

TOTAL NITROGEN IN LIQUEFIED PETROLEUM GASES BY ACID EXTRACTION-KJELDAHL PROCEDURE

UOP Method 432-65T

SCOPE

This method is for the determination of total nitrogen in liquefied petroleum gases in the region of 0.1 to several hundred parts per million.

OUTLINE OF METHOD

The method is patterned after the work of Milner, Zahner, Hepper, and Cowell¹. The liquefied gas sample is first drawn into an evacuated 1-1 stainless steel bomb, fitted at both ends with stainless steel valves and containing concentrated sulfuric acid. The bomb is rotated or shaken and the contents allowed to settle. The contents are drained into a prepared Kjeldahl flask and the gas is allowed to boil off. The standard Kjeldahl procedure is then followed, except that specially-purified reagents are used. Following digestion, the ammonia formed is distilled from a strongly alkaline solution containing sodium thiosulfate. The sodium thiosulfate precipitates the mercury (used as catalyst in the digestion) and permits quantitative distillation of ammonia. The ammonia is absorbed in a saturated boric acid solution containing methyl purple indicator and titrated with 0.005 *N* sulfuric acid.

APPARATUS

Balance, 5-kg maximum capacity

Beakers, 500- and 1000 - ml

Bombs, extraction and sample, 1-1 capacity. Non-magnetic stainless steel construction, fitted at both ends with non-magnetic stainless steel fittings and valves, and stainless steel connecting tube

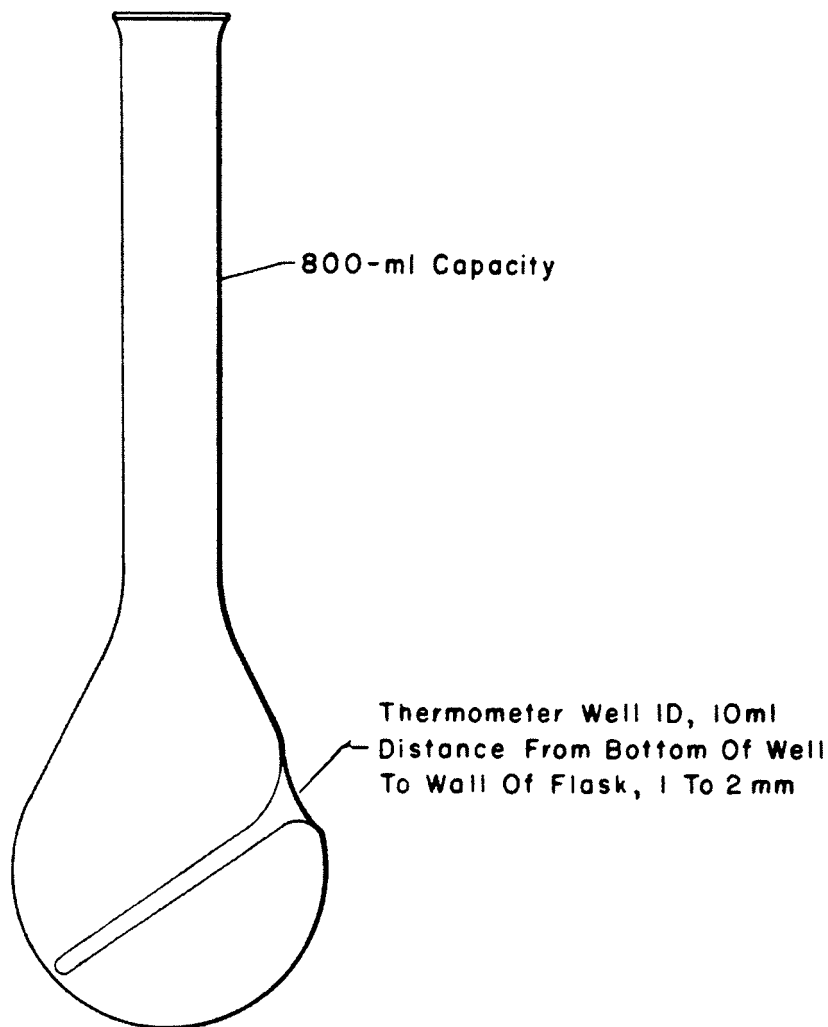
Digestion unit, Kjeldahl. If a commercial unit is used, the heater must be modified to provide a full range of heats. The following have been found satisfactory for heat control: The Precision Scientific Co., Type H, 750-watt heater with a variable transformer, or the Labconco Infinite Heat Control electric heater, available from E. H. Sargent and Co. by specifying Catalog No. S-63065.

Distillation unit, Kjeldahl. Any commercial or improvised setup may be used if it utilizes an 800 - ml Kjeldahl flask, condenser, and a Kjeldahl connecting bulb. This connecting bulb is available from E. H. Sargent and Co. by specifying Catalog No. S-63545 or S-63465.

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Kjeldahl Flask, 800-ml, With Thermometer Well

Flask, Erlenmeyer, 500-ml

Flask, Kjeldahl, 800-ml, with thermometer well (see illustration)

Graduates, glass stoppered, 100- and 500-ml

Hot plate

Pipets, 5-, 10-, 25-, 100-ml

Purification column. For sodium hydroxide (and sulfuric acid): Glass column, 150-cm long by 7-cm ID, tapered at one end to form a 6-mm dripper incorporating a coarse sintered glass plug, equipped with a water cooling jacket 135-cm long located 10 cm from the top of the column, and fitted at the other end to a one-liter reservoir. Design the top of the reservoir for attachment to an air pressure system. The water cooling feature is used for purifying the sodium hydroxide; air pressure but no cooling is used when purifying sulfuric acid.

Thermometer, total-immersion, gas-filled, 500 C maximum

Vacuum source, electric pump or water aspirator

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.

Because of the small concentration of nitrogen detected at the lower limit of analysis (less than 0.1 ppm), and the large amount of reagents used (700 g), it is imperative that all reagents be exceedingly low in nitrogen content. Reagents that contain more than trace concentrations of nitrogen compounds (see Note 1) must be specially purified.

Acetone

Boric acid solution, saturated. Dissolve approximately 40 g of boric acid crystals in 1 l of distilled water.

Carborundum boiling stones. Remove any nitrogenous matter by digesting a quantity of carborundum chips in boiling, concentrated sulfuric acid for 30 minutes. Rinse with copious quantities of water and oven-dry.

Mercury, redistilled. Store in a dropping bottle.

Methyl purple indicator, 0.1% aqueous solution. Store in a dropping bottle.

Pentane. Skellysolve "A" is satisfactory.

Potassium sulfate. Purify potassium sulfate by heating in an electric furnace for 12 hours at 500-600 C. It has been found convenient to use a porcelain dish large enough to hold a pound of crystals. Place a dish and contents in the furnace while the furnace is still cool to minimize spattering at higher temperatures. Store in a clean dry bottle.

Silica gel, 14-20 mesh, obtainable from Davison Chemical Co., Baltimore, Md., by specifying "Grade H, Type 3" (for caustic purification); and 60-200 mesh, obtainable from the same source by specifying "Code 950" (for purifying H₂SO₄).

Sodium hydroxide-thiosulfate solution, approximately 50% sodium hydroxide and 5% sodium thiosulfate pentahydrate (Na₂S₂O₃ • 5H₂O) when prepared. Fisher Scientific Company supplies a carbonate-free 50% sodium hydroxide solution, Cat. No. So-S-254.

Analyze the 50% sodium hydroxide solution for nitrogen content before using, as follows: Measure 110 ml of the 50% sodium hydroxide into an 800-ml Kjeldahl flask, add 400 ml of water and a few boiling chips. Distill about 200 ml into 20 ml of 4% boric acid solution contained in a 500-ml Erlenmeyer flask and titrate with 0.005 N sulfuric acid. If the nitrogen content is greater than 70 γ, the sodium hydroxide solution must be purified before further use; if less, use without purification.

Use the following procedure to purify the sodium hydroxide solution: Add 14-20 mesh silica gel to the 150-cm glass purification column to within 10 cm of the reservoir. Add enough solid glass beads to the top of the gel to prevent the bed from rising when the sodium hydroxide solution is added. Turn the water on and let the column cool for 15 minutes before the 50% sodium hydroxide solution is added. Charge 1000 ml of the 50% sodium hydroxide solution to the reservoir, connect the air line to the reservoir by means of a ground-glass joint and adjust the pressure to 2 psig. Discard the first 200-250 ml of the percolated solution. Continue charging the solution until a total of 3800 ml has been charged. Collect a heart-cut of 3000 ml and store in a clean 1-gal polyethylene bottle. Determine the nitrogen content of the percolated 50% sodium hydroxide before using.

Weigh 229 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystals into a 500-ml beaker, add 200 ml of water, 10 g of 50% sodium hydroxide solution and a few boiling chips. Boil until the solution turns yellow.

When the thiosulfate solution has cooled, pour it into a 1-gal polyethylene bottle. Add 4575g of the 50% sodium hydroxide solution (assaying no more than 70 $\gamma\text{N}/110$ ml) to the polyethylene bottle containing the thiosulfate solution. Shake well to ensure proper mixing.

Stopcock grease, Dow Corning silicone type, or equivalent

Sulfuric acid, 1:1. Mix equal volumes of concentrated sulfuric acid and water.

Sulfuric acid 0.01 N and 0.005 N. Standardize to 3 significant figures.

Sulfuric acid, concentrated, reagent grade. E. I. DuPont de Nemours and Co., 4251 S. Crawford Ave., Chicago, III. 60632, supplies sulfuric acid containing less than 1 ppm nitrogen. This is the only known commercial source of low nitrogen content sulfuric acid.

If the nitrogen content of the sulfuric acid is greater than 3 ppm, purification either by distillation² or by percolation through silica gel is necessary.

Distill concentrated sulfuric acid at atmospheric pressure in an all-glass system (see Note 2). Lubricate ground-glass joints with concentrated sulfuric acid. Cool the condenser by passing a rapid stream of air through the condenser jacket. Discard the initial 10% overhead and collect an 80% heart-cut in a clean, dry bottle. Discard the 10% bottoms.

An alternative method is to percolate the acid through a column of silica gel. Insert a small wad of glass wool into the column just above the dripper to hold the silica gel in the column. Load the column with 60 - 200 mesh silica gel to the bottom to the reservoir. Pack the column by tapping, to eliminate the possibility of channeling. Fill the reservoir with sulfuric acid and set the air pressure at 5 psig.

Allow about 1l of the sulfuric acid to percolate through the column or continue until the acid coming off is colorless. Discard the colored acid and collect the colorless acid in a clean, dry bottle.

Water, distilled or deionized. It is necessary to use water which has a consistent and low nitrogen content. Double-deionized water obtained from a deionizer in good condition has been found satisfactory. The term "double deionized" refers to water which has been processed in a central deionizer followed by reprocessing in a small laboratory deionizer.

Zinc metal, 20-30 mesh, granulated

PREPARATION OF APPARATUS

The extraction bomb should be cleaned as soon as possible after using (see Note 1). If it has not been cleaned, clean before reusing as follows:

Open both valves of the bomb and allow any gas remaining to vent itself from the bomb. Rinse the bomb with hot tap water for 5 to 10 minutes. After the bomb is cool, add 100 ml of 1:1 H_2SO_4 -water solution to the bomb and allow to set for 15 minutes. Drain the acid solution from the bomb and rinse with hot tap water until the exit water is clear. Rinse the bomb with distilled or deionized water, follow by an acetone wash. Drain all the acetone from the bomb and evacuate the bomb for 15 minutes in a vertical, valve-end down position to remove any remaining acetone.

PROCEDURE

The olefin content of the liquefied gas must be determined *before* extraction of the gas with sulfuric acid is carried out. This is because concentrated sulfur acid will react exothermically with olefins. Use UOP Method 358, "Bromine Index of Liquid Butane and Petroleum Distillates by Coulometric Titration" or a gas-liquid chromatographic analysis to determine the olefin content of a liquefied gas sample.

Extraction – LPG Less Than 15% Olefinic

Draw 60 ml of concentrated sulfuric acid into an evacuated 1-1 extraction bomb. Allow the acid to collect at one end of the bomb and then evacuate the bomb again, keeping it in a vertical position to avoid carrying acid into the vacuum line. Close the bomb valve and disconnect it from the vacuum source. Place the bomb in a box containing dry ice for a period of 15 minutes (see Note 3). Weigh the bomb to the nearest 0.5 g.

Slightly bleed the bomb containing the sample to remove any foreign matter that may be present in the valve. Weigh the bomb to the nearest 0.5 g and connect it to the evacuated extraction bomb by means of a stainless steel tube and fittings. The position of the sample bomb should be such that the liquefied gas will be forced into the extraction bomb by its own vapor pressure. Position the extraction bomb at a lower elevation than the sample bomb. The sample bomb, connecting tube and extraction bomb should all be in a vertical plane, perpendicular to the bench top. Open the valve of the sample bomb all the way. Open the valve of the extraction bomb 4 or 5 complete turns and then close it quickly. Close the valve on the sample bomb. Avoid taking more than 450 g of sample during sampling. As quickly as possible after sampling weigh the sample bomb to the nearest 0.5 g. The weight of sample taken is the weight difference.

Because of the danger of hydrostatic pressure developing if the extraction bomb is filled to capacity, the upper limit of safety has been set at 450 g of liquid butane, representing approximately 750 ml at 75 F.

If the sample weight is greater than 450 g, repeat the extraction on a fresh sample using new reagents and a clean bomb.

When sampling is completed, mix the contents of the extraction bomb by either shaking or rotating the bomb end-over-end. Accomplish rotation by attaching a heavy beaker clamp to the bomb and securing the shaft of the clamp to a ring stand. Maintain rotation for 2 minutes.

Empty the bomb (in a hood) into a prepared Kjeldahl flask containing 25 ± 0.5 g of heat-treated potassium sulfate crystals, 1.0 ± 0.2 g of mercury and a few carborundum boiling chips. Use care when emptying the bomb into the Kjeldahl flask. The extraction bomb must be held in a vertical position, with the valve opening *inside* the neck of the Kjeldahl flask. Open the valve slowly and let the vapor pressure of the liquefied gas force the acid and liquefied gas into the flask. Allow the extraction bomb to drain a few moments after the last of the gas has been ejected.

Allow the flask containing the acid extract to defrost and then place it in a warm bath to boil off the liquefied gas.

Extraction – LPG Greater Than 15% Olefinic

Dilute samples containing more than 15% olefins with pentane to a safe concentration before extraction as follows: Evacuate a 1-1 extraction bomb and draw in 60 ml of concentrated sulfuric acid. Evacuate the bomb again and draw in 100 ml of pentane. Cool the bomb in a dry ice chest for 10 minutes. Weigh the bomb and evacuate it again. Reweigh the bomb and observe any significant loss in weight due to the boil-off of pentane. The loss in weight should not exceed 5 g. Replace the evacuated extraction bomb, the connecting tube, and the sample bomb in the dry-ice chest for 20 - 30 minutes.

Remove the extraction bomb from the dry ice. Place it, with the connecting tube attached, in a bucket of ice water. Remove the sample bomb from the dry ice and weigh it to the nearest 0.5 g. Attach it to the connecting tube of the extraction bomb so that the sample is taken from the bottom of the sample bomb. Open the valve of the sample bomb fully. Open the valve of the extraction bomb 3 or 4 full turns and then close it in one continuous motion (see Note 3). Close the valve of the sample bomb, disconnect it from the connecting tube, and reweigh it to the nearest 0.5 g. The weight of sample taken is the weight difference. If the weight of the sample taken exceeds 400 g, repeat the sampling using fresh reagents and a clean extraction bomb.

Carefully remove the extraction bomb from the ice bucket and shake it 2 or 3 times. Immediately replace the bomb in the ice bucket and add more ice if necessary. Wait 10 minutes and repeat the shaking procedure. Continue shaking every 10 minutes until there is no evidence of the bomb warming up (see Note 4). After the initial heat of reaction has been dissipated, rotate the extraction bomb for a period of 2 minutes, as previously described for low-olefin samples. Transfer the acid and liquefied gas to a prepared Kjeldahl flask as previously described. Allow the excess gas in the flask to boil off in a hood. The sulfuric acid-soluble esters formed during the extraction step must be converted to the corresponding alcohols to avoid excessive frothing, long digestion time and the use of large amounts of additional sulfuric acid during digestion. Do this by adding about 100 ml of water in small amounts, swirling the flask after each addition. Place the flask on the digestion rack and distill off the alcohol and water at low to medium heat.

Digestion

Wrap the upper 1 to 2 inches of the neck of the Kjeldahl flask with glass wool to prevent condensed sulfuric acid from creeping around the lip of the flask and running down the neck toward the heating element. Place the flask on the digestion rack. Apply a medium heat (50-60 v); continue heating until frothing and charring cease, then maintain medium heat for 45 ± 15 minutes.

Starting the digestion with medium rather than low heat is practicable because of the small amount of hydrocarbon extracted by the sulfuric acid. This permits the digestion time to be shortened from the usual 5 to 6 hours to as little as 2 to 2-½ hours from start to finish.

When charring is completed and the contents of the flask are liquid, increase the heat over a 15-20 minute period until high heat (100-110 v) is applied. If severe frothing develops, lower the heat to medium (50-60 v) and add a small quantity (10-15 ml) of concentrated sulfuric acid.

Maintain the rate of boiling such that condensation of the acid vapor occurs 1/2 to 3/4 of the way up the neck of the flask. The reflux serves to wash back any particles of froth or char into the bulb of the flask. If necessary, add *small* amounts of acid to wash back any particles lodging high in the neck of the flask. Avoid using additional acid, if possible, by exercising care during initial charring.

Continue heating at the high rate until the liquid in the flask becomes colorless and is approximately 20 - 30 ml in volume. The temperature of the boiling liquid should be between 360-380 C, determined by carefully inserting a thermometer into the thermometer well of the Kjeldahl flask (see Notes 5 and 6). The digestion is timed when this temperature is reached and continues for 1 hour at the same reflux rate.

Too much sulfuric acid in the digestion flask results in a low digestion temperature and incomplete nitrogen recovery. Too small an acid volume results in an excessive digestion temperature and loss of nitrogen. If the volume is below 20 ml and the temperature exceeds 400 C, add additional low-nitrogen sulfuric acid. If the volume exceeds 30 ml and the temperature is below 375 C, increase the reflux rate so that the excess acid is distilled from the flask either by increasing the heat or by wrapping glass wool around the neck of the flask in order to insulate it. After a 20-30 ml level is attained and the temperature is between

360-380 °C, remove the glass wool (or decrease the heat) and continue digestion for 1 hour at the same reflux rate. Lake et al³ published an excellent detailed discussion of the effects of temperature on the nitrogen recovery.

When digestion is complete, turn off the heat and allow the flask to cool to room temperature. Add 400 ml of water in the following manner: Very cautiously and with continuous swirling, add about 50 ml of water. Continue adding water by increments, followed by swirling, until the salt cake dissolves. Then add the remaining water with continuous swirling. Cool the flask in an ice bath until cold to the touch.

Distillation

While the flask is cooling, thoroughly rinse the distillation apparatus with distilled or deionized water (see Note 7). Place 25 ml of saturated boric acid solution in a 500-ml Erlenmeyer flask. Place the flask on the distillation rack so that the condenser tip is well beneath the surface of the acid solution. Do not permit the condenser tip to press tightly against the bottom of the Erlenmeyer flask to avoid creating back-pressure.

When the digestion flask is cold, the receiver in place and the condenser is cold, add a pinch of granulated zinc to the Kjeldahl flask. Then, inclining the flask, carefully add 100-110 ml of the caustic-thiosulfate solution in such a manner so as to maintain 2 discrete layers. Quickly place the flask on the distillation rack, connect the spray trap and carefully swirl the flask so that there is a gradual but thorough mixing of the layers.

When mixing is completed, apply full heat and start the distillation. Continue distilling until “bumping” commences (see Note 8). At this point 150-200 ml of distillate will have been collected, enough to ensure that all the ammonia has been taken over. Use care not to allow any alkali to be carried over into the distillate during the distillation step, since even a trace in the distillate will increase basicity and cause erroneously high results. Use of the spray trap mentioned under APPARATUS, Kjeldahl distillation unit makes it virtually impossible for any caustic to be carried over into the distillate. In addition, distillation should not continue after “bumping” commences or a total of 200 ml is in the receiver (see Note 9). When either point is reached, turn off the heat, raise the Kjeldahl flask from the heating element and immediately lower the receiving flask so that the condenser tip is no longer submerged.

Titration

Add 4 drops of methyl purple indicator to the distillate and swirl to mix. Titrate with standard 0.005 *N* sulfuric acid to the point at which the solution just begins to exhibit a purple tint. When high nitrogen concentrations are anticipated, titrate with 0.01 *N* sulfuric acid.

Reagent Blank

Run a reagent blank each time a new lot of reagents is prepared, in the same manner as described for an unknown, with the exception that no extraction is required.

CALCULATIONS

$$\text{Nitrogen, wt - ppm} = \frac{14,000 \, N (V_A - V_B)}{W}$$

where:

- N** = normality of standard acid used for titration
- V_A** = volume of standard acid used to titrate the sample, ml
- V_B** = volume of standard acid used to titrate the blank, ml
- W** = weight of sample, g; when the sample is measured by volume,
- W** = ml sample × sp gr.

NOTES AND PRECAUTIONS

1. This one point cannot be emphasized too strongly: To obtain accurate results the analyst must use great care to avoid contamination by nitrogenous substances.
2. Distillation of sulfuric acid obviously presents some hazard. Have adequate personal protective facilities at hand; e.g., safety glasses, face shield, protective clothing, etc. Have sodium carbonate available to neutralize spills.
3. *Never* leave the extraction bomb unattended during the extraction step.
4. If the temperature of the extraction bomb cannot be controlled during the extraction of the high olefinic liquefied gas and the bomb has become hot to the touch, *immediately* open one of the valves, place the bomb in a vented, explosion-proof area and allow the heat and pressure to dissipate. The bomb should then be emptied and cleaned thoroughly before being used again.
5. Since the volume of acid in the Kjeldahl flask is difficult to determine, the use of temperature control is a more accurate method of maintaining the critical 20-30 volume of sulfuric acid. Determine the temperature of the boiling sulfuric acid solution by having a thermometer well in the Kjeldahl flask, such that the bottom of the well will be beneath the level of the acid, and carefully inserting the specified thermometer into the well.
6. *Do not* insert cotton or glass wool at the bottom of the thermometer well to act as a cushion for the thermometer. This would raise the bulb of the thermometer above the liquid level of the acid in the Kjeldahl flask, causing low temperature readings.
7. The last traces of ammonia must be removed from the distillation equipment to avoid possible contamination of subsequent samples after high nitrogen content samples have been distilled. Rinse the spray trap and condenser several times with water, then add 400 ml of water to the Kjeldahl flask and distill until 200 ml are recovered overhead. Rinse the spray trap and condenser again with distilled or deionized water. If both high- and low-nitrogen samples are routinely analyzed, reserve particular glassware for the low (0-1 ppm) nitrogen concentrations.
8. As soon as the contents of the Kjeldahl flask begin to “bump” during the distillation, turn off the heat immediately, since “bumping” can become violent. Use of a safety shield is recommended. Asbestos tape is helpful as a cushion to reduce flask breakage. Wind 1-inch width tape onto the ceramic plate so that the flask contacts the tape at 5 or 6 places.
9. The walls of the Kjeldahl flasks become thinner with continued use because of attack by the alkali added in the distillation step. Discard flasks after 40 to 50 analyses, or upon any visible evidence of weakening.

PRECISION

An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least 4 degrees of freedom.

Based on a limited amount of data duplicate results should not differ by more than 20% of the mean for the 1 - to 100-ppm N range.

TIME FOR ANALYSIS

Man-hours required for one analysis are 2 and 4 hours of elapsed time.

REFERENCES

1. Milner, O. I., Zahner, R. J., Heppner, L. S., and Cowell, W. H., *Anal. Chem.* 30, 1528 (1958).
2. Noble, E. D., *Anal. Chem.* 27, 1413 (1955).
3. Lake, G. R., McCutchan, P., Van Meter, R., and Neel, J. C., *Anal. Chem.* 23, 1634 (1951).