

NITROGEN IN PETROLEUM DISTILLATES AND HEAVY OILS BY ACID EXTRACTION OR DIRECT KJELDAHL PROCEDURE

UOP Method 384-76

SCOPE

This acid extraction method is specifically intended for the determination of combined nitrogen in petroleum distillates and heavy oils in concentrations ranging from 0.1 to 100 ppm. Non-extractable samples, and samples containing nitrogen concentrations ranging from 20 ppm to several percent, can be handled by a direct Kjeldahl analysis. The method applies to oil samples as well as a large variety of other materials; e.g., corrosion products, deposits, catalysts, etc.

The types of nitrogen compounds which can be determined are those which usually are determined by a macro-Kjeldahl procedure and include amines, amides, pyridines, pyrroles and quinolines. The method does not apply to organic nitro-compounds or to those containing a -N = N- linkage.

OUTLINE OF METHOD

The acid extraction method is patterned after the work of Milner, Zahner, Hepner and Cowell.¹ The sample is introduced into a separatory funnel and extracted twice with concentrated sulfuric acid. The sulfuric acid extract is then digested by the Kjeldahl procedure, employing specially purified reagents and rigid time and temperature control. 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 liberated ammonia is absorbed in a saturated boric acid solution containing methyl purple indicator and is determined by titration with 0.01 *N* or 0.005 *N* sulfuric acid.

The direct Kjeldahl analysis eliminates the acid extracting step. The sample is digested with concentrated sulfuric acid, following the standard Kjeldahl procedure except that specially purified reagents are used.

APPARATUS

Kjeldahl digestion unit. 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: "Type II," 750-w heater with a variable transformer, available from Precision Scientific Co., 3737 Cortland Ave., Chicago, IL 60647; or the "Labconco Infinite Heat Control" heater, Cat. No. S-63065, available from Sargent Welch, 7300 N. Linder Ave., Skokie, IL 60076.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 1964, 1976 UOP LLC
ALL RIGHTS RESERVED

UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Kjeldahl distillation unit. Any commercial or improvised setup may be used if it utilizes an 800- ml Kjeldahl flask, condenser and a spray trap.

Kjeldahl flask, 800 - ml, with thermometer well (see Fig. 1)

Purification columns. 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 1-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 water cooling is used when purifying sulfuric acid.

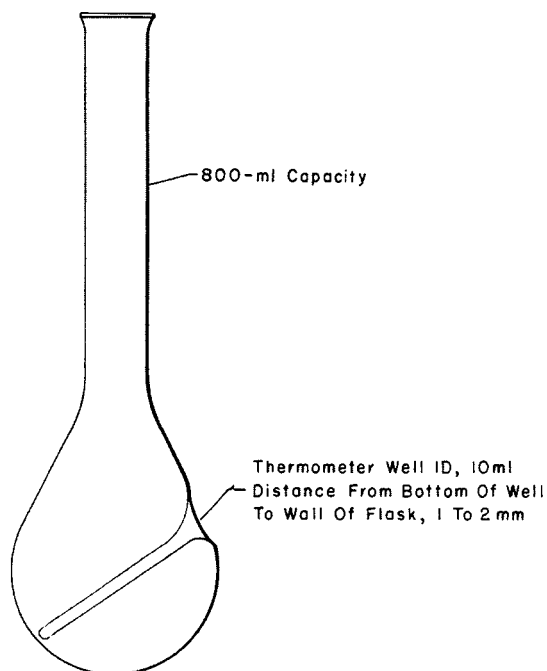


Figure 1

Kjeldahl Flask 800-ml, With Thermometer Well

For isooctane: Glass column 50 - cm long by 4 - cm ID, tapered at one end to form a 5-mm dripper, and fitted at the other end to a 1-liter reservoir.

Spray trap, (see Fig. 2)

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

The following conventional equipment is also required:

Beakers, 500- and 1000-ml

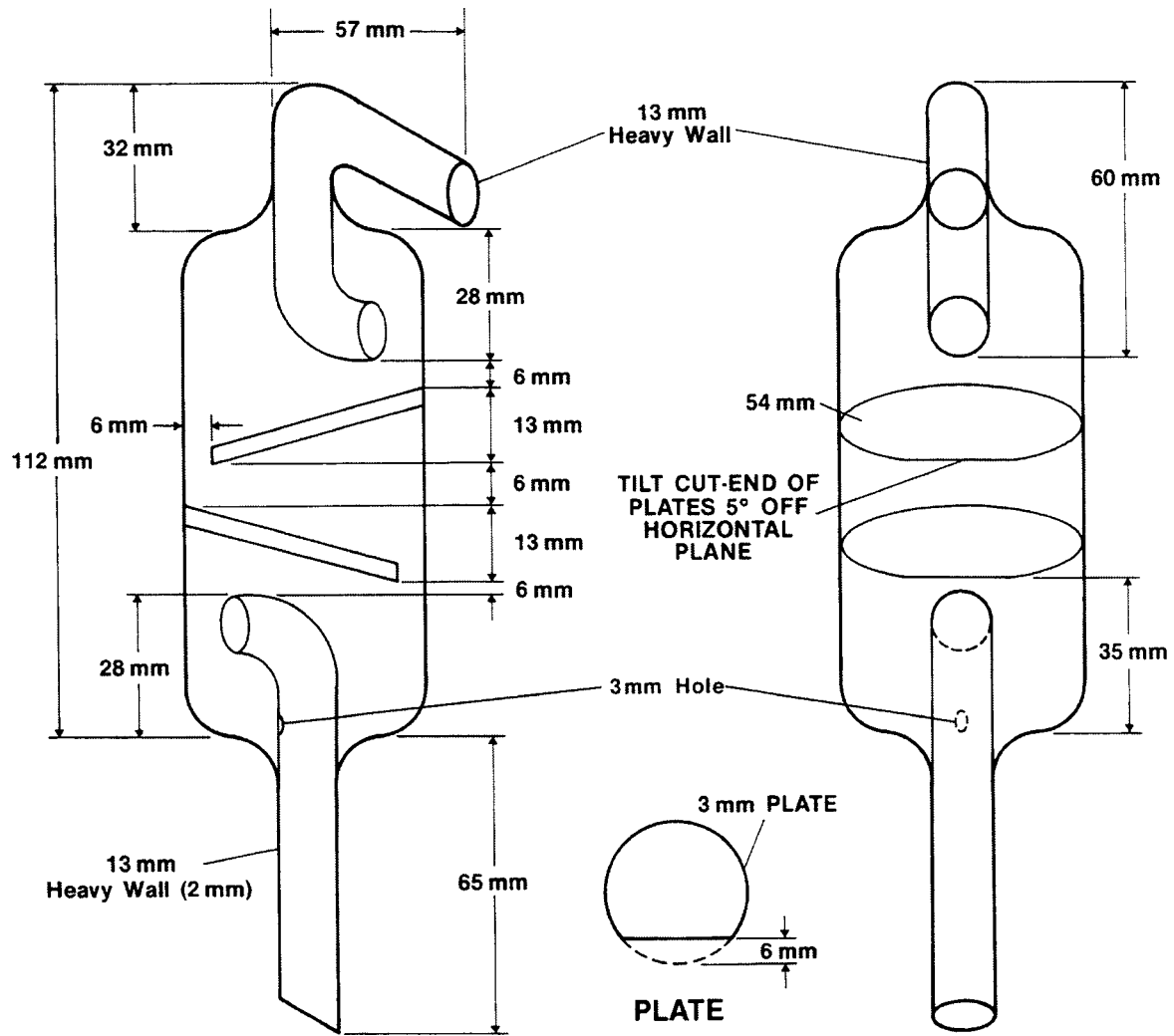


Figure 2
Spray Trap

Bottle, polyethylene, 1-gal

Flask, Erlenmeyer, 500-ml

Funnels, separatory, 500- and 1000-ml

Graduates, glass stoppered, 250- and 500-ml

Hot plate

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

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean double-deionized or freshly-distilled water unless otherwise specified.

Because of the small concentration of nitrogen detected (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. Accordingly, it is necessary to purify reagents found to contain more than trace concentrations of nitrogen compounds.

Boric acid, saturated. Dissolve approximately 40 g of boric acid crystals in 1-liter of 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 dry in an oven.

Isooctane. Purify by the following procedure: Fill the 50-cm glass column with 60-200 mesh silica gel to within 1 cm of the bottom of the reservoir. Insert a glass wool plug in the tapered end to prevent loss of gel. Charge 1 liter of isooctane to the reservoir and discard the first 100 ml percolated. Continue to charge the reservoir until a total of 4 liters of isooctane has been added. Collect a heart-cut of 3700 ml in a clean, dry 1-gal bottle. Discard the remaining isooctane and used silica gel.

Run a total nitrogen determination by the procedure of this method on every new batch of isooctane that is to be used in dilution.

Mercuric oxide

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

Potassium sulfate. Purify 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 the 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 Division, W. R. Grace & Co., 101 N. Charles St., Baltimore, MD 21203, by specifying Grade II, Type 3 (for caustic purification); and 60-200 mesh, obtainable from the same source by specifying Code 950 (for purifying isooctane and sulfuric acid).

Sodium hydroxide - thiosulfate solution, approximately 50% sodium hydroxide and 5% sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) when prepared. Fisher Scientific Co., 1458 N. Lamon, Chicago, IL 60651, 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 μg purify the solution before further use; if less, use without purification.

Use the following procedure, if necessary, to purify the sodium hydroxide solution: Add 14-20 mesh silica gel to the 150-cm glass 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 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 percolated. Continue charging the sodium hydroxide 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 it.

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 4575 g of the 50% sodium hydroxide solution (assaying no more than 70 γ /110 ml of 50% sodium hydroxide) to the polyethylene bottle containing the thiosulfate solution. Shake the bottle well to ensure proper mixing.

Stopcock grease. Dow-Corning Silicone Stopcock Grease has been found to be free of nitrogenous matter and is safe to use without fear of contamination, available from Sargent-Welch.

Sulfuric acid, 0.1 *N* and 0.005 *N*. Standardize by any acceptable method. Titration with tris(hydroxymethyl)aminomethane is recommended.

Sulfuric acid, concentrated. E. I. DuPont de Nemours and Company, 4251 S. Crawford Ave., Chicago, IL 60632, supplies a low nitrogen content sulfuric acid (less than 1 ppm nitrogen) and is the only known commercial source. Purification of this acid is not necessary.

If the nitrogen content of the sulfuric acid is greater than 3 ppm, purify it either by distillation³ or by percolation through silica gel.

Distill concentrated sulfuric acid at atmospheric pressure in an all-glass system (see Note 4). 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 for removing ammonia from sulfuric acid 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 of the reservoir. Pack the column by tapping, to eliminate the possibility of channeling of the sulfuric acid. Fill the reservoir with sulfuric acid and set the air pressure at 5 psig.

Allow about 1 liter 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.

Tris(hydroxymethyl)aminomethane, available as THAM from Fisher Scientific Company.

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 processing in a small deionizer in the laboratory.

Zinc metal, 20-30 mesh, granulated

PROCEDURE

Extraction of Naphthas

Sample size is determined by the nitrogen content. A convenient estimation can be made by first determining the basic nitrogen by UOP Method 313 or 269, using the result as a guide in selecting the sample volume from the table below.

Basic Nitrogen Range, ppm	Sample Volume, ml
0-0.5	400-700
0.5-1	300-400
1-5	200-300
5-10	100-200
10-20	50-200
20-100	20-50

For samples of 400 ml or less, place 35 ml of concentrated sulfuric acid in a 500-ml separatory funnel and add the sample. Stopper the funnel and shake for 1 minute, venting frequently and cooling if necessary under tap water. Allow the acid to settle to the bottom of the funnel, and then draw it off into a Kjeldahl flask fitted with a thermometer well (see illustration), containing 25 ± 0.5 g of *heat treated* potassium sulfate crystals, 1.1 ± 0.2 g of mercuric oxide and a few carborundum boiling chips. Add 35 ml more of concentrated sulfuric acid to the separatory funnel and again shake for 1 minute. Allow the acid to settle and then draw off the acid plus a small amount of sample, 1 or 2 ml, into the flask.

When the sample exceeds 400 ml, use a 1000-ml separatory funnel for extraction. Increase the time for shaking to 3 minutes.

Proceed next as directed in the section *Digestion*.

Extraction of Olefinic Stocks

Extraction of olefinic stocks presents some hazard because of the heat generated by reactions which occur when olefinic material is contacted with concentrated sulfuric acid. Samples containing greater than 10% olefins should be diluted with percolated isooctane to twice the volume taken for analysis. Shaking of the sample with concentrated sulfuric acid should be done slowly at first, with frequent venting of the separatory funnel and cooling under tap water. When the heat of reaction has been dissipated, continue to shake for 1 minute, settle and drain the acid layer into the Kjeldahl flask. Carry out the same procedure for a second extraction, then follow the instructions in the last part of the section *Extraction of Naphthas*.

Proceed next as directed in the section *Digestion*.

Extraction of Heavy Oils

Determine the amount of sample to be taken on the basis of expected nitrogen content as indicated in the table for naphtha samples. Transfer a weighed sample to a separatory funnel containing 30 ml of concentrated sulfuric acid. Add a volume of percolated isooctane equal to that of the sample and follow the extraction procedure described under *Extraction of Naphthas*.

Proceed next as directed in the section *Digestion*.

Extraction of Oils Semi-Solid at Room Temperature

Determine the amount of sample to be taken on the basis of expected nitrogen content as indicated in the table for naphtha samples. Warm the semi-solid oil until it is liquid and homogeneous. Transfer a weighed sample to a separatory funnel containing 35 ml of concentrated sulfuric acid. Add a volume of percolated isooctane equal to that of the sample and follow the extraction procedure described under *Extraction of Naphthas*.

Proceed next as described under *Digestion*.

Direct Sampling for High-Nitrogen Samples

The extraction step is unnecessary for samples containing more than 100 ppm nitrogen. Analyze the sample directly by the following procedure.

Pipet or weigh the sample into the 800-ml Kjeldahl flask fitted with a thermometer well, add 25 ± 0.5 g of heat-treated potassium sulfate crystals, 1.1 ± 0.2 g of mercuric oxide, a few carborundum boiling chips and 70 ml of concentrated sulfuric acid. The amount of sample taken for analysis depends on the nitrogen content and is selected as suggested in the following table.

Estimated Nitrogen, ppm	Sample Weight, g
20-50	3-5
50-100	1-3
100-500	0.5-1
500-1000	0.1-0.5
> 1000	0.1

The above sample sizes are based on a minimum titration of 1 ml of 0.005 *N* sulfuric acid.

The Kjeldahl method can be applied to a wide variety of materials other than oil samples; e.g., corrosion products, deposits, catalysts, etc. Exact instructions for such a diverse group of samples cannot be given here. The analyst must use his judgment in deciding size of sample, course of the digestion and normality of titrant. However, the 1-hr digestion at 360-380 C described under *Digestion* must be followed.

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 this medium heat for 45 ± 15 minutes.

Starting the digestion with a medium rather than a low heat is practicable because of the small amount of hydrocarbon that is extracted by the concentrated sulfuric acid. This permits the digestion time to be shortened from the usual 5 to 6 hours to as little as 2 to 2-1/2 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 so 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 into the bulb of the flask any particles of froth or char. If necessary, add *small* amounts of acid to wash back any particles lodged high in the neck of the flask. Avoid this use of additional acid, if possible, by exercising care during the 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 and 380 C, determined by carefully inserting a thermometer into the thermometer well of the Kjeldahl flask (see Note 6 and 7). The digestion is timed when this temperature is reached and continued for 1 hour at the same reflux rate.

Too large a volume of 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. Do not allow the volume to decrease so that the temperature exceeds 380 C. Add additional low-nitrogen sulfuric acid as required to keep the temperature at the maximum of 380 C. 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; accomplish this either by increasing the heat or by wrapping glass wool around the neck of the flask in order to insulate it. After a 20 to 30 ml level is attained and the temperature is between 360 and 380 C, remove the glass wool (or decrease the heat) and continue digestion for 1 hour at the same reflux rate. Lake, et al.² have published an excellent detailed discussion of the effects of temperature on the nitrogen recovery.

When the digestion is completed, 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 by increments, followed by swirling, until the salt cake dissolves in the hot solution. Then add the remaining volume of 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 water (see Note 5). 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 liquid. In order to avoid objectionable pressure build up, do not permit the condenser tip to press tightly against the bottom of the Erlenmeyer flask.

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 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 2). At this point 150-200 ml of distillate will have been collected, a sufficient amount to ensure that all the ammonia has been taken over. Care must be used not to allow any alkali to be carried over into the distillate during the distillation, since even a trace of caustic in the distillate will increase the basicity and cause erroneously high results. Use of the spray trap mentioned under *APPARATUS, Kjeldahl distillation unit*, has been found to make it virtually impossible for any caustic to be carried over. In addition, distillation should not continue after bumping commences or a total of 200 ml is in the receiver (see Note 3). 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 the distillate 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 0.1 *N* sulfuric acid until the endpoint is being approached. Finish the titration with 0.005 *N* sulfuric acid.

Reagent Blank

A reagent blank *must* be run each time a new lot of reagents is prepared. Run the reagent blank in the same manner as described for an unknown, with the exception that 100 ml of isooctane is extracted.

MERCURY REMOVAL FROM USED KJELDAHL SOLUTIONS

In order to minimize mercury residues going to the drain, solutions remaining in the Kjeldahl flasks after distillation are accumulated (settled) in gallon containers overnight and filtered.

An acceptable filtration setup would include a Buchner funnel, a vacuum filtration flask and a source of vacuum. Using 15 cm filter paper and adequate vacuum, one gallon of solution can be filtered in four hours.

Overnight settling and filtration using Whatman 42 paper are required to reduce mercury concentration to 20-40 wt-ppm in the filtrate.

Mercury collected on the filter paper should be treated as a solid toxic waste and stored until enough is collected to be sent for commercial processing to recover the mercury.⁴

CALCULATIONS

$$\text{Nitrogen, wt-ppm} = \frac{14,000 (VN + V_1N_1 - V_A N_1)}{W}$$

or

$$\text{Nitrogen, wt-\%} = \frac{1.4 (VN + V_1N_1 - V_A N_1)}{W}$$

where:

N = normality of strong standard acid

N₁ = normality of weak standard acid

V = volume of strong acid used in titrating sample, ml

V₁ = volume of weak acid used in titrating sample, ml

V_A = volume of standard acid used in titrating the blank, ml

W = weight of sample, g; or ml sample $\times$ sp gr, when sample is measured by volume

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. As soon as the contents of the Kjeldahl flask begin to “bump” during the distillation, turn off the heat immediately, since the bumping can become violent. Use of a safety shield is recommended. Asbestos tape has been helpful as a cushion to reduce flask breakage. Wind 1-inch width tape onto the ceramic plate in such a manner that the flask contacts the tape at 5 or 6 places.

3. The walls of the Kjeldahl flasks become thinner with continued use because of attack by the alkali added in the distillation step. Flasks should be discarded after 40 or 50 analyses, or upon any visible evidence of weakening.

4. 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.

5. The last traces of ammonia must be removed from the distillation equipment to avoid possible contamination of subsequent samples after high nitrogen content 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 water. If high and low nitrogen samples are both routinely analyzed, it is desirable to reserve particular glassware for the low (0-1 ppm) nitrogen determinations.

6. 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 ml volume of sulfuric acid. The temperature of the boiling sulfuric acid solution can be determined by a thermometer well inserted into the Kjeldahl flask so that the bottom of the well is beneath the liquid level of the sulfuric acid. A full-immersion, gas-filled, 500 C maximum thermometer can be used to measure the temperature of the boiling solution.

7. *Do not* insert any cotton or glass wool at the bottom of the thermometer well to act as a cushion for the thermometer. Such a cushion would raise the mercury bulb of the thermometer above the liquid level of the sulfuric acid in the Kjeldahl flask and give low temperature readings.

PRECISION

Duplicate determinations run in the same laboratory by the same operator on the same equipment should not differ from the mean by more than the percent relative in the table below.

Total Nitrogen, ppm	Percent, Relative
0.5	20
5	11
45	5
500	2

The estimated standard deviation was calculated to be 0.35 at the 16-ppm level, based on 5 replicate samples; 1.38 at the 54-ppm level, based on 6 replicates.

TIME FOR ANALYSIS

One man-hour is required for one analysis and 4 hours of elapsed time.

REFERENCES

1. Milner, O. I., Zahner, R. J., Hepner, L. S., and Cowell, W. H., *Anal. Chem.* **30**, 1528 (1958)
2. Lake, G. R., McCutchan, P., Van Meter, R., and Neel, J. C., *Anal. Chem.* **23**, 1634 (1951)
3. Nobel, E. D., *Anal. Chem.* **27**, 1413 (1955)
4. Mima, M. J., "Safe and Simple Method for the Disposal of Mercury-Containing Wastes from Kjeldahl Analysis." *Anal. Chem.* **46**, 14 (1974)