



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
- UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₂-C₄ Fractions," www.astm.org
- UOP Method 939, "Basic Nitrogen in LPG by Ion Chromatography," www.astm.org
- UOP Method 981 "Trace Nitrogen in Liquid Hydrocarbons by Oxidative Combustion with Chemiluminescence Detection," www.astm.org
- UOP Method 999, "Precision Statements in UOP Methods," 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 The acid extract is withdrawn and analyzed for total nitrogen by chemiluminescence, utilizing ASTM Method D4629, "Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative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".

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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.

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- μ 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.

4. Allow the cylinder to cool to room temperature. Tare the cylinder and record the tare mass to the nearest 0.1 g.
5. Clean the 300-mL cylinder in the same manner as directed for the 1000-mL cylinder except that the 300-mL cylinder does not need to be weighed.

Sample Collection

Sample must be initially collected, in accordance with UOP Method 516, “Sampling of Gasolines, Distillate Fuels and C₂-C₄ Fractions,” in a Sulfinert™ coated cylinder to prevent loss of nitrogen compounds to the cylinder walls. Transfer sufficient LPG from the collection cylinder into the 1000-mL extraction cylinder to fill it approximately half full with liquid. Weigh the cylinder and determine the mass of the LPG transferred by subtracting the tare mass from *Cylinder Preparation*, Step 4. The mass of the LPG will be approximately 250 g but should never exceed 300 g when the cylinder is half full with liquid. In no case should a cylinder be filled completely with liquid because the hydrostatic pressure in the cylinder will exceed the rated pressure of the cylinder, if the liquid expands after filling.

- The LPG sample size should be adjusted at the source, based on the nitrogen concentration. A sample size of 250 g was selected to analyze samples containing 300 mass-ppm N or less. If the nitrogen content is greater than 300 mass-ppm, the LPG sample size must be adjusted as shown in Table 1. Higher nitrogen concentrations also require the use of more extractant, as described later in the method.
 - The ratio of extractant to LPG must never be less than the values shown in Table 1. If larger volumes of extractant are injected accidentally, the analysis is still accurate.
1. Reweigh the cylinder and record the LPG sample mass, to the nearest 0.1 g, on a tag to be attached to the cylinder as the final cylinder mass minus the tare mass from *Cylinder Preparation*, Step 4.
 2. Measure and record the pressure in the half-filled 1000-mL cylinder using the pressure gauge (0-20,000 kPa (3000 psi)) and indicate the pressure on a tag to be attached to the cylinder.
 - The pressure of the sample cylinder should not exceed 3500 kPa (500 psi). If the pressure is greater than 3500 kPa (500 psi), the sample is likely not pure LPG or the cylinder is liquid full and should not be analyzed. Consult with the plant engineer or originator of the sample.

Table 1
Quantities of LPG and Extractant to Use
for Various Nitrogen Concentrations

<u>Mass of LPG, g</u>	<u>N, mass-ppm</u>	<u>Extractant, g</u>
250	0.1 to 300	50 g
50	300 to 3,000	100 g
25	3,000 to 30,000	250 g

Extraction

1. Mount the 300-mL acid injection cylinder vertically on the ring stand with the clamps and attach a vacuum hose to a male adapter at the open valve at the top of the cylinder but keep the bottom valve closed. Apply vacuum to the cylinder at the open top valve.
2. Note the appropriate volume of 2N acetic acid solution to be added to the 300-mL acid injection cylinder based on the nitrogen content of the LPG and Table 1 and measure the acid into an appropriately sized graduated cylinder.
3. Use a piece of Tygon™ tubing to connect the polyethylene “Poly-Flo” tubing to the male adapter at the bottom valve, so that the polyethylene tubing is submerged at the bottom of the graduated cylinder containing the appropriate volume of acetic acid and slowly open the bottom valve to

withdraw the acetic acid with vacuum into the 300-mL cylinder. Next, close first the lower, then the upper valve and disconnect the vacuum hose.

- Take care to control the rate of withdrawal of the acetic acid into the evacuated 300-mL cylinder so that none of the acid is aspirated out of the opened top valve.
4. Assemble the cylinders attached to the helium tank as shown in the figure below and pressurize the 300-mL cylinder with helium, until the pressure in the 300-mL cylinder exceeds the pressure in the 1000-mL cylinder by approximately 350 kPa (50 psi).
 - The pressure in the LPG sample cylinder was recorded in *Sample Collection*, Step 3. If no record is present, the pressure must be measured by attaching the cylinder to the ring stand in a vertical position, attaching a gauge to the top of the cylinder, and measuring the pressure. For this method, the pressure should not exceed 3500 kPa (500 psi) but in no case should the pressure in the cylinder exceed the safe operating pressure of the vessel, typically 12000 kPa (1800 psi).
 - The two cylinders are attached vertically to a ring stand, positioned in a hood, using the clamps. The bottom valve of the top cylinder is attached to the top valve of the lower LPG sample cylinder with the straight stainless-steel connector. Any substitute connector tube should be no more than 51 mm (2 inches) in length and the shortest possible section of straight, stainless steel tubing and fittings should be used to minimize hold up of the acetic acid. Ensure that all fittings are leak free at the pressure in the 300-mL cylinder. The cylinder assembly is shown in the Figure (see Step 6), without indicating the location of the ring stand and clamps.
 5. Open slowly the bottom valve of the top (300-mL) cylinder.
 6. Open the top valve of the 1000-mL extraction cylinder.
 - The sound of the 2N acetic acid solution being forced into the LPG sample should be audible.

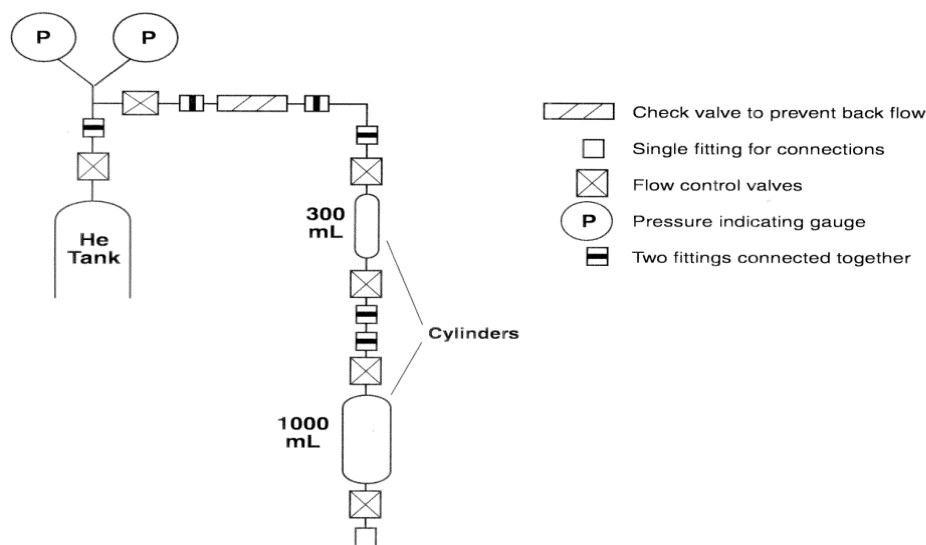


Figure
Cylinder Assembly

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7. Close the top valve of the extraction cylinder and then close the helium cylinder valves.
 - Development of heat of the extraction cylinder is not expected. If, however, the cylinder should warm up due to caustic or other impurities in the sample, immediately stop the analysis and consult with the plant engineers or originators of the sample.
8. Disconnect the helium tubing connection at the top valve of the 300-mL cylinder slowly to relieve pressure. Disconnect the 300-mL cylinder from the extraction cylinder. Remove the extraction cylinder from the ring stand and reweigh the extraction cylinder to determine the mass of the acid added (± 0.1 g).

- The 1000-mL extraction cylinder is plugged at both ends after weighing, using the stainless-steel plugs.
9. Mix the LPG and acid mixture thoroughly by inverting and rotating the cylinder for at least 30 minutes. Use a rocking, rotating motion to thoroughly extract the nitrogen compounds or use a mechanical extractor (See *Note 2*).
 - Nitrogen species can adsorb on the walls of the cylinder; therefore, the acetic acid solution must contact the entire interior surface.
 10. Reattach the 1000-mL extraction sample cylinder to the ring stand in a vertical position and allow the contents to separate.
 - Separation can occur in 10 minutes. However, the individual LPG will affect the length of time required for separation and some experimentation may be needed to establish a suitable settling time. Longer periods are required for LPG containing ethers, alcohols or other non-paraffinic impurities.
 11. Drain the acid extract from the extraction cylinder by partially opening the bottom valve of the extraction cylinder into a clean, dry Erlenmeyer flask placed under the valve.
 - The sample pressure will force the separated acid extract out of the cylinder. If the valve is opened too far, the acid solution may spatter; use appropriate personal protection equipment. Usually the acetic acid drains as a milky acid-gas emulsion, which separates easily in a few minutes.
 - Not all the acid needs to be drained, just enough for subsequent analysis. It is preferred to leave some acid in the extraction cylinder, as splashing may occur when all the acid is drained and LPG begins to come out.
 12. Decant a portion of the acid extract from the Erlenmeyer flask into a 15-mL sample vial and analyze the acid extract on the chemiluminescence nitrogen analyzer as directed in ASTM Method D 4629 and according to the following procedure.

Preparation of Standard Solutions

Pyridine stock solution, 1000 µgN/mL

Weigh 1.129 ± 0.001 g of pyridine to the nearest 0.001g into a clean, dry 200 mL volumetric flask. Dilute to the mark with 2 N acetic acid solution. Cap and mix well.

- If the pyridine cannot be dispensed with sufficient precision to achieve the exact 1.129 g weight, substitute the exact weight added for the 1.129 in Equation 1, and correct the subsequent dilutions.

Equation 1 shows the calculation of the concentration of nitrogen in the stock solution:

$$1000 \text{ µgN/mL} = \frac{(1.129)(17.71)}{200} \quad (1)$$

where:

- 1.129** = weight of pyridine, g
- 200** = dilution volume, mL
- 17.71** = concentration of N in pyridine, %

Calibration standard solution, 100 µgN/mL

Dispense 10 ml of the pyridine stock solution with a volumetric pipette into a clean, dry 100-mL volumetric flask. Dilute to the mark with 2N acetic acid solution. Cap the flask and mix well.

Calibration standard solutions, 10, 5, 1, 0.5, 0.2 µgN/mL

Prepare a series of 5 working standards by serial dilution of the standard solution with 2N acetic acid solution as follows:

10 µgN/mL standard- Dispense 20 mL of the 100 µgN/mL standard with a pipet into a clean, dry 200-mL volumetric flask. Dilute to the mark with the 2N acetic acid. Cap the flask and mix well.

5 µgN/mL standard - Dispense 10 mL of the 100 µgN/mL standard with a pipet into a clean, dry 200-mL volumetric flask. Dilute to the mark with the 2N acetic acid. Cap the flask and mix well.

1.0 µgN/mL standard - Dispense 20 mL of the 10 µgN/mL standard with a pipet into a clean, dry 200-mL volumetric flask. Dilute to the mark with the 2N acetic acid. Cap the flask and mix well.

0.5 µgN/mL standard - Dispense 20 mL of the 5 µgN/mL standard with a pipet into a clean, dry 200-mL volumetric flask. Dilute to the mark with 2N acetic acid. Cap the flask and mix well.

0.2 µgN/mL standard - Dispense 4 mL of the 10 µgN/mL standard with a pipet into a clean, dry 200-mL volumetric flask. Dilute to the mark with 2N acetic acid. Cap the flask and mix well.

The stock solution can be retained, if refrigerated, for up to 1 year. The standard solutions can be retained, if refrigerated, for 3 months.

Instrument Set Up

Set up the nitrogen analyzer according to the manufacturer's instructions. Connect the cyclone trap to the furnace outlet to prevent water in the gases from overloading the membrane drier. Allow the instrument to warm-up and the baseline to stabilize before injecting samples. Establish analysis parameters for the 2 N acetic acid samples. Suggested operating conditions for the Mitsubishi NSX-2100V analyzer are listed in Table 2. If another instrument is used, see that instrument's manual for the appropriate setup instructions.

Table 2
Suggested Operating Conditions for NSX-2100 V instrument

Upper temperature	600°C
Lower temperature	800°C
Argon Main	100 mL/min
Oxygen Main	500 mL/min
Ozone	200 mL/min
Detection start waiting time	0 sec
End time	300 sec
Sampling/Injection parameters:	
Fill rate	5 µL/sec
Post Fill delay	5 sec
Injection rate	0.6 µL/sec
Post inject delay	10 sec

Calibration

1. Fill the rinse bottle with deionized water and pre-fill bottle with methanol.
2. Fill autosampler vials, one each, with the 2N acetic acid (blank) and the 0.2, 0.5, 1, 5, 10 µg/mL nitrogen calibration standards.
3. Before starting to measure calibration standards run a few blanks of 2N acetic acid to condition the instrument and to remove any residual contamination. The response should be stable before proceeding.
4. Run a calibration program with multiple 20 µL injections of the solvent blank and each standard stored in the instrument software. It is recommended to inject each standard or blank at least 4 times. The instrument will average the results of the injections of each standard and the blank.

- Relative standard deviation (RSD), as calculated by the instrument for the blank, should be within 25%. The RSD for the standards should be within 15%.
5. Create a regression line using the instrument software using the blank and the five standards. Set the regression line to “ $y=bx+c$ ”. The calibration method will be saved automatically.
 6. Check the calibration curve by analyzing 0.5 µgN/mL and 1.0 µgN/mL standards as unknowns, (enter “1”, as a density). The standards should be run in triplicate. The instrument will average the results of the triplicate injections.

Sample Analysis

1. Enter the sample parameters into the software, this include sample ID, sample volume that is to be injected (usually 20µL), density (“1” for samples diluted in 2N acetic acid) and appropriate injection program, (the programs are stored under “ASC-250L” and they are established prior to the calibration).
 - Each sample should be injected at least three times to obtain an average result.
 - If the nitrogen concentration of the extract exceeds the concentration of the highest standard, the extract must be diluted with 2N acetic acid until the standards span the concentration of the diluted extract.
2. Before starting to measure samples run a few blanks of 2N acetic acid to condition the instrument and to remove any residual contamination. The response should be stable before proceeding.
3. Fill the autosampler vials with the samples and place the vials onto the autosampler rack according to the saved method.
4. Inject and analyze the samples using the instrument software.

Calculations

Verify that the acetic acid sample concentration is spanned by the calibration standards. The sample response must be read from the instrument, and the concentration of the extract must be calculated manually using Equation 2, rounding the result to two significant figures at or above 1 mg/kg, and to one significant figure below 1 mg/kg.

$$\text{Concentration of the combined nitrogen in the LPG, mg/kg} = \frac{S M}{L} \quad (2)$$

where:

L = mass of the LPG, g

M = mass of the acetic acid extract added to the LPG cylinder, g

S = combined nitrogen concentration of the acetic acid extract, density corrected, as read from the instrument, mass-ppm (mg/kg).

Notes

1. Cleaning of the interior, wetted surfaces of the cylinders and attached valves with the cleaning solvents can be performed as follows:
 - a. Mount the cylinder vertically on the ring stand in the hood and open both valves.
 - b. Evacuate the cylinder, by pressing a vacuum hose against the top cylinder valve by hand to create some vacuum in the cylinder.
 - c. Draw the solvent into the cylinder by submersing the bottom valve in the solvent held in the 100-mL polypropylene beaker. Close first the bottom, then the top cylinder valve.

- d. Remove the cylinder from the ring stand and rotate and invert the cylinder manually for about two minutes.
 - e. Reattach the cylinder to the ring stand and place the polypropylene beaker under the lower valve. Open both valves to drain the solvent from the cylinder and observe the color. Then discard the rinse.
 - f. Repeat the rinse with the solvent until the rinse is colorless. Then repeat Steps a through f, alternating the valves that are cleaned, until all the solvent required has been used to clean the cylinder and valves.
2. The extraction or cleaning procedure can be automated by using any commercial mixer that inverts the cylinders regularly as described. Alternatively, a device for the extraction can be constructed as described in the *Appendix*.
 3. The vacuum pump is required to reduce the pressure in the analyzer detector to improve sensitivity, and also to draw the combustion product gas into the detector. This requires a pump capable of handling high flow rates. Pump stability is very important as pressure fluctuations will strongly affect sensitivity.
 4. The Perma Pure membrane drier and the cyclone trap is used to remove the water produced during combustion. If not removed, the water vapor would enter the analyzer detector and result in a reduction of the chemiluminescence intensity.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining impurities in four LPG samples. One sample was analyzed by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence.

Table 3
Repeatability and Site Precision, mg/kg

<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>
2.6	0.10	0.4	0.20	0.9
0.6	0.03	0.1	0.04	0.1

The data in Table 3 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The labor required for the analysis is 4 hours and the elapsed time is also 4 hours.

Suggested Suppliers

Burdick & Jackson, 1953 S. Harvey St., Muskegon, MI 49442, USA, 1-973-455-5268,
www.bandj.com

COSA XENTAUR Corp., 84G Horseblock Rd., Yaphank, NY 11980, USA, 1-631-345-3434,
distributor for Mitsubishi Chemical Analytech, 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084,
Japan, +81-467-86-3864, www.cosa-instrument.com

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300,
www.fishersci.com

Lesman Instruments, 135 Bernice Drive, Bensenville, IL 60106 USA, 1-630-595-8400,
www.lesman.com

Matheson Tri Gas, 150 Allen Rd # 302, Basking Ridge, NJ 07920, USA, 1-908-991-9200,
www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA, 1-814-353-1300, www.restek.com

Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103, USA, 1-314-771-5765, www.sigma-aldrich.com

Swagelok Company, 29500 Solon Rd., Solon, OH 44139, USA, 1-440-248-4600,
www.swagelok.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

Appendix

Agitation Apparatus

A device to provide the agitation necessary for the extraction may be constructed as described.

Materials

Extractor, special construction, consisting of the following:

Hex nuts, plain steel, grade 8, McMaster-Carr, Cat. No. 90499A033, 16 required

Jar mill, Glen Mills

Polycarbonate sheet, “Hyzod”, general purpose, ½-inch thickness, Piper Plastics, Cat. No. GP-9100

Rod, alloy steel, B-7, coarse thread, ½-inch-13, approximately 4 m (158 inches) required, cut to length, McMaster-Carr, Cat. No. 98957A636

Rubber-Mat, V-rib, corrugated, heavy duty, 0.25-inch thickness, McMaster-Carr, Cat. No. 6973T12

Washers, flat steel, 24 needed, McMaster-Carr, Cat. No. 90108A033

Wing-nuts, iron, diameter ½ “-13, 8 needed, McMaster-Carr, Cat. No. 90876A166

Procedure

Any machine or carpenter shop familiar in the arts can fabricate the optional extractor as follows:

1. Trace two 500-mm (20-inch diameter) circular patterns on a rigid material, such as heavy polycarbonate sheet.
2. Cut two circular wheels from the polycarbonate in Step 1 and sand or polish the edges until smooth.
3. Drill 16-mm holes into the wheels for placement of the axles and clamps in the positions shown in Fig. A-1.
4. Glue a piece of rubber-mat (80 x 200 mm) into the center of each wheel between the clamp holes (Figures A-1 and A-3). These mats will serve as a cushion for the stainless-steel LPG cylinder(s).
5. Connect the wheels as shown in Figs. A-2 and A-3, using the threaded rods, washers and nuts as indicated.
6. Heat treat and bend a length of threaded rod with an acetylene-oxygen torch into four equal size U-shaped clamps using an empty stainless-steel cylinder as a form. Cut off and grind smooth the ends of each U-shaped clamp at a height of 160 mm. Insert two clamps for each cylinder into the appropriate holes in the center of each wheel and secure the clamp in place with the washers and wingnuts as shown in Fig. A-3 and A-4.
7. Attach the cylinder(s) to the extractor using the clamps as shown in Fig. A-4.
 - Two extractions can be performed simultaneously, as indicated in Fig. A-2.
8. Place the extractor onto the jar mill and turn on the mill.
9. Proceed with Extraction, Step 10, in the body of the method. Operate the mixer for 30 minutes per extraction.

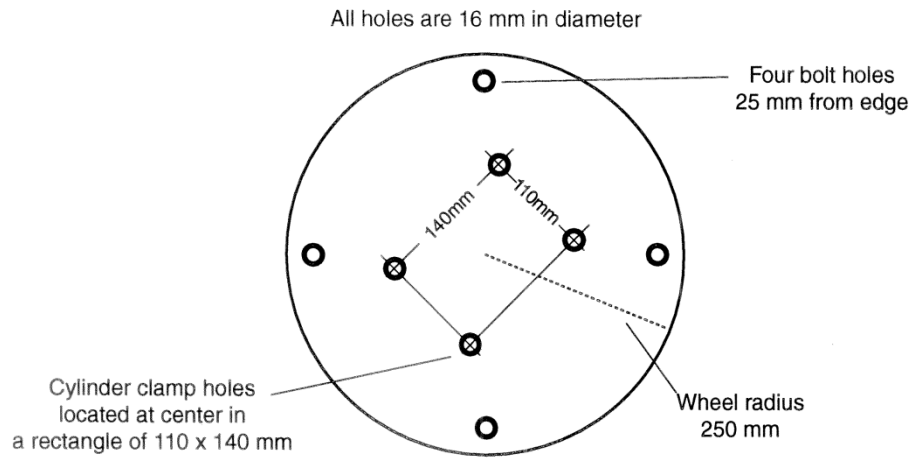


Figure A-1
Extractor Wheel (2 Required)
Showing Dimensions and Holes

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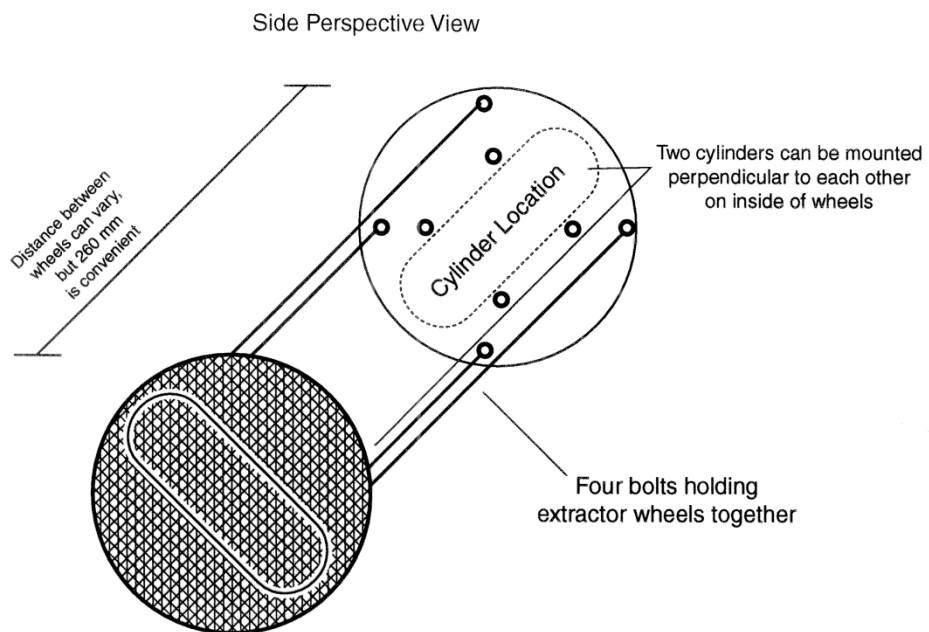


Figure A-2
Assembled Extractor Wheels, Showing Bolts
and Cylinder Locations

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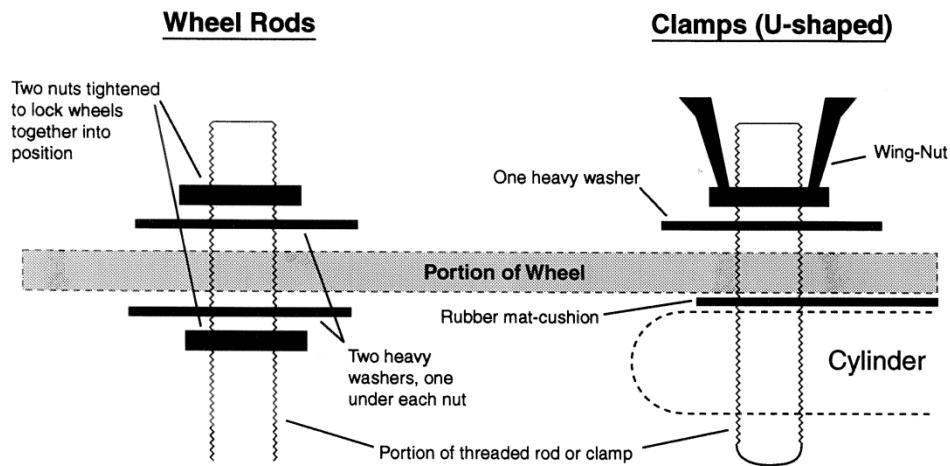


Figure A-3
Detail Showing Nuts and Washers on Extractor-Wheel Bolts
or Clamps, Side View

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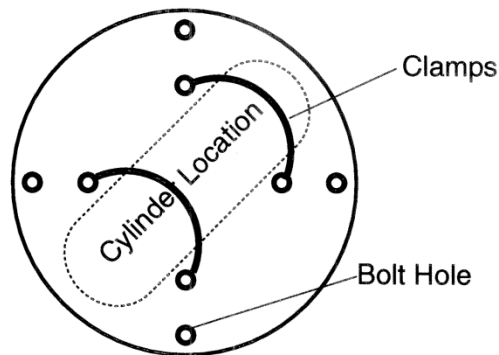


Figure A-4
Cylinder Clamped to Extractor Wheel,
Not to Scale

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Suggested Suppliers

Glen Mills Inc., 220 Delawanna Ave., Clifton, NJ 07014 USA (973-777-0777) www.glenmills.com

McMaster-Carr Supply Co., 600 County Line Rd., Elmhurst, IL USA 60126-2081 (708-833-0300)

Piper Plastics Inc., 1921 Industrial Dr., Libertyville, IL 60048 USA (708-367-0110)