

BASIC NITROGEN IN GASES BY LOW TEMPERATURE ACID SCRUBBING

UOP Method 315-59

SCOPE

This is a method for determining basic nitrogen compounds in refinery gases in the region of 0.1 to several hundred parts per million. It can be used for gases which are largely condensable by dry ice-acetone mixture, such as stabilizer gas and polymerization unit feed stocks; and also for gases which are low in condensables, such as recycle gas from catalytic reforming units or catalytic hydrogen treating units. The procedure will not distinguish between ammonia and low-boiling amines.

OUTLINE OF METHOD

The sample is passed into an essentially non-aqueous solution of sulfuric acid in acetone, kept at dry ice-acetone temperature, where the condensable hydrocarbons and basic compounds are retained. Quantitative retention of the basic compounds is ensured by low-temperature scrubbing through an acid solution and also by condensation of the bases along with the hydrocarbons.

Following sampling, the weight of condensables is determined and then they are evaporated. The remaining solution of sulfuric acid in acetone is diluted with water and analyzed for basic nitrogen by a conventional Kjeldahl distillation; i.e., strong alkali is added and the bases distilled into a solution of boric acid. The volatilized bases are titrated with standard acid to the methyl purple endpoint.

It is preferred that samples be taken directly into the apparatus at the refinery for analyses to avoid loss of ammonia by adsorption on the steel walls. However, if necessary to remove a sample for further laboratory study, a stainless steel cylinder with stainless steel fittings and valves should be used.

APPARATUS

(a) General

Cylinder, stainless steel with stainless steel fittings and valves, 1- to 2-liter

Flask, Kjeldahl, 800-ml

Gas meter, wet test

Distillation apparatus, Kjeldahl

Pipet, gas sampling, 1-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).

- (b) For samples having low content of condensables

Flask, condensing, glass, as shown in Fig. 1

Flask, Dewar, 1-qt

Trap, evaporation, filled with glass rods as shown in Fig. 2. Fit with **3** 19/38 male and female glass joints to fit condensing flask shown in Fig. 1.

- (c) For samples having high content of condensables

Flask, condensing, glass, as shown in Fig. 2

Flask, Dewar, 1-gal

Trap, evaporation, filled with glass rods as shown in Fig. 2.

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 deionized or distilled water.

Acetone

Boiling chips

Boric acid, saturated aqueous solution

Dry ice

Methyl purple indicator, approximately 1%, aqueous. Available from Fleisher Chemical Co., Washington, D. C. 20004

Sodium hydroxide, 50% aqueous solution. Fisher Scientific Co. supplies a carbonate-free 50% NaOH solution, Cat. No. 50-S-254. Heat the solution, strip with high-purity nitrogen to remove ammonia, filter through glass wool and store in a polyethylene bottle.

Sulfuric acid, standard solutions, 0.01 *N* and 0.005 *N*

Sulfuric acid, 1% by volume

PROCEDURE

I. Sampling

Samples taken in stainless steel cylinders must be analyzed within 24 hours following sampling. It has been found that samples taken in stainless steel cylinders, equipped with stainless steel fittings and valves, show a loss of approximately 10% of the basic nitrogen content per day of storage. This loss is probably due to adsorption of basic nitrogen on the interior walls of the cylinder.

The apparatus and procedure used for obtaining the sample vary slightly according to the type of sample being analyzed. Samples having a low content of condensables require the procedure given in *Section A*. Samples having a high content of condensables require the procedure given in *Section B*.

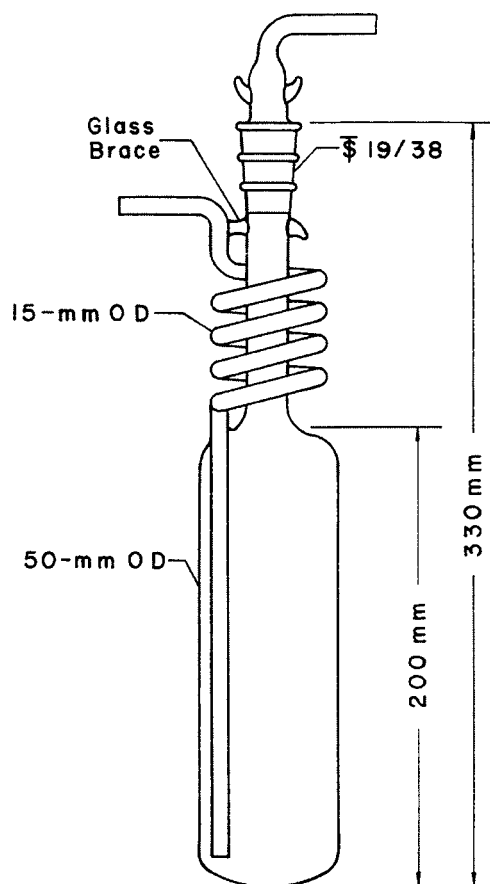


Figure 1

Condensing Flask for Sample Having Low Content of Condensables

A. Samples Having Low Content of Condensables

Partially fill the 1-qt Dewar flask with acetone and cautiously add crushed dry ice until the effervescence, which is violent at first, practically ceases. Add 50 ml of the sulfuric acid in acetone solution into the small dry condensing flask (Fig. 1) and carefully dip it into the dry ice-acetone bath. Cautiously add excess dry ice and additional acetone to fill the Dewar flask. Continue to add dry ice as required throughout the sampling period to maintain an excess.

Connect the evaporation trap to the condensing flask. Pour 25 ml of 1% sulfuric acid into the top of the evaporation trap and allow the acid to drain into the condensing flask in order that the glass rod packing is wet with sulfuric acid. Connect the exit tube of the evaporation trap to the wet test meter. Record the initial reading of the meter, the temperature and the barometric pressure. Connect the sample tap to the inlet tube of the condensing flask and introduce the sample into the flask. The rate of passage of gas through the meter should not exceed 6 cu ft/hr. Collect a sample of uncondensed gas in the gas sampling pipet and determine the specific gravity of the gas against air. This can be collected from the outlet of the wet test meter after metering has begun.

When sufficient sample has been taken (as much as 20 cu ft is needed for samples having very low concentrations of basic nitrogen) stop the flow and record the final meter reading. Note: The amount

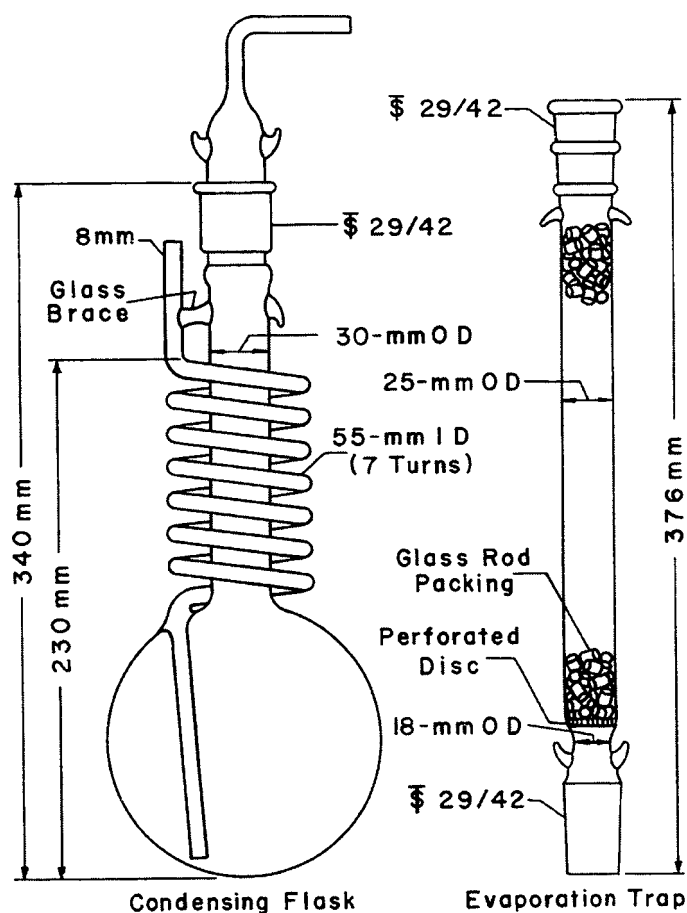


Figure 2

Condensing Flask and Accessories for Sample Having High Content of Condensables

of condensables ordinarily present in a catalytic reformer recycle gas is negligible and can be ignored. However, if it is desired to include the condensables in the sample weight, proceed as in *Section B - 2*.

Disconnect the exit tube from the wet test meter and remove the condensing flask, with attached evaporation trap, from the dry ice trap. Add water to the evaporation trap and allow it to drain into the condensing flask. Detach the evaporation trap from the condensing flask and quantitatively transfer the solution to a Kjeldahl flask. Wash the condensing flask with water and add the washings to the Kjeldahl flask to bring total volume to 400 ml. This solution should be acidic. If it is not, too large a sample has been taken. Discard it and take a smaller sample. Cool the contents of the Kjeldahl flask in an ice bath. Distill as described in *Section II, "Distillation and Titration."*

B. Samples Having High Content of Condensables

The procedure used for obtaining samples having a high content of condensables also varies slightly, depending on what method is used to determine the amount of sample taken. For cases where the total sample is measured as a gas, use the procedure given in *Section B - 1*. For cases where the amount of sample is determined from the weight of condensables plus the volume of non-condensables, follow the procedure given in *Section B - 2*.

1. *Cases Where the Total Sample Is Measured as a Gas*

Follow the procedure given in *Section A*, using the large condensing flask (Fig. 2) to obtain the sample. Determine the specific gravity of the total gas sample (i.e. before passage through the condensing flask) compared to air. This sample may be obtained during the course of the analysis by stopping the sampling of the gas and obtaining the sample for the gravity determination directly from the sample tap.

When sufficient sample has been taken stop its flow, detach the inlet tube of the condensing flask from the sample tap and close the inlet tube of the flask by a small cork stopper. Remove the flask from the dry ice trap and let it stand on a cork ring. Disconnect the exit tube from the evaporation trap and pour 25 ml of 1% sulfuric acid into the evaporation trap. Reconnect the exit tube to the trap and allow the condensed gases to evaporate and pass through the meter. This step can be hastened by careful immersion of the flask in a water bath at 60 C. Since the gases are flammable and may contain poisonous hydrogen sulfide, vent them to a hood or outdoors. When all the condensed gases have evaporated, record the final meter reading.

Detach the exit tube from the evaporation trap and wash it with water, allowing the washings to drain into the condensing flask. Quantitatively transfer the solution to a Kjeldahl flask, adding water to bring total volume to 400 ml and cool in an ice bath. Distill as described in *Section II*, "*Distillation and Titration*."

2. *Cases Where the Amount of Sample Is Determined from the Weight of Condensables and the Volume of Non-Condensables*

Follow the procedure given in *Section A*, but use the large condensing flask (Fig. 2) with the following additions: Obtain the weight of the condensing flask containing the sulfuric acid in acetone solution prior to sampling by carefully dipping the flask into the dry ice-acetone bath until all the coils of the flask are immersed. Remove the flask from the bath, quickly wipe the bottom, set it upon a cork ring on a pan balance, weigh rapidly to the nearest gram and record this as tare weight. Determine the specific gravity of the uncondensed gas sample (i.e. after passage through the condensing flask) compared to air. The gas sample used to determine the specific gravity can be collected from the outlet of the wet test meter after the passage of sufficient gas to flush the meter. If the sample contains only condensables, the sample will be completely retained in the condensing flask, and the meter will indicate no gas passage.

When sufficient sample has been taken, stop its flow, detach the condensing flask and rapidly weigh as before. Record the net weight and meter reading. In most cases a 400 g sample is adequate, but the amount of sample should be increased when extremely low concentrations are involved.

Place the condensing flask on a cork ring in a hood. Replace the evaporation trap and add 25 ml of 0.005 *N* aqueous sulfuric acid. The rapid evaporation of the condensables will keep a "plug" of 0.005 *N* sulfuric acid from draining through to the condensing flask. The possible loss of basic nitrogen through rapid evaporation thus is held to a minimum since the gas must bubble through this liquid "plug". Vent the condensed gases to the atmosphere and do not pass them through the wet test meter. Again the precaution of venting to a hood or outdoors should be observed.

When all the condensed gases have been evaporated, pour 100 ml of water into the top of the evaporation trap. Allow water to drain through to the condensing flask. Transfer the solution quantitatively to a Kjeldahl flask. Wash the condensing flask and coils with additional water and transfer to the Kjeldahl flask until the total volume is brought to 400 ml. Cool the solution in an ice bath.

II. Distillation and Titration

Place a 500-ml Erlenmeyer flask containing 25 ml of boric acid solution under the condenser of the Kjeldahl distillation apparatus so that the tip is well beneath the surface of the liquid. Add a few boiling

chips to the cooled contents of the Kjeldahl flask. Slowly pour 25 ml of nitrogen-stripped 50% sodium hydroxide solution down the inclined neck of the Kjeldahl flask. Connect the flask to the distillation condenser and swirl the flask contents.

Heat the distillation flask so that rapid boiling is established and maintained. When the volume of liquid in the receiving flask reaches approximately 130 ml, lower the receiver to expose the condenser tip and rinse it with water. After about 1 minute of additional distillation, turn off the heat and allow the condenser tube to drain.

The distillate receiver contents may contain a hydrocarbon layer resulting from liquid hydrocarbon contained in the sample. To facilitate the titration and avoid interference in detecting color change of the indicator, transfer the distillate to a separatory funnel and separate the hydrocarbon layer from the aqueous layer. Return the aqueous layer to the receiver flask, wash the hydrocarbon with water and add the washings to the receiver flask.

Add 5 drops of methyl purple indicator and titrate the receiver contents with standard sulfuric acid until, first, the green color fades into gray and then, just beyond, to the point where the gray assumes the first faint tinge of purplish pink. The strength of sulfuric acid for the titration is governed by the basic nitrogen content — for samples which have low concentration use 0.005 *N* acid; for those with higher concentration use 0.01 *N* acid.

In some cases the distillate will be slightly turbid, due to the presence of hydrocarbons of higher molecular weight than butane. If the turbidity is such that the endpoint cannot be seen sharply, extraction with methyl isobutyl ketone is necessary.

Transfer the turbid distillate to a 500-ml separatory funnel and add 50 ml of water-washed methyl isobutyl ketone. Shake for 2 minutes and allow the aqueous layer to separate from the hydrocarbon layer. Draw off the aqueous portion into a 500-ml Erlenmeyer flask. Add 25 ml of water to the separatory funnel and shake for 2 minutes. Allow the layers to separate and draw off the aqueous layer into the Erlenmeyer flask. Add 5 drops of methyl purple indicator and titrate with standard sulfuric acid to the purplish pink endpoint.

Determine a reagent blank by following the distillation and titration procedure. Use the same amount of reagents as in the analysis.

CALCULATIONS

A. Weight of Non - Condensed Gas

$$\text{Non - condensed gas, g} = V \times C \times 34.61 \times G$$

where:

C = factor for converting the metered gas volume to STP (standard temperature and pressure of 60 F and 760 mm of Hg, Note 1)

G = specific gravity of non - condensed gas (sp gr of air = 1.000)

V = metered volume before correction to STP, cu ft

Note 1 — **C** can be conveniently ascertained from the Gas Volume Correction Charts, Figs. 3 and 4. Alternatively, it can be calculated from the formula:

$$C = \frac{(P - P_w)}{760} \times \frac{520}{460 + t}$$

where:

P = meter pressure, mm Hg

P_w = vapor pressure of water at temperature *t*, mm Hg

t = meter temperature, °F

B. Calculations Based on Weight of Sample, wt-ppm Basic Nitrogen

$$\text{Basic nitrogen, wt-ppm} = \frac{(A - B) \times N \times 14000}{W}$$

where:

A = volume of standard acid required to titrate sample, ml

B = volume of standard acid required to titrate blank, ml

N = normality of standard acid

W = total weight of sample (includes condensed and uncondensed gas), g

Both methods assume that the gas is saturated with water when it is metered. For greatest accuracy it is desirable to insert a water saturator upstream from the wet test meter.

C. Calculations Based on Volume of Sample, mol-ppm NH₃

$$\text{NH}_3, \text{ mol-ppm} = \frac{(A - B) \times N \times 837}{V \times C}$$

where:

V = metered volume before correction to STP, cu ft

A, B, C and **N** are as previously defined

PRECAUTIONS

Due to the extremely low concentrations of basic nitrogen sought, care must be taken to prevent contamination from outside sources. Use clean equipment and reagents which are suitable for Kjeldahl determinations.

Keep the distillation receiver away from flames during the distillation step because flammable vapors may be present.

Avoid the development of excessive hydrostatic pressure when using a steel cylinder for sample transfer by not filling the cylinder to more than 75% of its liquid capacity.

PRECISION

The following data should be used for judging the acceptability of results.

Duplicate results by the same operator should be considered suspect if they differ by more than the amounts tabulated below. These data are based on analyses of butane samples.

Range	
<u>Wt-ppm Basic N</u>	<u>Repeatability</u>
0.0 to 0.5	0.05
0.5 to 1.0	0.15
1.0 to 10	0.2

REFERENCE

Donn, L. and Levin, H., *Ind. Eng. Chem., Anal. Ed.*, **18**, 596 (1946)

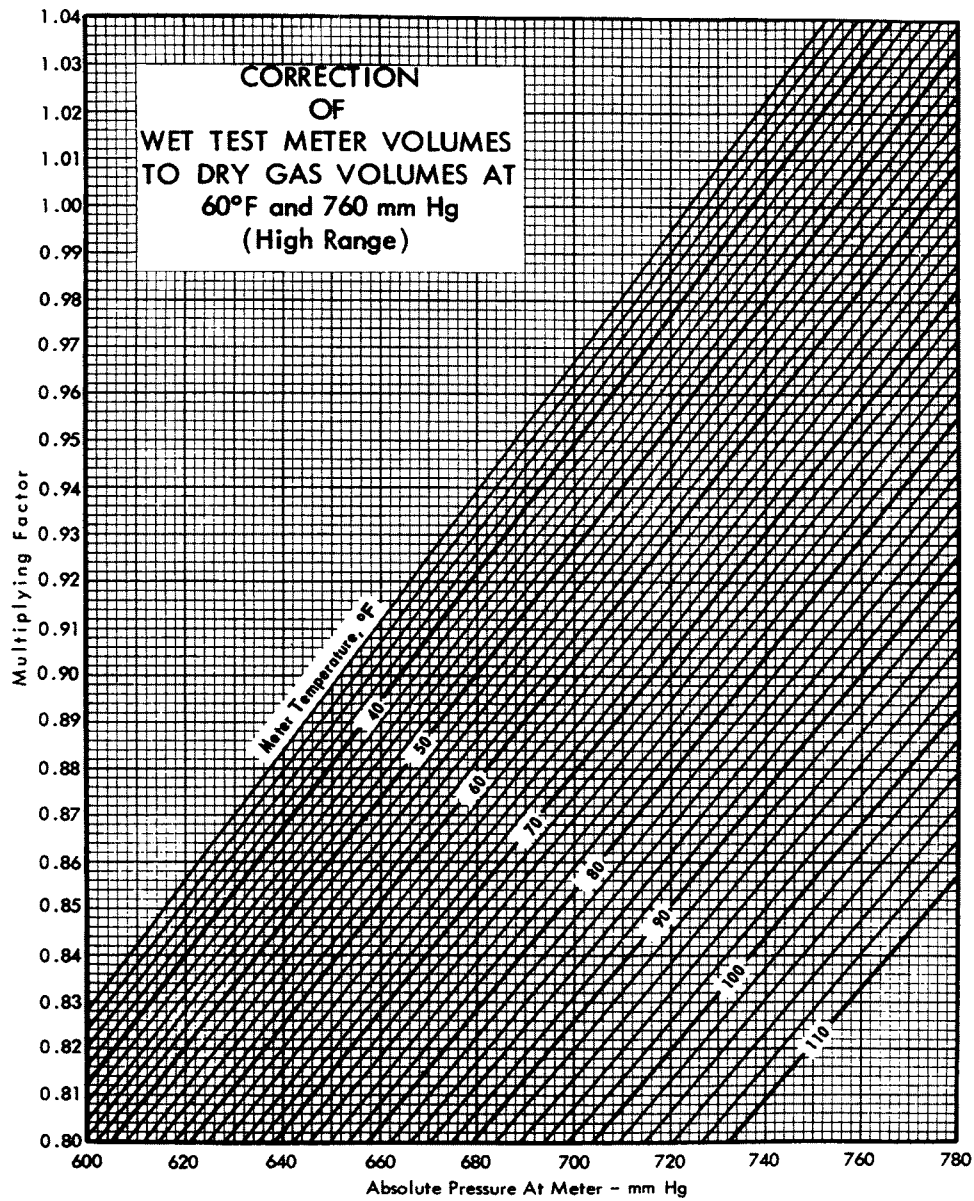


Figure 3

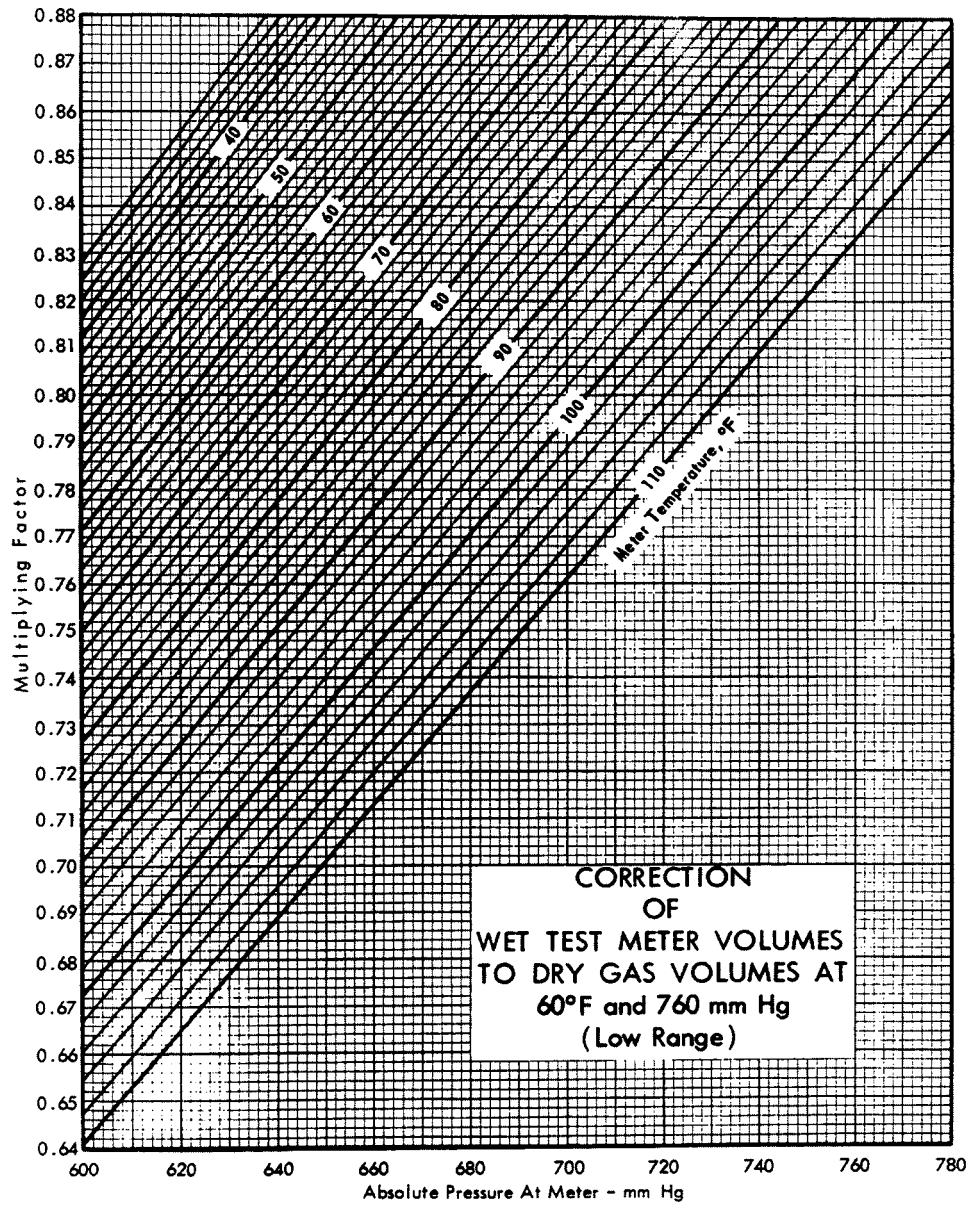


Figure 4