, to prepare an Absolute Calibration Blend Standard with known analyte basic nitrogen concentrations ranging between 0.5 to 1.5 mass-ppm. Mix each serial dilution thoroughly.
  - For best precision, serial dilutions must be performed at a dilution ratio of 1:100 or less.
5. Determine the basic nitrogen concentration for each analyte in each serial dilution, to three significant figures, using Eq. 2. The final serial dilution standard is named the Absolute Calibration Blend Standard.

$$F = \frac{EG}{H} \quad (2)$$

where:

**E** = mass-ppm nitrogen for each analyte in the Stock Calibration Blend

**F** = mass-ppm nitrogen for each analyte in the Absolute Calibration Blend Standard (*Calibration Procedure 1*) or in the Representative Calibration Blend Standard (*Calibration Procedure 2*)

**G** = mass of Stock Calibration Blend used, g

**H** = total mass of Absolute Calibration Blend Standard (*Calibration Procedure 1*) or Representative Calibration Blend Standard (*Calibration Procedure 2*), g

6. Inject 50 μL of Absolute Calibration Blend Standard into the ion chromatograph, that is operating according to the procedure in *Chromatographic Technique*, and immediately start the integrator and chart recorder. Collect data on the integrator until the last analyte has eluted.

7. Identify the analytes on the resulting chromatogram and determine their individual peak areas.
  - Analytes typically elute in the order of their ionic radius. For example, tertiary amines will elute before secondary amines of the same carbon number. Watch for interfering sodium and potassium peaks that may be detected. Correct identification of peaks must be confirmed by preparing individual analyte standards and analyzing each separately.
8. Determine the analyte response factor, to three significant figures, for each compound in the Absolute Calibration Blend Standard using Eq. 3.

$$J = \frac{F}{K} \quad (3)$$

where:

- F** = previously defined, Eq. 2
- J** = response factor for each analyte
- K** = peak area of analyte, from chromatogram

9. Analyze the Absolute Calibration Blend Standard in duplicate each day a sample analysis is performed.
10. Average the Response Factors obtained from the duplicate chromatograms of the Absolute Calibration Blend to determine the Absolute Response Factors for each analyte.

## Calibration Procedure 2

Use this procedure when the composition of the sample is unknown or if individual analytes are unresolved. In this procedure, a Representative Calibration Blend is prepared that is used to calculate Representative Calibration Response Factors that approximate those typically obtained from other analytes that elute in the same region of the chromatogram.

1. Prepare a Stock Calibration Blend by weighing in one sample vial, 0.1 g each, ammonium chloride, dimethylamine hydrochloride, diethylamine, dipropylamine and dibutylamine; and record the mass of each standard pure (A, Eq. 1) to the nearest 0.1 mg.
2. Dissolve the standard pure in approximately 10 g of 0.4-N acetic acid. Record the total mass (B, Eq. 1) of this Stock Calibration Blend to the nearest 0.1 mg. Mix the Stock Calibration Blend thoroughly to ensure that all components are brought into solution.
3. Determine the mass-ppm nitrogen for each analyte in the Stock Calibration Blend, to three significant figures, using Eq. 1.
4. Perform serial dilutions by mass (sample diluent: 0.4-N acetic acid) of the Stock Calibration Blend prepared in Step 2 to prepare a Representative Calibration Blend Standard with known analyte basic nitrogen concentrations ranging between 0.5 to 1.5 mass-ppm. Mix each serial dilution thoroughly.
  - For best precision, serial dilutions must be performed at a dilution ratio of 1:100 or less.
5. Determine the final nitrogen concentration for each analyte in the Representative Calibration Blend Standard, to three significant figures, using Eq. 2.

6. Inject 50  $\mu\text{L}$  of the Representative Calibration Blend Standard into the ion chromatograph, that is operating according to the procedure in *Chromatographic Technique*, and immediately start the integrator and chart recorder. Collect data on the integrator until the di-*n*-butylamine peak has fully eluted.
7. Identify and integrate the peak areas for each standard cation in the Representative Calibration Blend by comparing the resulting chromatogram with a typical Representative Calibration Blend, shown in Fig. 2.
8. Determine the response factors to three significant figures for each compound in the Representative Calibration Blend Standard using Eq. 3.
9. Analyze the Representative Calibration Blend Standard in duplicate each day that a sample analysis is performed.
10. Average the response factors obtained from the duplicate chromatograms of the Representative Calibration Blend to determine the Representative Response Factors. Use the ammonium ion response factor for Species Group 1, the dimethylamine response factor for Species Group 2, the diethylamine response factor for Species Group 3, the dipropylamine response factor for Species Group 4, and the di-*n*-butylamine response factor for Species Group 5. See Step 4 of *Sample Analysis* for definition of Species Groups.

## CALCULATIONS

Calculate the concentration of each individual basic nitrogen species (*Calibration Procedure 1*) or Species Group (*Calibration Procedure 2*) in the acetic acid extract, rounding the result to two significant figures at or above one mass-ppm, and to one significant figure below one mass-ppm, using Eq. 4.

$$N = \frac{JM W}{X} \quad (4)$$

where:

**J** = Absolute Response Factor (*Calibration Procedure 1*) or Representative Response Factor (*Calibration Procedure 2*) for individual basic nitrogen species or Species Group, previously defined, Eq. 3

**M** = peak area of individual basic nitrogen species or Species Group from chromatogram

**N** = mass-ppm nitrogen from individual basic nitrogen species or Species Group

**W** = mass of acetic acid extract (*Sample Analysis*, Step 1), g

**X** = total diluted sample mass (*Sample Analysis*, Step 2), g

Calculate the total concentration of basic nitrogen in the acetic acid extract (T) by summing the results above for each individual basic nitrogen species or Species Group in the acetic acid extract, rounding the result to two significant figures at or above one mass-ppm, and to one significant figure below one mass-ppm.

Calculate the concentration of the basic nitrogen in the LPG sample in mass-ppm, as follows, rounding the result to two significant figures at or above one mass-ppm, and to one significant figure below one mass-ppm, using Eq. 5.

$$P = \frac{TR}{S} \quad (5)$$

where:

- P** = concentration of basic nitrogen in the LPG sample, mass-ppm
- R** = mass of the acetic acid added to the LPG cylinder, g
- S** = mass of the LPG extracted (from UOP Method 936), g
- T** = total concentration of basic nitrogen in the acetic acid extract, mass-ppm

Concentrations at or above 10,000 mass-ppm can be converted to mass-% by dividing the mass-ppm value by 10,000.

## NOTE

Calculate % nitrogen in any single nitrogen containing compound to three significant figures as follows:

$$D = \frac{1401}{Y} \quad (6)$$

where:

- D** = previously defined, Eq. 1
- Y** = formula atomic mass of compound
- 1401** = atomic mass of nitrogen times 100 to convert to %

## PRECISION

The following precision data only reflect the variability inherent in the ion chromatographic analysis. The precision analysis was performed on synthetic blends prepared in 2-*N* acetic acid, eliminating any variability expected by the acid extraction procedure.

### Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in the Table. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences listed in the Table at the concentrations listed (95% probability).

### Reproducibility

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

**Table**  
**Repeatability**

| <b><u>Component</u></b>            | <b><u>Concentration,<br/>mass-ppm, N</u></b> | <b><u>Within-Lab esd,<br/>mass-ppm, N</u></b> | <b><u>Allowable<br/>Difference,<br/>mass-ppm, N</u></b> |
|------------------------------------|----------------------------------------------|-----------------------------------------------|---------------------------------------------------------|
| <b>Ammonium Ion</b>                | <b>480</b>                                   | <b>8.4</b>                                    | <b>28</b>                                               |
|                                    | <b>4.9</b>                                   | <b>0.41</b>                                   | <b>1.4</b>                                              |
| <b>Dimethylamine</b>               | <b>380</b>                                   | <b>5.8</b>                                    | <b>19</b>                                               |
|                                    | <b>3.8</b>                                   | <b>0.16</b>                                   | <b>0.5</b>                                              |
| <b>Diethylamine</b>                | <b>460</b>                                   | <b>8.1</b>                                    | <b>27</b>                                               |
|                                    | <b>4.5</b>                                   | <b>0.21</b>                                   | <b>0.7</b>                                              |
| <b>Dipropylamine</b>               | <b>370</b>                                   | <b>8.4</b>                                    | <b>28</b>                                               |
|                                    | <b>3.5</b>                                   | <b>0.25</b>                                   | <b>0.8</b>                                              |
| <b>Di-<i>n</i>-<br/>butylamine</b> | <b>250</b>                                   | <b>8.3</b>                                    | <b>28</b>                                               |
|                                    | <b>2.6</b>                                   | <b>0.18</b>                                   | <b>0.6</b>                                              |

### TIME FOR ANALYSIS

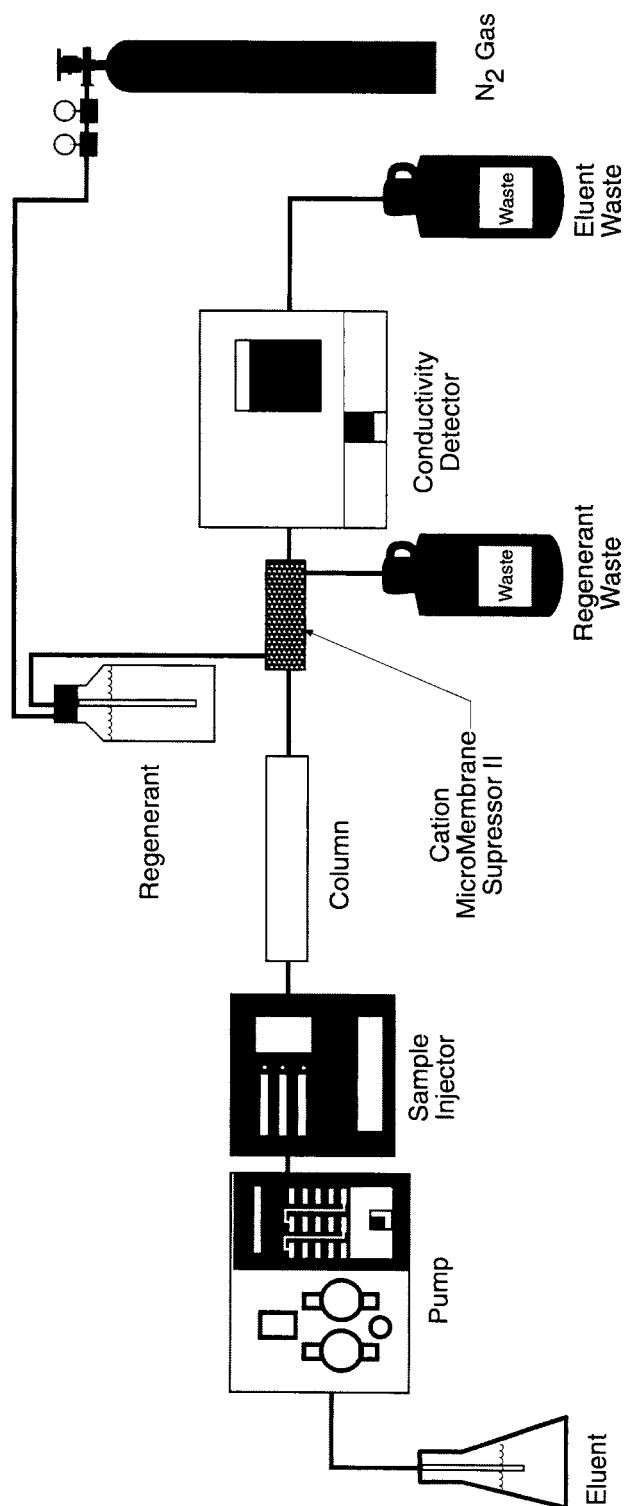
The labor required for the analysis, including the extraction procedure according to UOP Method 936, is 3 hours and the elapsed time is 3.5 hours.

### REFERENCE

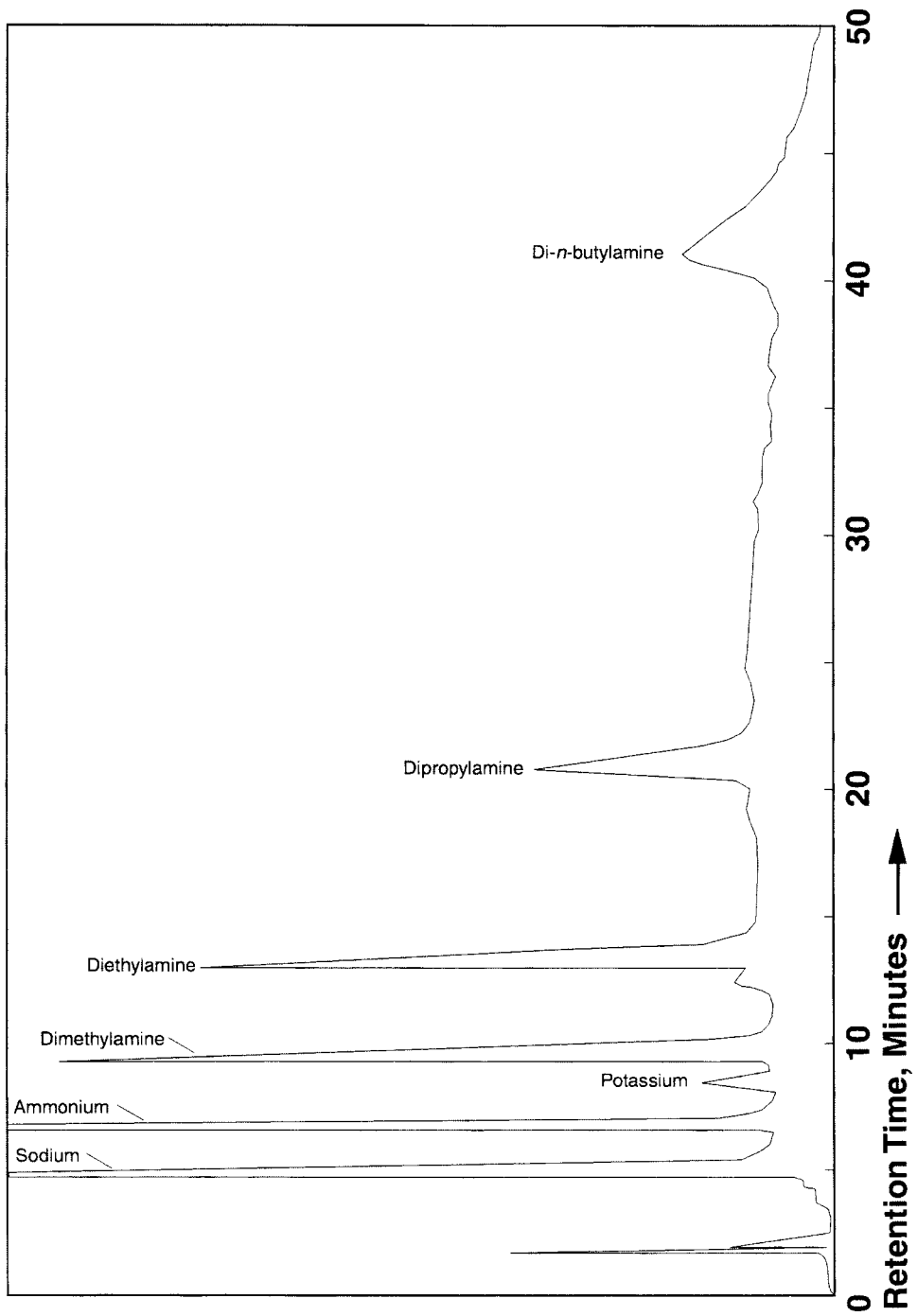
UOP Method 936, "Combined Nitrogen in LPG by Chemiluminescence"

### SUGGESTED SUPPLIERS

Aldrich Chemical Co., 1001 W. St. Paul Ave., Milwaukee, WI 53233, (414-273-3850)  
 Dionex Corporation, 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088-3603 (408-737-0700)  
 Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)  
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)  
 Millipore Corp., Waters Chromatography Division, 34 Maple Street, Milford, MA 01757 (508-478-2000)  
 Rainin Instrument Co., 1715 64th St., Emeryville, CA 94608-1097 (415-654-9142)  
 Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048 (814-359-3441)



**Figure 1**  
Chromatographic System Assembly



**Figure 2**  
Typical Chromatogram