

TOTAL AMINE IN SOLUTIONS

UOP Method 828-81

SCOPE

This method is for determining total amine in amine solutions by the Kjeldahl technique. The molecular weight of the amine in the sample must be known or assumed to make the proper calculation. An amine concentration of 1 to 50 wt-% is typically determined.

OUTLINE OF METHOD

The amine sample is digested with concentrated sulfuric acid using specially purified reagents and precise time and temperature control. Following digestion, the ammonia formed is distilled from a strongly alkaline solution containing sodium thiosulfate. The liberated ammonia is absorbed in a saturated boric acid solution containing methyl purple indicator and is determined by titration with 0.05 *M* and 0.0025 *M* sulfuric acid.

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.; or the "Labconco Infinite Heat Control" heater, Cat. No. S-63065, available from Sargent-Welch Scientific Co., or equivalent apparatus.

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

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

Spray trap. (see Fig. 2), available from UOP Inc.

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

The following conventional equipment is also required:

Balance, capable of weighing to 0.1 mg

Beakers, 500- and 1000-mL

Bottle, polyethylene, 4-liter

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).

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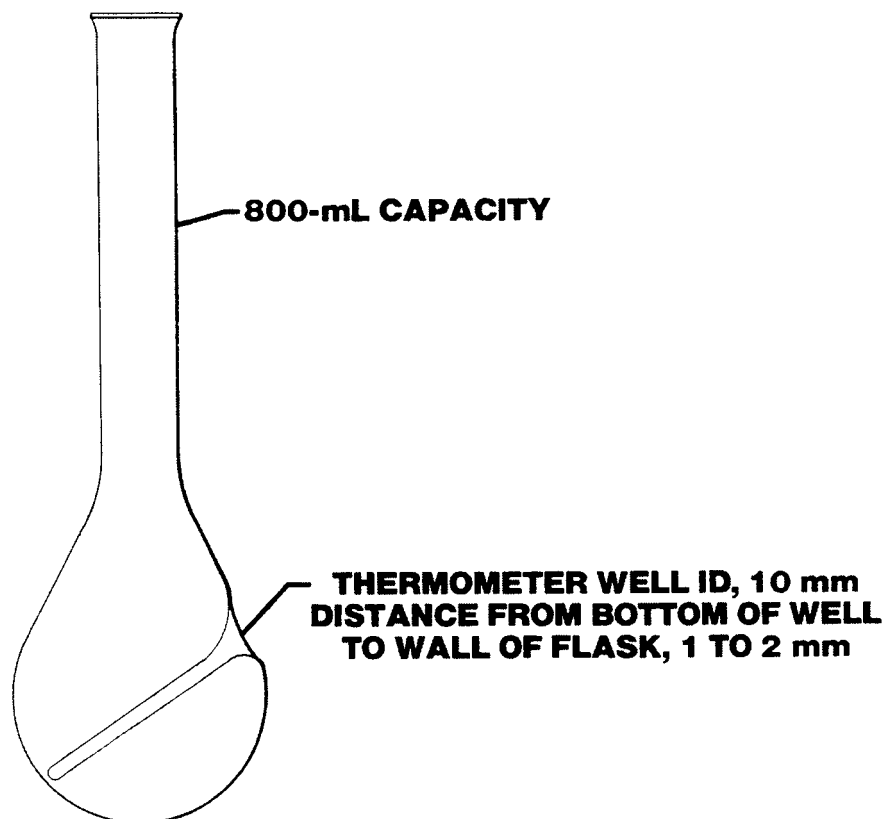


Figure 1

Kjeldahl Flask 800-mL, With Thermometer Well

Cylinder, graduated, 250- and 500-mL

Flask, Erlenmeyer, 500-mL

Flask, volumetric, 100-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.

Boiling chips, carborundum. 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. Available from Arthur H. Thomas Co., Cat. No. 1590-D30, or equivalent.

Boric acid, saturated. Dissolve approximately 40 g of boric acid crystals in one-liter of water.

Mercuric oxide

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

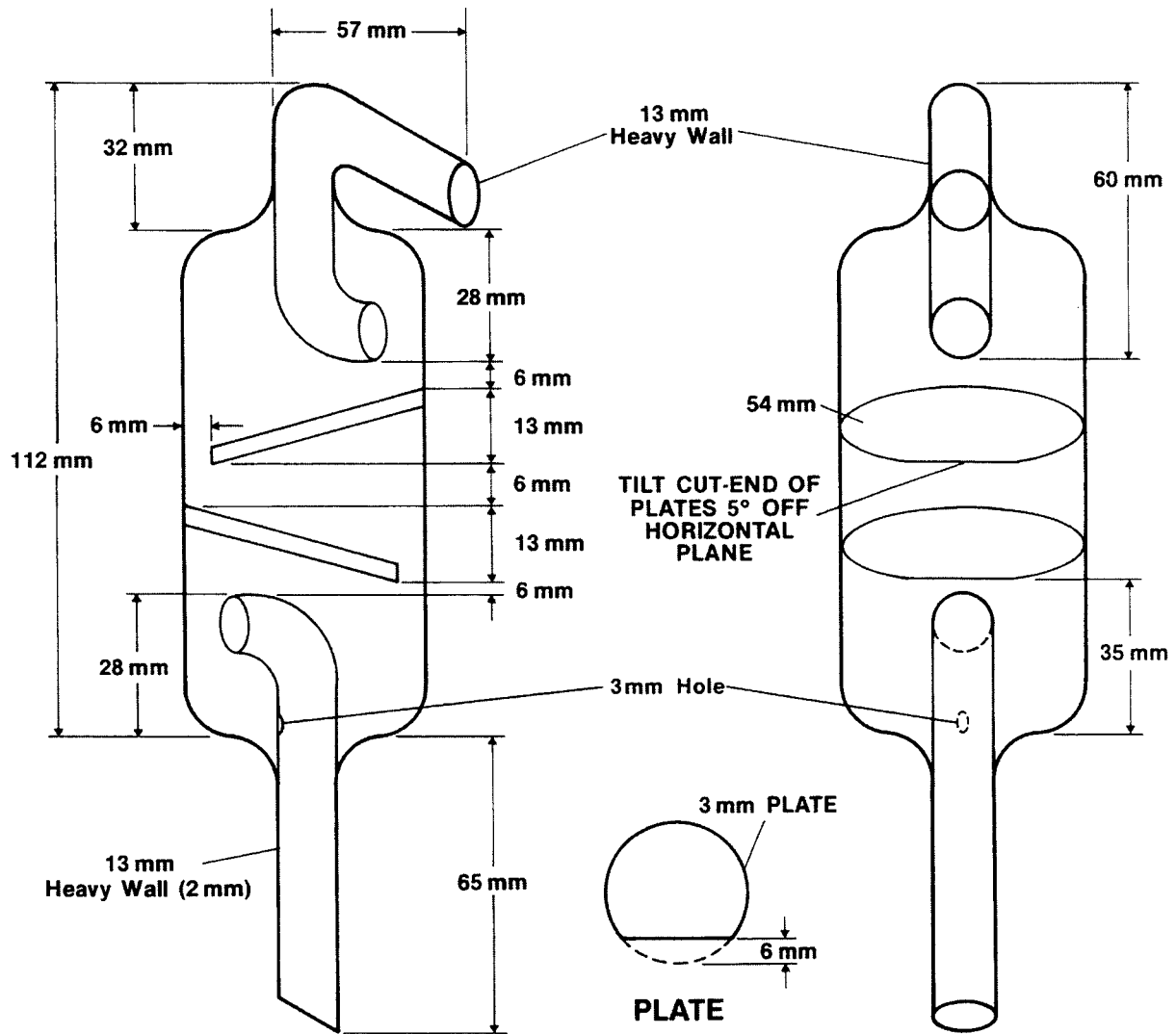


Figure 2
Spray Temp

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.

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., supplies a carbonate-free 50% sodium hydroxide solution, Cat. No. So-S-254.

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, 10g of 50% sodium hydroxide solution and few boiling chips. Boil until the solution turns yellow.

When the thiosulfate solution has cooled, pour it into a 4-liter polyethylene bottle. Add 4575 g of the 50% sodium hydroxide solution 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 Scientific Co., or equivalent.

Sulfuric acid, 0.05 M and 0.0025 M. Standardize by any acceptable method. Titration with tris(hydroxymethyl) aminomethane is recommended.

Sulfuric acid, concentrated. E. I. DuPont de Nemours and Company, 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.

Tris(hydroxymethyl)aminomethane, available as THAM from Fisher Scientific Co., or equivalent

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

Direct Sampling for High-Nitrogen Samples

Weigh one-gram to the nearest 0.1 mg of the sample into a 100-mL volumetric flask and dilute to the mark with water. Mix the contents and pipet a 10-mL aliquot into the 800-mL Kjeldahl flask modified 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. Add the acid slowly while the flask is inclined and rotate it in order to wet the inner wall.

Digestion

Prior to starting the analysis, put on protective clothing (see Notes 2, 3 and 4).

Wrap the upper 2 to 5 cm 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 practical 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 Notes 6 and 7). The digestion is timed when this temperature is reached and continued for one 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 380 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 one hour at the same reflux rate.

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 0.05 *M* sulfuric acid until the endpoint is being approached. Finish the titration with 0.0025 *M* sulfuric acid until a purple tint is exhibited.

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, using 0.0025 *M* sulfuric acid for the titration.

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 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, four liters of solution can be filtered in four hours.

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

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.

CALCULATIONS

Calculate the wt-% amine in the sample where it is assumed that all the free amine present corresponds to either MEA, mol-wt 61, or DEA, mol-wt 105.

$$\text{Amine, wt-\%} = \frac{0.2A(VM + V_1M_1 - V_aM_1)}{W}$$

where:

- A** = molecular weight of the amine
- M** = molarity of strong standard sulfuric acid
- M₁** = molarity of weak standard sulfuric acid
- V** = volume of strong standard sulfuric acid used in titrating the sample, mL
- V₁** = volume of weak standard sulfuric acid used in titrating the sample, mL
- V_a** = volume of weak standard sulfuric acid used in titrating the blank, mL
- W** = weight of sample in 10-mL aliquot, g

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 begins to “bump” during the distillation, turn off the heat immediately, since the bumping can become violent. Use of a safety shield is recommended. Glass wool has been helpful as a cushion to reduce flask breakage. Wind 2.5-cm 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 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.

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 to 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

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.

TIME FOR ANALYSIS

The elapsed time for one analysis is 4 hours. The labor requirement is one hour.

REFERENCES

1. UOP Method 384
2. Method SM-33, The Girdler Corp., Louisville, KY

SUGGESTED SUPPLIERS

E. I. DuPont de Nemours and Co., 4251 S. Crawford Ave., Chicago, IL 60632
Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143
Precision Scientific Co., 3737 Cortland Ave., Chicago, IL 60647
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
Arthur H. Thomas Co., P.O. Box 779, Philadelphia, PA 19105
UOP Inc., Ten UOP Plaza, Des Plaines, IL 60016