

BASIC NITROGEN IN GASES BY ACID SCRUBBING

UOP Method 430-70T

SCOPE

This method is intended for determination of basic nitrogen in gases in the range of 0.05 to several hundred weight parts per million. It can be used for liquefied gases, such as stabilizer gas and polymerization unit feed stocks; also for gases such as hydrogen recycle gas from catalytic hydrotreating units. A titrimetric analysis used for samples containing more than 3 wt-ppm nitrogen determines the sum of ammonia and amines. A spectrophotometric analysis used below 3 wt-ppm nitrogen determines only ammonia.

OUTLINE OF METHOD

The gas is passed into a gas washing bottle containing dilute acid which removes ammonia and amines. Ammonia determination may be concluded spectrophotometrically by conversion to indophenol, this procedure being recommended for samples containing less than 3 ppm of ammonia. Ammonia and volatile amines may also be determined by conventional Kjeldahl distillation; i.e., strong alkali is added and the ammonia, with such amines as are volatilized by a Kjeldahl distillation, is distilled into a solution of boric acid. The volatilized bases are titrated with standard acid to the methyl purple endpoint.

It is preferable to scrub samples at the sample source and to analyze the scrubber solutions in the laboratory, since samples taken in a bomb lose ammonia because of adsorption on bomb walls. However, if it is necessary to transport a sample for laboratory scrubbing, a stainless steel cylinder equipped with stainless steel fittings and valves is used.

In the case of hydrogen recycle gas, sampling is carried out directly on the unit.

APPARATUS

General

Bomb, stainless steel, 1- to 2- liter, equipped with stainless steel fittings and 2 valves. The stainless steel should be of non-magnetic quality.

Expansion valve, laboratory, 18-8 Whitey stainless steel valve and fittings. Wrap the valve with electrical heating tape using a variable transformer to control the temperature of the heating tape. (See Fig. 1 for laboratory expansion valve set-up.)

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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Expansion valve, refinery, 18-8 Whitey stainless steel valve and fittings. Since electrically heated expansion valves are not permissible in refineries, a hot water expansion system is used for scrubbing of an on-stream sample (see Fig. 2 for refinery expansion valve apparatus set-up).

Gas meter, wet test, a calibrated gas receiver or, alternatively, a Toledo Scale or balance capable of weighing 2-5 kg to the nearest 0.5 g

Scrubbers, gas, modified Dreschel type, tall-form, fritted cylinder, porosity "C", F joint 29/42, Pyrex, Corning No. 31770, 250-ml capacity, 200-mm height to F cone, 51-mm OD

Spectrophotometric Method

For scrubblings containing less than 3 ppm, but not less than 0.05 ppm of ammonia:

Absorption cell, spectrophotometric, 5-cm cell path

Cylinder, graduated, mixing, F stopper, calibrated, 50-ml capacity

Flasks, volumetric, 50- and 200-ml

Pipets, 2-, 4-, 10-, and 20-ml

Spectrophotometer

Water bath, 70 ± 1 C

Titrimetric Method

For scrubblings containing more than 3 ppm of ammonia and volatile amines:

Burets, 50-ml

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, such as E. H. Sargent & Co., Cat. No. S - 63545 or S - 63465.

Flasks, Erlenmeyer, 500-ml

Flask, Kjeldahl, 800-ml

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified (see Note 1). References to water mean deionized or distilled water.

Spectrophotometric Method

Hydrochloric acid, 0.001 N

Manganese sulfate, 0.00024 M. Dissolve 53 mg of manganese sulfate tetrahydrate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, in 200 ml of water, add 25 ml of acetone, dilute to 1 liter with water and mix.

Nitrogen standard solutions, (Stock Solutions “A” and “B”. Dry NH_4Cl for one hour at 110 C. Weigh exactly 0.7638 g of the dried salt, transfer to a 1-liter volumetric flask and dilute to the mark with freshly distilled or deionized water. This is Stock Solution “A” and contains 200 $\gamma\text{N/ml}$. Pipet 25 ml of Stock Solution “A” into a 500-ml volumetric flask and dilute to the mark with freshly distilled or deionized water. This is Stock Solution “B” and contains 10 $\gamma\text{N/ml}$.

Sodium hypochlorite, 0.90 g of available chlorine per 100 ml. Commercial bleach, such as “Clorox,” is suitable for preparing this solution by diluting 180 ml with water to 500 ml. Determine the activity of the solution by iodometric titration. (Add potassium iodide and dilute sulfuric acid to allow the available chlorine to oxidize iodide ion to iodine. Use 0.1 *N* sodium thiosulfate as titrant and 1% starch indicator solution). While this reagent is reasonably stable, discard it at 1- to 2- week intervals. Always use a fresh bottle of bleach when preparing a new batch.

Sodium phenolate solution. Dissolve 25.0 g of phenol in 150 ml of water. Dissolve 10.8 g of sodium hydroxide in 100 ml of water containing boiling chips. Boil the sodium hydroxide solution until approximately 50 ml remains (see Note 2). Add the ammonia-free sodium hydroxide solution to the phenol and dilute the mixture to 250 ml with water. Prepare this solution fresh daily.

Titrimetric Method

Boiling chips. Carborundum crystals supplied by Cenco Instruments Corp. are satisfactory.

Boric acid, saturated aqueous solution

Methyl purple indicator, 0.1% aqueous solution, available from Fleisher Chemical Co., Benjamin Franklin Station, Washington, D. C. 20004

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

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

Sulfuric acid, 20 wt-% aqueous solution. Dilute approximately 123 ml of concentrated acid by cautiously adding the acid to about 800 ml of chilled, deionized water. Dilute to a final volume of 1 liter.

BOMB SAMPLING

Sample a refinery unit stream in the following manner: Flush the sample line to remove dirt, water and air. Connect a clean (see Notes 3 and 4) and dry 1-liter stainless steel bomb to the sample tap, using steel pipe or tubing. Do *not* use copper tubing or brass fittings. Arrange the bomb in a vertical position and then open the top valve of the bomb all the way. Open the valve of the sample line. Slowly open the valve on the bottom of the bomb. Allow enough vapor to flow upward through the bomb to purge the sample line and bomb of all air. Close the top valve of the bomb completely and then open the bottom valve of the bomb all the way. Open the top valve of bomb enough to allow liquid to vent from the top valve for 2 to 5 minutes. Close the top valve of the bomb and then the bottom valve of the bomb. Close the valve on the sample line. Disconnect the bomb from the sample line and immediately vent off about 100 ml of liquid from the bottom valve while the bomb is in a vertical position. Measure the 100-ml outage by allowing the liquid to flow out of the bomb at the fastest possible rate into a flask or beaker marked at the 100-ml volume. Connect the bomb to an electrical ground during venting. Avoid transferring the sample from one bomb to another whenever possible.

Samples taken in stainless steel bombs must be analyzed no later than 24 hours after sampling. Losses amount to approximately 10% of the basic nitrogen content per day of storage, and probably result from adsorption of basic nitrogen on the interior walls.

GAS SCRUBBING

In the Laboratory

If the scrubbing of the sample is to be carried out in the laboratory, use an electrically-heated gas expansion valve. Fig. 1 shows the bomb attached to the expansion valve apparatus. Wrap the heating tape only around the valve and *not* on the upstream tubing. Heating the tubing upstream from the valve causes boiling of the liquid in the sample line and permits ammonia to migrate back into the bomb. The temperature of the expansion valve, 70 - 80 F, is controlled by a variable transformer. During the actual scrubbing, the valve on the sample bomb is wide open. The expansion valve is also the flow control. If the valve on the bomb is used to control the flow, distillation will occur at the valve because of the cooling effect of the expanding gas. This, in turn, could result in leaving the heavier molecular weight amines behind. Weight of the sample scrubbed can be determined either by metering or by bomb weight difference.

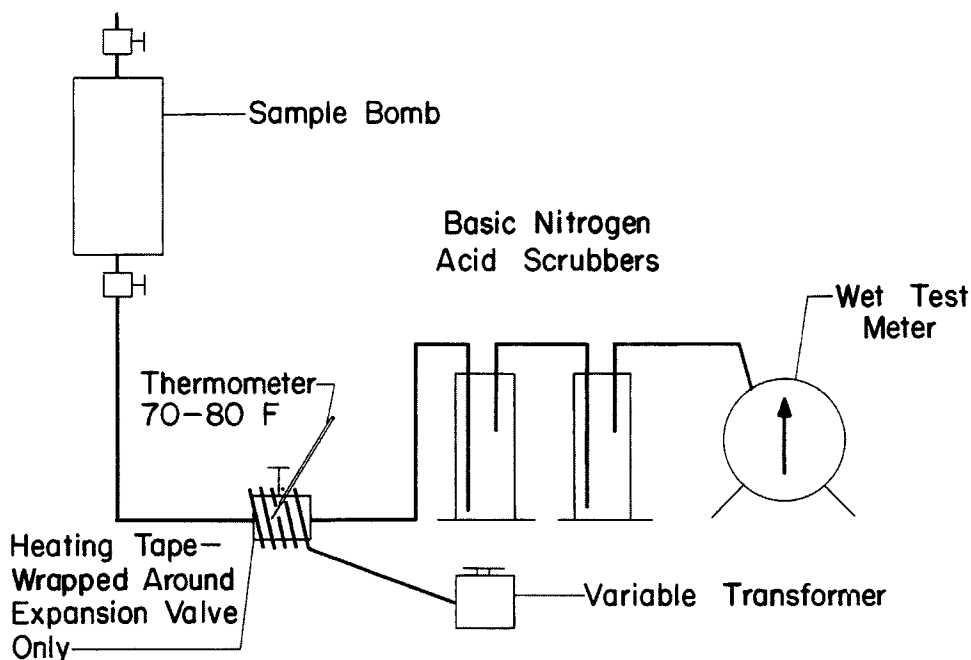


Figure 1

Laboratory Gas Expansion Valve and Scrubbing Apparatus

Prepare 2 gas scrubbers. If it is estimated that the concentration will be less than 3 ppm of ammonia, put 130 ml of 0.001 *N* hydrochloric acid in each scrubber and, after scrubbing, proceed with the spectrophotometric method. Otherwise, put 150 ml of 20% sulfuric acid in each scrubber and, after scrubbing, proceed with the titrimetric method.

Attach the sample source to the inlet of the first scrubber. Attach the exit tube of the gas scrubber to the inlet of the second scrubber which contains 130 ml of the same scrubber solution. The second scrubber should contain no ammonia after scrubbing, and is used only as a check, whenever required, to determine if the first stage of scrubbing has been quantitative.

Attach a wet test meter to the exit tube of the second gas scrubber. Adjust the gas flow to a rate of 1.5-2.0 cu ft/hr. The scrubbing time required depends on the concentration of ammonia in the gas stream.

Recommended Scrubbing Conditions

Expected ppm NH ₃	Scrubbing Rate, cu ft/hr	Method	Size of Sample, cu ft
0.05	2	Spectrophotometric	6
2.5	2	Spectrophotometric	1
3.0	2	Titrimetric	1

Record the scrubbing rate in cubic feet per hour and duration of scrubbing for calculations, as well as meter pressure in millimeters of mercury and meter temperature in degrees Fahrenheit.

In the Refinery

When the scrubbing of a gas sample is to be carried out in a refinery, an electrically-heated expansion valve cannot be used because of the danger of explosion. Therefore, an expansion valve heated by warm water is employed. Fig. 2 shows the vaporization apparatus used in on-stream scrubbing at the refinery and sources of heat and coolant.

A cold water jacket upstream of the expansion valve is necessary when using warm water to heat the valve. Heating the line upstream from the valve by conduction would cause boiling of the liquid in the line and result in migration of the ammonia upstream.

Use the scrubbing conditions previously specified.

PROCEDURE

A. Spectrophotometric Method for 0.05-3.0 ppm of Ammonia

Transfer the contents of the first scrubber to a 200-ml volumetric flask. Wash the gas bottle and fritted tip with water and blow out any liquid held up in the fritted tip to achieve quantitative transfer. Dilute the sample to 200 ml with water and mix.

Transfer 20 ml of the diluted scrubber solution to a 50-ml mixing cylinder. Add 2 ml of manganese sulfate solution. Dilute to 36 ml with water, mix well and add 10 ml of sodium phenolate solution. Add 4 ml of sodium hypochlorite reagent, mix well and heat 10 minutes at 70 C. Cool in ice water to room temperature. Transfer a portion of the cooled solution to fill a 5-cm cell and measure the absorbance at 625 mμ using water as reference.

At this point prepare a standard solution of known nitrogen content as follows: Pipet 1 ml of Stock Solution "B" into a 50-ml mixing cylinder and dilute to 34 ml with water. Make up this solution to a final volume of 50 ml in the same manner as the sample solution. It will contain 10 γ of nitrogen per 50 ml. Run a standard solution with each group of samples because small variations can affect the color intensity.

Determine a reagent blank by substituting for the sample scrubber solution 130 ml of unused scrubber acid and repeating the above procedure.

If there is reason to suspect less than quantitative absorption in the first scrubber (e.g., surges in gas flow) determine the ammonia in the second scrubber in the same manner.

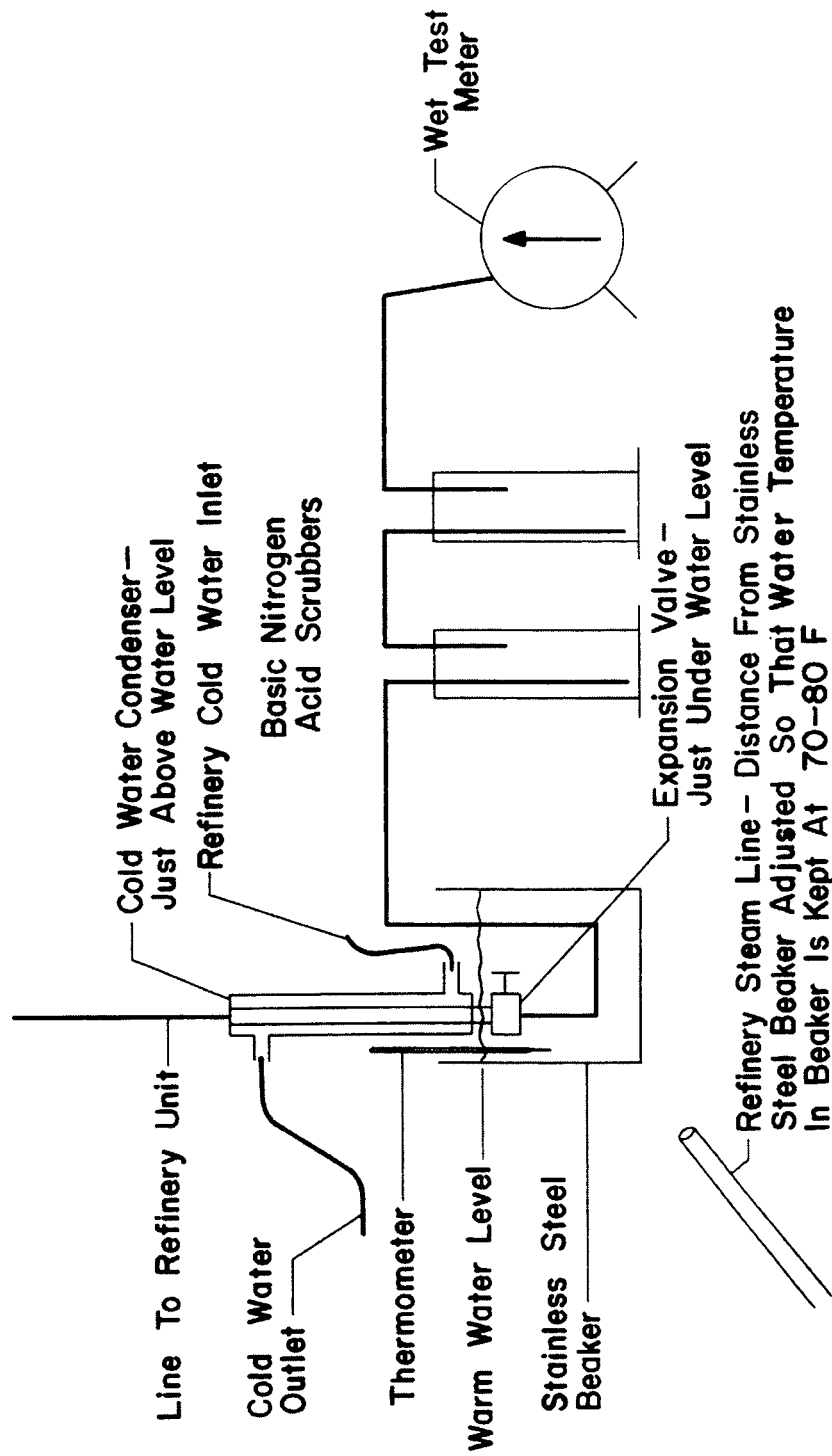


Figure 2

Refinery Gas Expansion Valve And Scrubbing Apparatus

B. Titrimetric Method for More than 3 ppm of Ammonia

Transfer the contents of the first scrubber to an 800-ml Kjeldahl flask using sufficient water in washing the bottle and fritted tip to bring the total volume to about 400 ml. Cool the flask in an ice bath and add a few boiling chips. While the flask is cooling, thoroughly rinse the distillation apparatus with freshly distilled or deionized water. Place 25 ml of the boric acid solution in a 500-ml Erlenmeyer flask and position it on the distillation rack so that the condenser tip is 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 causing any pressure build-up.

When the digestion flask is cold and the receiver is in place, slowly pour 100 ml of the low-nitrogen 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 flask so that rapid boiling is established and maintained. When the volume of liquid in the receiving flask reaches 130 ml, lower the receiver to expose the condenser tip and rinse it with water. After about one minute of additional distillation, turn off the heat and allow the condenser tube to drain (see Note 5).

If the distillate contains a hydrocarbon layer, remove it by transferring the receiver contents to a separatory funnel and returning the aqueous phase to the receiver. Weigh the hydrocarbon condensate and record the weight.

Add 5 drops of methyl purple indicator to the aqueous phase and titrate with standard 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 normality of sulfuric acid for the titration is governed by the basic nitrogen content: for samples which have low concentrations use 0.005 *N* acid; 0.01 *N* acid for higher concentrations.

Determine a reagent blank by following the distillation and titration procedure, substituting for the sample scrubber solution 130 ml of unused scrubber acid.

If there is reason to suspect less than quantitative absorption in the first scrubber (e.g., surges in gas flow) determine the ammonia in the second scrubber in the same manner.

CALCULATIONS

Spectrophotometric Method

$$\text{Basic nitrogen, wt - ppm} = \frac{GQ(A_s - A_b)}{A_k R (28.3 \text{ VCD} + g)}$$

where:

- G** = nitrogen in the 50 ml of 10- γ standard solution, γ
- A_s** = absorbance of the color developed sample solution at 625 m μ
- A_b** = absorbance of the color developed blank solution at 625 m μ
- A_k** = absorbance of the color developed standard solution at 625 m μ
- Q** = volume to which scrubber solution is originally diluted, ml
- R** = volume of aliquot taken for measurement, ml
- V** = metered volume at temperature *t* and system pressure, cu ft

D = gas density at 760 mm Hg and 60 F, g/l (obtain by ASTM Method D 1070 or UOP Method 113)

g = weight of hydrocarbon condensate collected in gas washing bottles and separated in separatory funnel, g

C = correction factor. Ascertain from the appropriate gas volume correction charts supplied. Alternatively, calculate from the formula:

$$C = \left(\frac{P - p}{760} \right) \left(\frac{520}{460 + t} \right)$$

where:

P = pressure of gas in wet test meter, mm Hg. (The sum of atmospheric pressure plus pressure on the meter.)

p = vapor pressure of water at temperature *t*, mm Hg (literature)

t = meter temperature, °F

Alternatively, it is often desirable to express the nitrogen concentration in mol-ppm, particularly when the sample is completely gaseous and contains no liquid condensate. Calculate as follows:

$$\text{Basic nitrogen, mol - ppm} = \frac{0.0596 \text{ GQ} (A_s - A_b)}{A_k \text{ VCR}}$$

where the various symbols are as defined previously.

Titrimetric Method

$$\text{Basic nitrogen, wt - ppm} = \frac{495 N (A - B)}{\text{VCD} + g}$$

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

g, V, C and D = as previously defined under *Spectrophotometric Method*

Alternatively, as above to express the nitrogen concentration in mol - ppm, calculate as follows:

$$\text{Basic nitrogen, mol - ppm} = \frac{834 N (A - B)}{\text{VC}}$$

where all symbols are as defined previously.

NOTES

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. Use care in removing ammonia from the 50% sodium hydroxide solution. Good safety practice is to use a new beaker for each lot of sodium hydroxide and, during heating of the solution, insert the glass beaker inside a stainless steel beaker.

3. Clean the stainless steel bomb thoroughly before taking a sample and after the analysis is completed. The following procedure is suggested:

- a. Empty the contents of the bomb in a safe place.
- b. Rinse the bomb with hot water for 5-10 minutes.
- c. After the bomb has cooled, introduce 100 ml of 1:1 H₂SO₄ and water solution into the bomb and let it stand for 15 minutes.
- d. Drain the acid solution from the bomb and again rinse with hot water until the exit water is clear.
- e. Follow with a distilled or deionized water rinse and a final rinse with acetone. Blow the bomb with air until it is dry.
- f. Tag the bomb "Clean and Dry".

4. Do not use bombs employed for sampling and subsequent analysis for nitrogen to sample streams to be analyzed for sulfur. High and erroneous sulfur determinations will result because these bombs are cleaned with sulfuric acid.

5. After distillation of high-nitrogen content samples, remove the last traces of ammonia from the equipment to avoid possible contamination of subsequent samples. Rinse the flask and condenser several times with water; then add 400 ml of water to the flask and distill until 200 ml is overhead. If high and low nitrogen samples are both routinely analyzed, it is desirable to reserve special glassware for low-nitrogen determinations.

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 it is believed that duplicate results should not differ from the mean by more than the following amounts:

Method	Nitrogen Level, wt-ppm	Allowable Difference, wt-ppm
Spectrophotometric	0.3	0.2
	0.8	0.4
	2.0	0.8
Titration	7.0	0.8
	45.0	2.0

TIME FOR ANALYSIS

Time requirements for one analysis are 2 man-hours and 4 hours elapsed time.

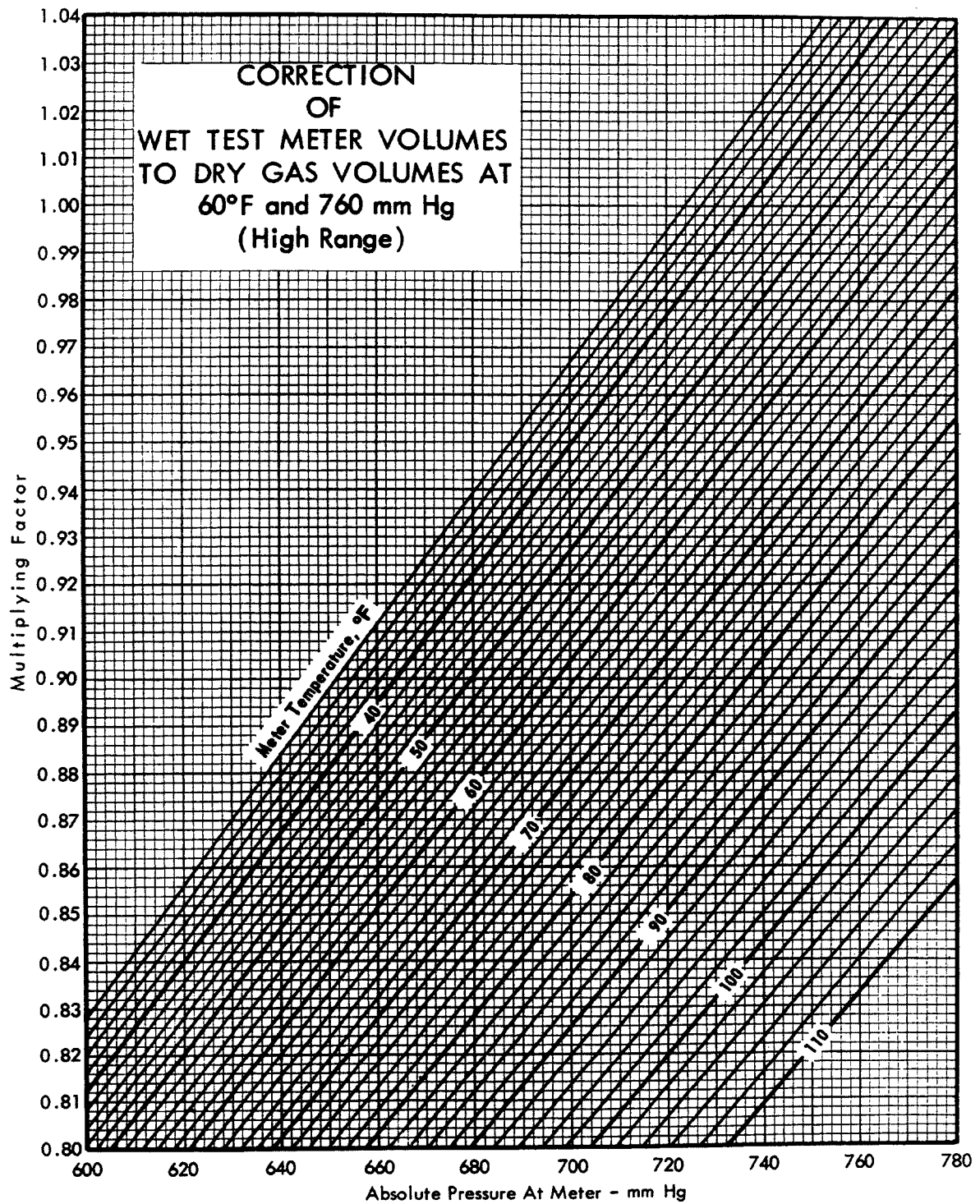


Figure 3

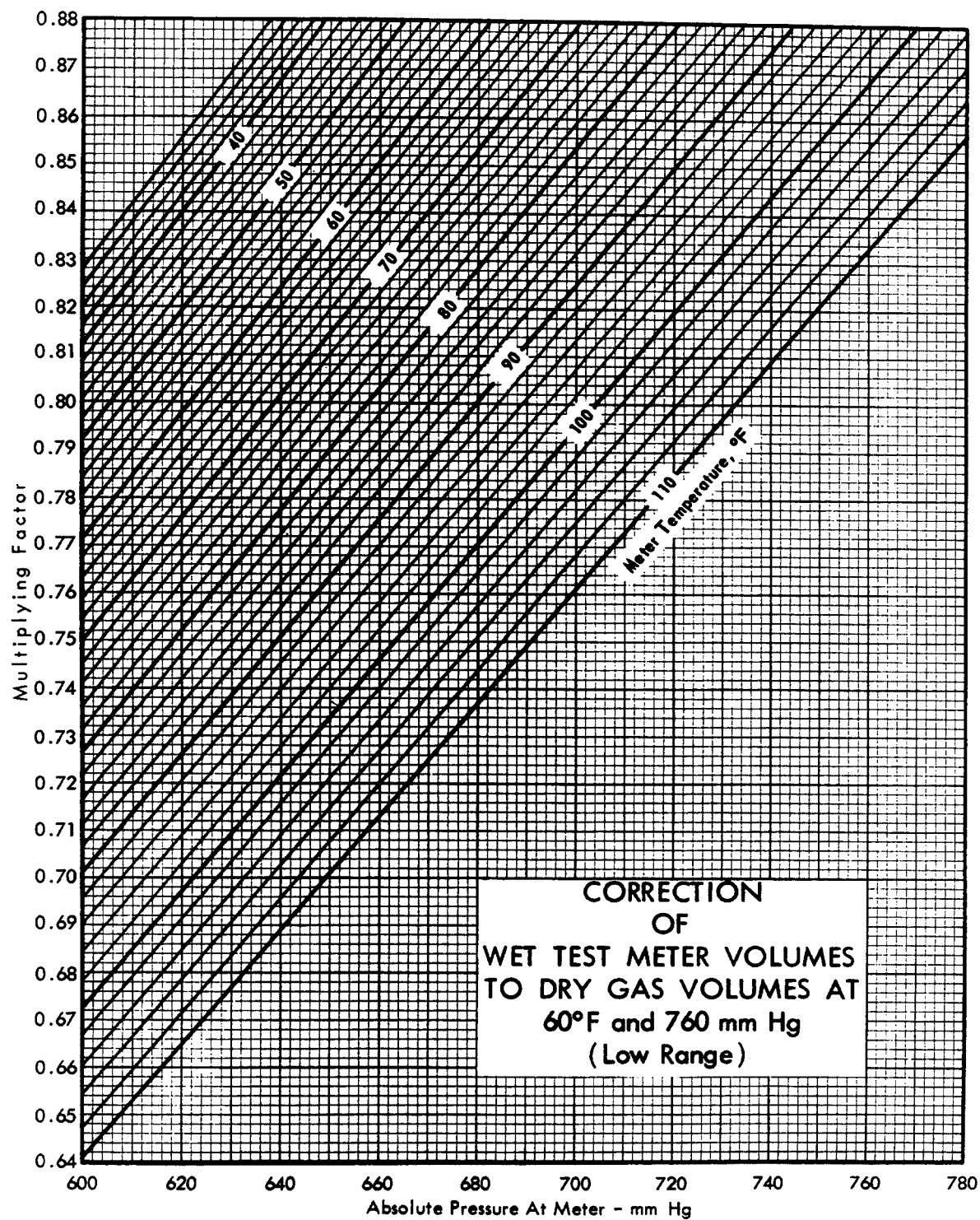


Figure 4