



## Combined Nitrogen in LPG including Propylene by Chemiluminescence

---

### UOP Method 936-20

#### Scope

This method is for determining combined nitrogen in liquefied petroleum gas (LPG), including propylene. The method determines all nitrogen compounds that are extractable by aqueous acid, including ammonia, amines, nitriles and amides. The method is particularly useful for LPG samples containing nitrogen species, such as ammonia and amines, which can readily adsorb on stainless steel surfaces in contact with the LPG. The procedure yields quantitative results in the range of 0.2 mass-ppm (mg/kg) to 3 mass%.

The method is also used as a preparation step for the analysis of basic nitrogen in LPG by UOP Method 939, "Basic Nitrogen in LPG by Ion Chromatography."

#### References

- ASTM Method D4629, "Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection," [www.astm.org](http://www.astm.org)
- UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C<sub>2</sub>-C<sub>4</sub> Fractions," [www.astm.org](http://www.astm.org)
- UOP Method 939, "Basic Nitrogen in LPG by Ion Chromatography," [www.astm.org](http://www.astm.org)
- UOP Method 981 "Trace Nitrogen in Liquid Hydrocarbons by Oxidative Combustion with Chemiluminescence Detection," [www.astm.org](http://www.astm.org)
- UOP Method 999, "Precision Statements in UOP Methods," [www.astm.org](http://www.astm.org)

#### Outline of Method

Nitrogen compounds are quantitatively extracted from an LPG, including propylene sample using a solution of 2N acetic acid in water. A measured mass of LPG is transferred to a cleaned, silica coated sample extraction cylinder. A known amount of acid solution is added to a second cylinder, the two vessels are connected and the acid solution is transferred under helium pressure into the sample extraction cylinder. The nitrogen components are extracted into the acid solution by mixing the liquids for several minutes. The LPG and acid extract are allowed to separate. The acid extract is withdrawn and analyzed for total nitrogen by chemiluminescence, utilizing ASTM Method D4629, "Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection".

**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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).**

© COPYRIGHT 1995, 2016, 2020 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, [www.astm.org](http://www.astm.org), or by contacting Customer Service at [service@astm.org](mailto:service@astm.org), 610.832.9555 FAX, or 610.832.9585 PHONE.

This is a preview. [Click here to purchase the full publication.](#)

## Apparatus

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

*Adapter*, male, 2 required, for charging the acetic acid cylinder, Swagelok, Cat. No. SS-4-TA-1-4 (see also *Connector*)

*Balance*, readability 0.001 g

*Balance*, readability 0.1 g, capacity 4000 g

*Beaker*, polypropylene, 100-mL, Fisher Scientific, Cat. No. 02-591-27

*Clamps*, for ring stand and sample cylinders, several required, with holders and cast-iron ring, Fisher Scientific, Cat. Nos. 05-769-8Q, 05-754 and 14-050CQ, respectively

*Connector*, stainless steel, used to connect the 300-mL and the 1000-mL cylinders vertically together and consisting of a male connector, Swagelok, Cat. No. SS-400-1-4 joined together with one male adapter, Swagelok, Cat. No. SS-4-TA-1-4.

*Cylinder*, collection, for initial sample collection from process stream, stainless steel, Sulfinert™ coated, 1000-mL, with valve and valve with outage tube, Restek, Cat. Nos. 24134, 21400, and 21402-038 respectively.

*Cylinder*, extraction, type 304 stainless steel, high pressure, 12,400 kPa gauge (1800 psi) maximum working pressure, 1000-mL capacity, Swagelok, Cat. Nos. 304L-HDF4-1000. Equip the cylinders with two stainless steel valves each, Swagelok, Cat. No. SS-16DKM4-F4, and two pipe-plugs each, Cajon, quarter-inch P-male-NPT, Swagelok, Cat. No. SS-4-P.

*Cylinder*, acid injection, type 304 stainless steel, high pressure, 12,400 kPa gauge (1800 psi) maximum working pressure, 300-mL capacity, Swagelok, Cat. Nos. 304L-HDF4-300. Equip the cylinders with two stainless steel valves each, Swagelok, Cat. No. SS-16DKM4-F4, and two pipe-plugs each, Cajon, quarter-inch P-male-NPT, Swagelok, Cat. No. SS-4-P.

*Cylinders*, graduated, borosilicate glass, 50-, 100- and 250-mL, Fisher Scientific, Cat. Nos. 08-556C, D and E, respectively

*Extractor* (optional), special construction, see *Appendix*

*Flask*, Erlenmeyer, 50-mL, Fisher Scientific, Cat. No. FB-500-50

*Flasks*, volumetric, 100-, 200-, 1000-, and 2000-mL, with caps, Fisher Scientific, Cat. Nos. 10-210-5C, -5D, -5G, and -5H, respectively. Several of each are required, see *Reagents and Materials and Procedure*.

*Gage*, pressure, 0-20,000 kPa gage (0-3000 psig), 2-inch diameter, ¼"-inch MNPT, used for testing the pressure of an unknown LPG sample gas cylinder, Matheson Gas Products, Model 63-2233

Hood, laboratory

*Nitrogen Chemiluminescence Analyzer*, with attached furnace, autosampler, vacuum pump, controls and computer. This method was developed and validated using the Mitsubishi analyzer NSX-2100V, with ND-210 Nitrogen Detector and STC-210 Sample Temperature Controller. The procedure for analysis may be different for other instruments and all other instruments need to be validated before using for this method.

The Mitsubishi analyzer must be equipped with the following accessories:

*Autosampler*, Mitsubishi Model ASC-250L, COSA Xentaur Corporation

*Autosampler syringes*, gas tight, 50- $\mu$ L, Mitsubishi, Cat. No. MC18525, COSA Xentaur Corporation

*Autosampler vials*, rinse, Mitsubishi Cat. No. TX3LSW, COSA Xentaur Corporation

*Cyclone trap*, Cat. No. MC 1914, COSA Xentaur Corporation

*Membrane drier*, Perma Pure MD-110-24F-4 or Mitsubishi Tube Dryer, Cat. No. TN6RPC, COSA Xentaur Corporation (see *Note 4*)

*Sample Temperature Controller*, Mitsubishi Model STC-210, COSA Xentaur Corporation

*Vacuum pump*, Vacuubrand MD4CNT and Ulvac GLS-050 vacuum pumps meet this requirement; other vacuum pumps must be evaluated before use, COSA Xentaur Corporation (see *Note 3*)

*Oven*, drying, capable of maintaining 105°C

*Pipet*, Mohr, 1-, 5- and 25-mL, Fisher Scientific, Cat. Nos. 13-665-F, -K and -N, respectively

*Pipet*, volumetric, Class A, 50-mL, 20-mL, 10- mL, 4-mL Fisher Scientific, Cat. No. 13-650-2S, 13-650-2N, 13-650-2L, 13-650-2E, respectively.

*Pipet filler*, Fisher Scientific, Cat. No. 13-681-102A

*Refrigerator*, laboratory

*Regulators*, inert gas, two-stage, Matheson Tri-Gas, Models 3810A-580 (used for the nitrogen analyzer) and 3030-580 (used for acetic acid transfer between cylinders)

*Regulator*, oxygen, two-stage, high purity, Matheson Tri-Gas, Model 3810A-540, cleaned for oxygen service by the supplier, used with Nitrogen Analyzer

*Ring stand*, with rectangular base, 170- x 280-mm base with 910-mm rod, Fisher Scientific, Cat. No. 14670D

*Tubing*, polyethylene, "Poly-Flo", for charging acetic acid cylinder, 6.4-mm (0.25-inch) OD, Lesman Instruments, Cat. No. 1FRPE4

*Tubing*, Tygon, R3603, for charging acetic acid cylinder 6.4-mm (1/4") OD, Fisher Scientific, Cat. No. 14-169-3C

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

*Vacuum pump*, aspirator, Nalgene, Fisher Scientific, Cat. No. 09-960-2, or house vacuum

*Valve*, check, 20,700 kPa gauge (3000 psig), Matheson Tri-Gas, Model 400V

## 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 water.

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

*Acetic acid*, approximately 2N. Prepare two liters by slowly adding 232 mL of glacial 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.

*Acetone*, certified, Honeywell Burdick & Jackson, Cat. No. AH010-4PC

*Helium*, ultra-high purity, 99.999%, local supply

*Ice*, water

*Isooctane*, certified, Honeywell Burdick & Jackson, Cat. No. 362-1L

*Isooctane-acetone*, 9 to 1, Measure 900 mL of isooctane into a 1000-mL volumetric flask and fill with acetone to the mark. Cap and mix thoroughly by inverting at least ten times.

*Methanol*, certified, Honeywell Burdick & Jackson, Cat. No. AH230-4PC

*Methanol-acetone*, 1 to 1. Measure 500 mL of acetone with a graduated cylinder into a 1000-mL volumetric flask and fill to the mark with methanol. Cap the flask and mix by inverting at least ten times.

*Nitrogen*, high purity, 99.99%, local supply

*Oxygen*, 99.98%, ultra-high purity, local supply

*pH paper*, CF strips, 0 to 14 pH units, Fisher Scientific, Cat. No. 09-876-17

*Pyridine*, 99.9%, Millipore Sigma-Aldrich, Cat. No. 27,040-7

*Sulfuric acid*, reagent grade, ACS, 95.5%, Fisher Scientific, Cat. No. A300-212

*Sulfuric acid*, 10%. Prepare one liter by slowly adding 100 mL of concentrated sulfuric acid from a graduated cylinder to approximately 800 mL of water in a 1000-mL volumetric flask while cooling in ice water. After the heat of dilution dissipates, dilute to volume with water. Mix thoroughly by capping the flask and inverting at least 10 times.

*Teflon-tape*, PTFE, roll, 12.5-mm (0.5-inch), Fisher Scientific, Cat. No. 14-831-300A

*Vials*, sample, for extracted sample, VWR International, Cat. No. 16087-068,

*Water*, deionized or distilled

## Procedure

The analyst is expected to be familiar with general laboratory techniques, nitrogen analysis, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

### Cylinder Preparation

1. Clean the interior surfaces of the 1000-mL extraction cylinder and valves as follows: Rinse the cylinder with a 100-mL portion of the isooctane-acetone mixture and follow with a 100-mL rinse of the methanol-acetone mixture until the rinse is colorless. Rinse with one 100-mL portion of the 10% sulfuric acid solution. Rinse with water until the rinse is neutral to the pH paper. Appropriately discard the washes.
  - If any of the rinses are colored or dirty upon draining, repeat that rinse until the drained material is clear.
2. Remove the water by rinsing the 1000-mL cylinder and valves with two successive 100-mL portions of the methanol-acetone and discard the rinses.
  - Rinsing with the solvents, in the order given, removes adsorbed nitrogen compounds. Any convenient procedure that assures contact of the wetted valve and cylinder surfaces with solvents may be used. One workable procedure is outlined in *Note 1*.
3. Flush the cylinder with nitrogen to remove the remaining solvents and then dry in the drying oven for at least one hour at 105°C.