

HYDROGEN CHLORIDE IN GAS STREAMS BY POTENTIOMETRIC TITRATION

UOP Method 405-67T

SCOPE

This is a method for determining low concentrations of hydrogen chloride in gas systems, such as Platforming Process recycle gas streams. The lower limit of hydrogen chloride detection varies inversely with gas sample size. At least 40 to 50 cu ft is desired for a lower detection limit of 0.1 mol-ppm hydrogen chloride.

The procedures of this method are more rapid than colorimetric or turbidimetric procedures but larger gas samples are required for comparable lower detection limits.

OUTLINE OF METHOD

The gas sample is passed through a scrubbing apparatus containing water. Hydrogen chloride is quantitatively retained and titrated potentiometrically with standard silver nitrate solution. Hydrogen sulfide interference is eliminated by a peroxide treatment prior to titration.

APPARATUS

Beaker, titration, 250-ml glass

Bottles, gas washing, 250-ml, with coarse fritted cylinder. Corning Glass Works Code No. 441450, or equivalent

Electrodes:

Reference, glass. Beckman 4990-80, or equivalent

Indicating, silver-silver sulfide. Beckman 1264, or equivalent

Flask, volumetric, 250-ml

Needle valve, 1/8-inch, non-magnetic stainless steel

Pipets, volumetric, 5-, 25-, 50-ml

Potentiometric titration apparatus, automatic or manual

Wet-test meter or calibrated dry-type volume meter

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).

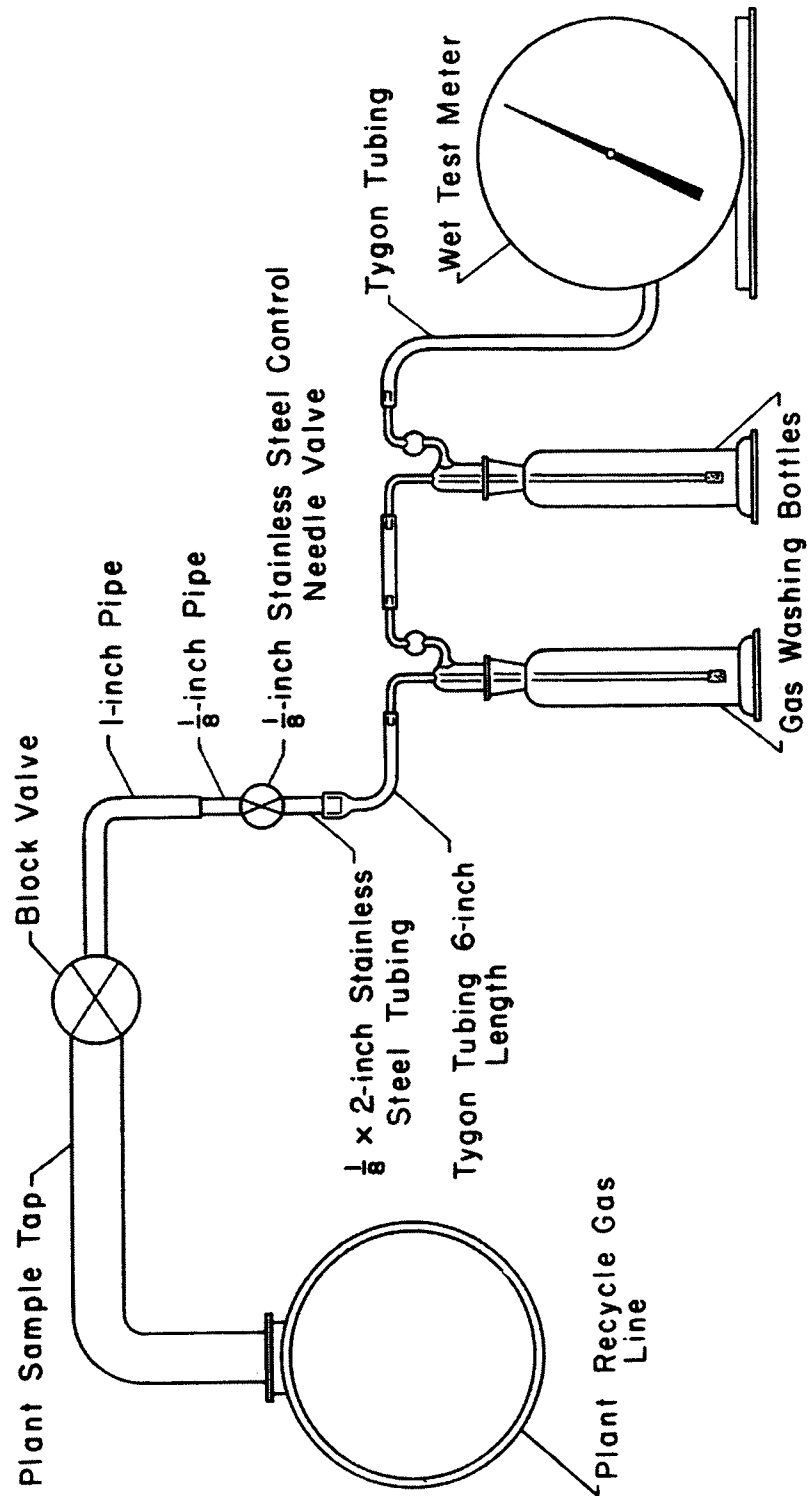


Figure 1

Sampling Of A Typical Refinery Recycle Gas Line
For Chloride Content

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 exist, unless otherwise specified. Water, where specified, means deionized or triple-distilled water. All solutions are aqueous.

Acetone

Hydrogen peroxide, 6% solution

Nitric acid, 35% solution. Dilute 1 volume of concentrated nitric acid with 1 volume of water.

Silver nitrate, 0.01 *N* solution. Standardize to 3 significant figures.

PROCEDURE

See Fig. 1 as an example of how sampling should be carried out in order to obtain the most reliable results.

Purge the fitting on the gas sample source sufficiently to ensure that water and foreign material have been removed. Wash the flow control valve and Tygon tubing thoroughly with water and acetone followed by drying with chloride-free air or vacuum before attaching to the sample source.

Add enough water to the 2 gas-washing bottles so that the liquid level is at least 1-1/2 to 2 inches above the fritted dispersion cylinder. Attach the clean and dry Tygon tubing from the 1/8-inch needle valve to the first gas-washing bottle. Avoid using tubing greater than 12 inches long to minimize excessive absorption of hydrogen chloride on the tubing wall during the scrubbing operation.

Connect the outlet of the second gas-washing bottle to a wet test or dry type gas volume meter that has been calibrated to ensure accurate gas volume measurement. Wire all the Tygon tubing connections to prevent possible sample leakage. Adjust the flow rate of the gas sample with the 1/8-inch needle valve to 1 to 2 cu ft/hr. Add more water to the gas-washing bottle if the level drops to less than 1 inch above the dispersion cylinder. Vent the metered gas to the atmosphere. Record the total volume of gas passed through the gas-washing bottles. Scrub an appropriately sized gas sample that will require a minimum titration of 1.0 ml of 0.01 *N* silver nitrate. The following is a list of suggested sample sizes to be taken for varying concentrations of hydrogen chloride in the gas:

HCl, mol-ppm	Suggested Minimum Sample Size, cu ft
0.1 - 0.4	60 - 20
0.4 - 0.8	20 - 10
0.8 - 2.0	10 - 4
> 2.0	4 - 1

Take extreme care to avoid contamination. Reserve glassware especially for this method or thoroughly rinse it with acetone and water before use. Devote special attention to fritted glass articles. Glassware in refinery laboratories may be contaminated with trace amounts of sulfides or bromine compounds from leaded gasoline. These must be scrupulously removed since sulfides, mercaptans, cyanides, cyanates and all halogen compounds interfere.

In all operations remember that human perspiration contains sodium chloride. Therefore, avoid touching the inside surfaces of absorbers, the ground surfaces of stoppers, or other surfaces which may come in contact with the sample solutions or reagents.

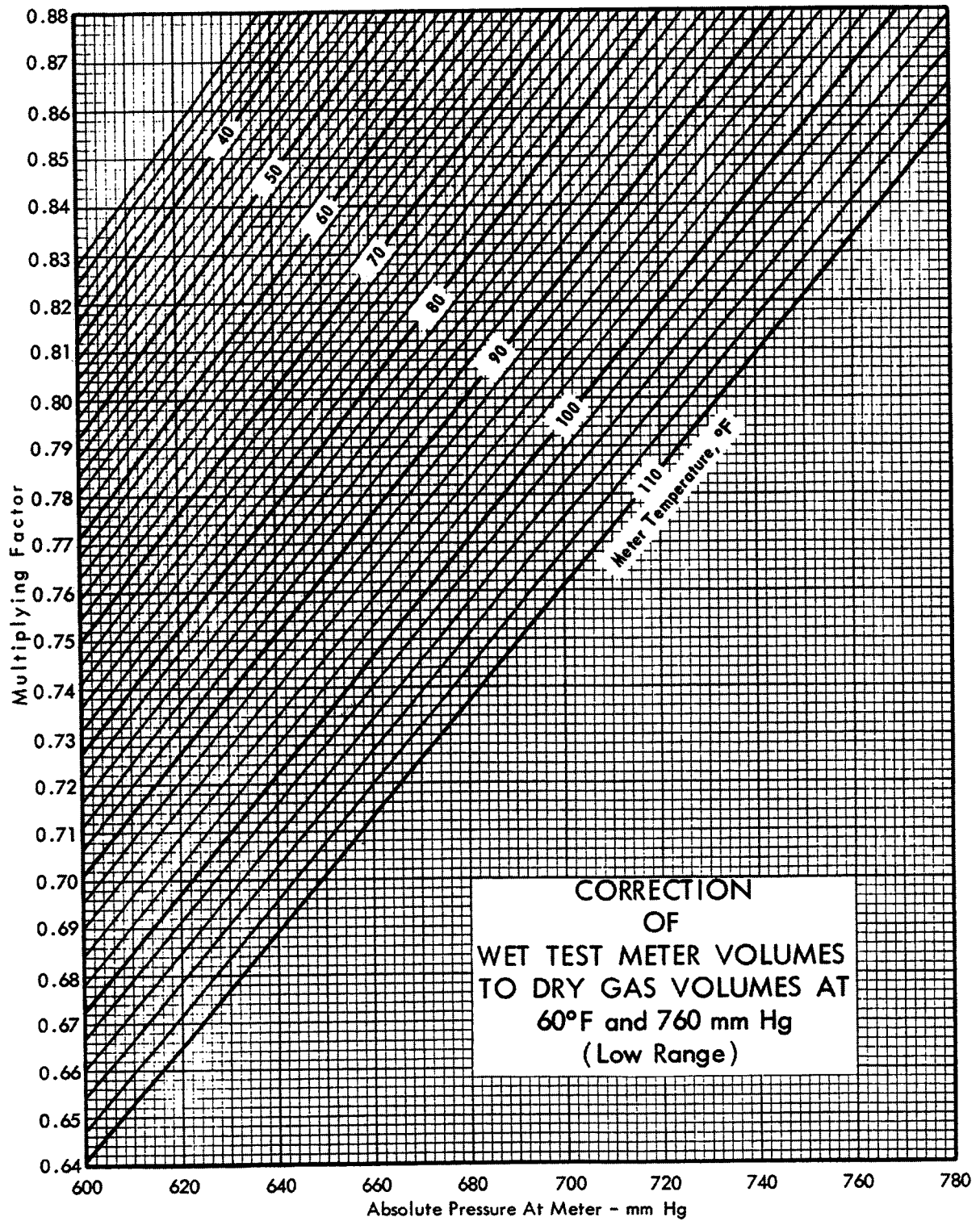


Figure 2

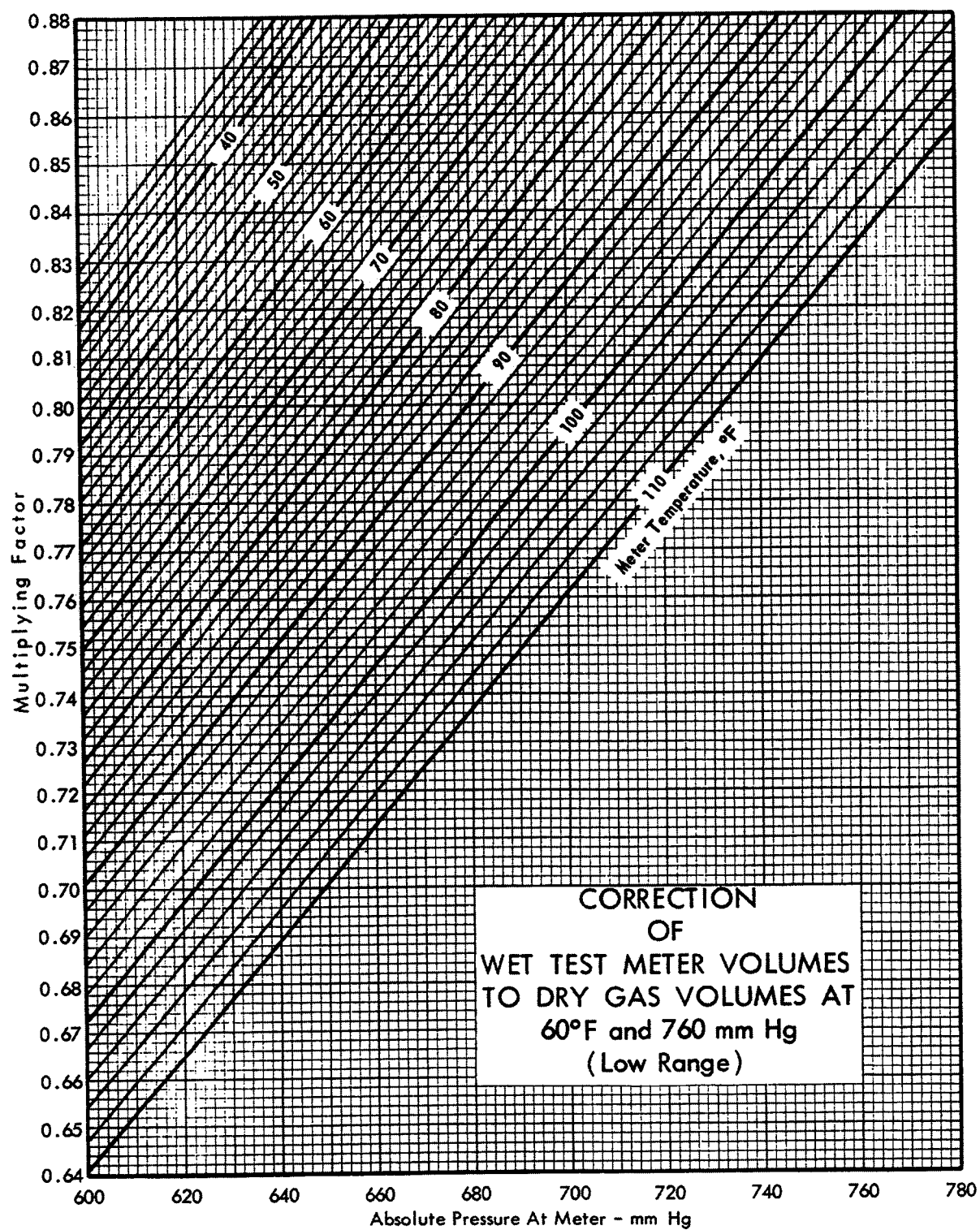


Figure 3

Following the scrubbing operation, quantitatively transfer the contents of the gas-washing bottles to a titration beaker with water (see Note). Disconnect and wash the 1/8-inch needle valve and the tubing connecting the needle valve to the gas washing bottle with water. Add the washings to the titration beaker. Add 1 ml of the 6% hydrogen peroxide and gently boil the scrubber solution and washings for approximately 5 minutes to dispel excess peroxide.

The peroxide treatment is employed to prevent hydrogen sulfide and mercaptans from interfering in the subsequent titration step but it may be omitted when such impurities are known to be absent. Use larger quantities of the peroxide solution when the total hydrogen sulfide and mercaptan content exceeds 25 mg.

Cool the solution to room temperature, add 2 or 3 drops of nitric acid, assemble the glass and silver - silver chloride electrode system, and titrate potentiometrically with 0.01 *N* silver nitrate solution.

If organic chlorides are present in the gas stream, *do not* transport the scrubber sample solution to an area for analysis that involves a time lag greater than one day between sampling and analysis.

CALCULATIONS

$$\text{Hydrogen chloride, mol - ppm} = \frac{836 M N}{V F}$$

where:

M = volume of titrant used, ml

N = normality of standard silver nitrate solution

V = volume of gas sample, as metered, cu ft

F = gas volume correction factor for conversion to dry gas at 760 mm Hg, 60 F. Determine this from Figs. 2 and 3, or calculate it as follows:

$$F = \frac{520}{460 + t} \times \frac{P - P_w}{760}$$

where:

t = temperature of wet test meter, °F

P = barometric pressure, mm Hg

P_w = vapor pressure of water at t, mm Hg

NOTES AND PRECAUTIONS

An increase in chloride values of scrubbed recycle gas stream samples upon aging in an aqueous solution would indicate that hydrolysis of organic chlorides is taking place. It is therefore essential that recycle gas samples scrubbed for hydrogen chloride content be analyzed the same day.

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 by more than 20% of the mean in the range from 0.1 to 1 mol-ppm.

TIME FOR ANALYSIS

One man-hour and 2 hours elapsed time are required for 1 analysis.