

CHLORINE IN HYDROGEN GAS BY A COLORIMETRIC PROCEDURE

UOP Method 317-66T

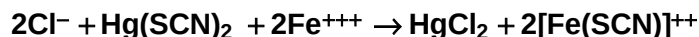
SCOPE

This method can be used for the determination of chlorine in compressed hydrogen gas or for the determination of hydrogen chloride in other gas systems, such as refinery recycle gases. The method as applied to compressed hydrogen does not distinguish between chlorine and hydrogen chloride and the results are expressed in terms of mol ppm of chlorine. For recycle gas analysis, the chlorine is in the form of hydrogen chloride and is expressed as such. Two to six cubic feet of sample is sufficient to detect a chlorine or hydrogen chloride content equal to or greater than 1 mol ppm. Chlorine content in the range of 0.1 to 1.0 mol ppm can be determined by the use of a proportionately larger sample.

OUTLINE OF METHOD

A. For Compressed Hydrogen

The gas sample is scrubbed with a dilute hydrogen peroxide solution to collect the chlorine and convert it to ionic chloride. The solution from the scrubber is made basic, heated to destroy excess peroxide and concentrated to a smaller volume. The resulting concentrate is acidified and the chloride content determined by a colorimetric method. This is based on the liberation of thiocyanate ions from mercuric thiocyanate by chloride ion and measurement of the colored ferric thiocyanate complex:



B. For Recycle Gases

The gas sample is scrubbed with water and the scrubber solution is acidified and boiled to remove hydrogen sulfide. An aliquot is then used to determine chloride by the colorimetric method described above.

APPARATUS

Buret, 10-ml, with 0.02-ml subdivisions

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).

Flasks, Erlenmeyer, 125-ml; volumetric, 25-, 50-, 500- and 1000-ml

Gas washing bottle, 250-ml, with coarse fritted cylinder

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

Pipets, volumetric, 2-, 5-, and 20-ml

Pipets, 10-ml, serological, graduated in 0.1-ml divisions

Spectrophotometer, Coleman Model 14, or equivalent instrument, equipped with 20 × 40-mm rectangular cuvettes

Wet test meter, or equivalent

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 triple-distilled water.

Ferric ammonium sulfate, 0.25 *M* in approximately 9 *M* nitric acid. Place 60.3 g of $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in a 500-ml volumetric flask. Add approximately 100 ml of water. Carefully add 281 ml of concentrated nitric acid. When the salt is dissolved, dilute to the mark with water. In some cases not all the salt will dissolve. When this occurs, filter the solution through a fine sintered-glass filter before diluting.

Hydrogen peroxide, 3%

Lead acetate test paper

Mercuric thiocyanate. Saturated solution in ethyl alcohol. Keep in a brown glass bottle, preferably stored in a dark place, as deterioration of this solution is accelerated by light. Denatured alcohol is satisfactory if it is chloride-free.

Nitric acid, 1:1. Mix equal volumes of concentrated nitric acid and water.

Phenolphthalein indicator solution, 1%, alcoholic

Sodium chloride solution, 0.01 mg Cl/ml. Place exactly 0.1646 g of sodium chloride in a 1-l volumetric flask. Dissolve the salt completely in water. Dilute to volume with water and mix thoroughly. Quantitatively transfer a 100-ml aliquot of the resulting solution to another 1-l flask. Dilute to volume with water. The final stock solution now contains 0.01 mg Cl/ml.

Sodium carbonate, approximately 0.2 *N*

PREPARATION OF CALIBRATION CURVE

Add by 10-ml buret exactly 0.5-, 1.0-, 2.0-, 4.0-, 6.0-, 8.0- and 10.0-ml portions of the 0.01-mg Cl/ml stock solution to seven 25-ml volumetric flasks, respectively. Dilute each portion to about 20 ml with water. Add exactly 2.0 ml of the 0.25 *M* ferric ammonium sulfate solution to each flask. Swirl to mix well. Add exactly 2.0 ml of saturated alcoholic mercuric thiocyanate solution to each flask. Swirl to mix. Dilute to the mark with water and mix thoroughly.

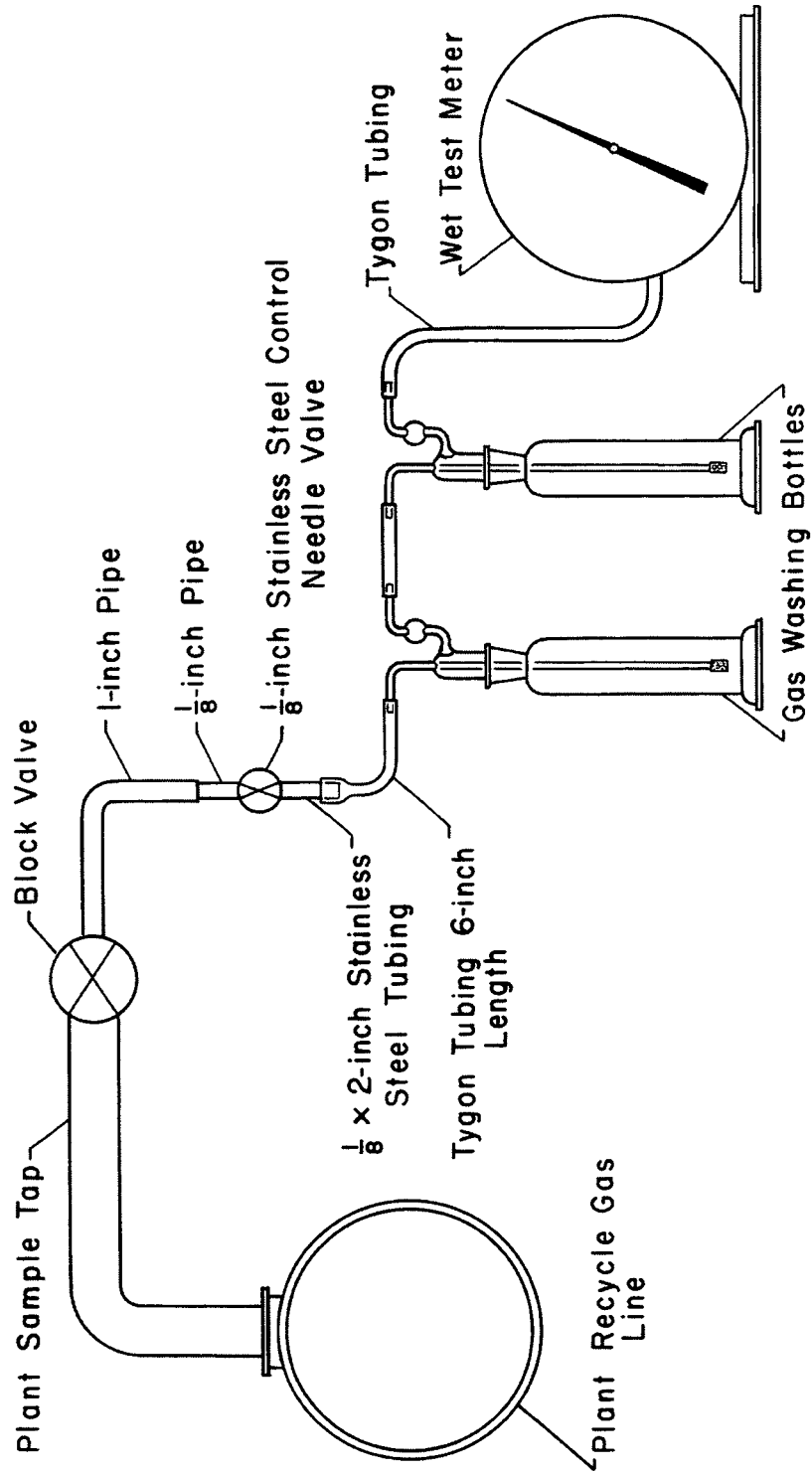


Figure 1

Sampling Of A Typical Refinery Recycle Gas Line
For Chloride Content

At the same time prepare a pair of reagent blanks by pouring 15 to 20 ml of water into each of two 25-ml volumetric flasks. Add exactly 2.0 ml of the 0.25 *M* ferric ammonium sulfate solution to each flask. Mix well. Add exactly 2.0 ml of the saturated alcoholic mercuric thiocyanate solution to each flask and mix well. Dilute to the mark with water and mix thoroughly.

Allow the colored complex to develop for about 10 minutes. Measure the absorbance at 460 m μ in the 20 $\times$ 40-mm cuvette, using distilled water as the reference. Subtract the average absorbance noted for the reagent blanks from the other readings. Plot the data as net absorbance vs. milligrams Cl per 25 ml.

PROCEDURE

Take extreme care to avoid contamination. Reserve glassware for chloride use or thoroughly rinse it with acetone and distilled water before use. Devote special attention to fritted glass articles, such as the gas washing bottles. 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 will come in contact with absorber solutions or reagents.

After the equipment and reagents to be used have been checked for possible chloride contamination as described under "Blank Determination" below, select the procedure (Sections A and B) appropriate to the sample.

A. For Compressed Hydrogen

See Figure 1 for the proper sequence of assembling the scrubbing train from the needle control valve to the wet test meter.

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 distilled water and acetone followed by drying with chloride-free air or vacuum before attaching the flow control valve to the sample source. Charge the gas-washing bottles with 40 ml of 3% hydrogen peroxide, making sure that the fritted dispersion cylinder has a liquid head of 1-1/2 to 2 inches. Attach the clean and dry Tygon tubing from the 1/8-inch needle valve to the gas-washing bottle, using a rubber stopper or a ground glass joint adapter. Avoid using tubing greater than 1 ft in length to minimize excessive adsorption of hydrogen chloride on the tubing wall during the scrubbing operation. Connect the outlet of the gas-washing bottle to a wet test meter that has been calibrated to ensure accurate gas volume measurements. Wire all the Tygon tubing connections to prevent possible leakage of sample. Adjust the flow rate of the gas sample with the 1/8-inch needle valve to 1 to 2 cu ft/hr. Vent the metered gas to the atmosphere. Record the total volume of gas passed through the gas-washing bottle. Sample 2 to 6 cu ft of gas, depending on the expected concentration of chloride in the sample.

Following the scrubbing operation, quantitatively transfer the contents of the gas-washing bottles to a 125-ml Erlenmeyer flask with water. 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 Erlenmeyer flask. Add about 2 ml of 0.2 *N* sodium carbonate solution and boil to bring the volume of liquid to about 15 ml. Add a drop of phenolphthalein indicator solution and nitric acid (1:1) drop by drop until the solution is acidic; then add 2 drops in excess. Quantitatively transfer this solution to a 50-ml volumetric flask. Dilute the contents to the mark with water and mix thoroughly. Use the solution directly for color development (Section C). If organic chlorides are present in the gas stream, *do not* transport the absorber sample solution to an area for analysis that requires a time greater than one day between sampling and analysis.

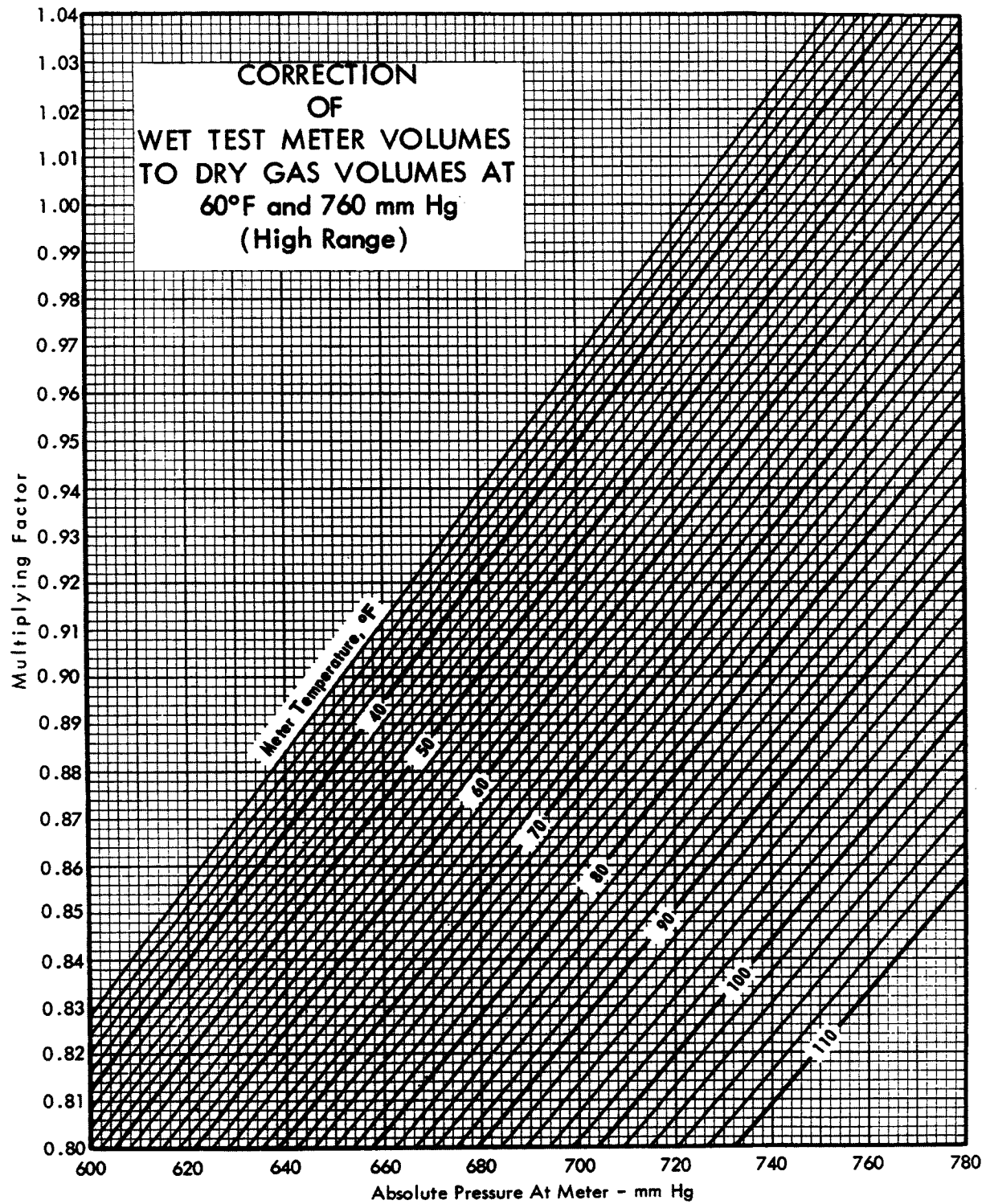


Figure 2

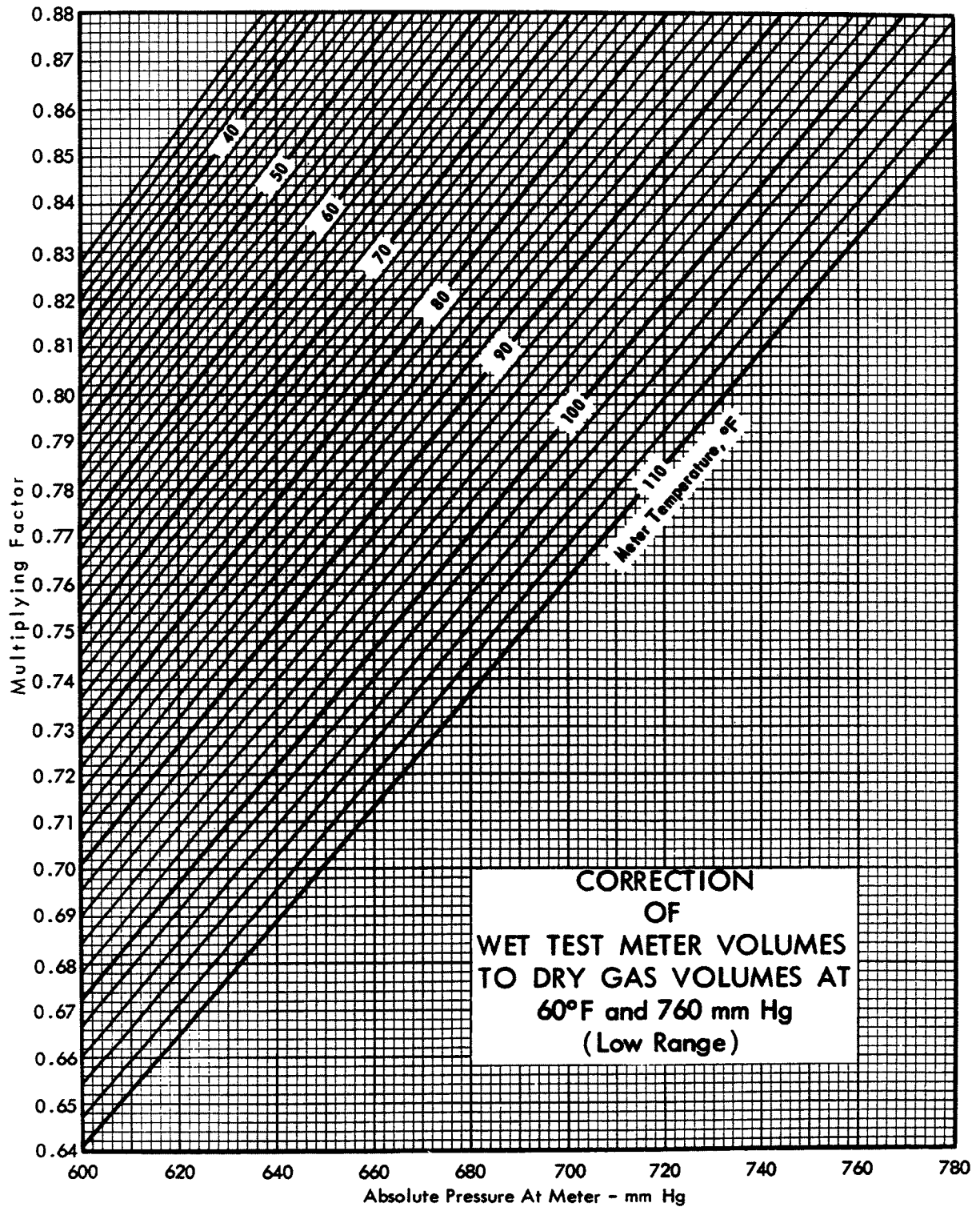


Figure 3

B. For Recycle Gases

See Figure 1 for arrangement of the sampling train to obtain the most reliable results.

Charge each of the gas-washing bottles with 40 ml of water. Follow the same sampling procedures as outlined in Section "A". Record the volume taken as sample, using 2 to 6 cu ft of gas. Wash the needle valve and tubing connecting the needle valve to the gas-washing bottle with water. Add the washings to the absorber solution in the gas-washing bottle.

Acidify the absorber solution with 10 drops of 1:1 nitric acid. Test a drop of the solution with lead acetate paper by dipping a clean stirring rod in the solution and touching it to the paper. If no sulfide ion is present, transfer the solution directly to a 50-ml volumetric flask. If sulfide is present (brown or black spot forms on the paper), transfer the solution to a 125-ml Erlenmeyer flask and boil gently for 30 minutes. Test again with lead acetate paper. If the test still is positive, continue until the test is negative, indicating the absence of sulfide. It is important that the original volume of solution be maintained by adding chloride-free water while boiling. When the solution is sulfide-free, concentrate it to about 30-ml, transfer it quantitatively to a 50-ml volumetric flask with water and dilute it to the mark. Use this solution directly for color development.

C. Color Development

Pipet a 20-ml aliquot of the solution from either of the above procedures to a 25-ml volumetric flask. Add exactly 2.0 ml of the 0.25 *M* ferric ammonium sulfate solution and mix well. Add exactly 2.0 ml of the saturated mercuric thiocyanate solution and mix. Dilute to the mark with water and mix thoroughly. Allow the colored complex to develop for about 10 minutes. Measure the absorbance at 460 mμ in the 40-mm cuvette, using distilled water as the reference.

D. Blank Determination

Run a reagent blank each time a new batch of any one of the reagents is prepared. In addition, if analyses are made only occasionally, so that reagents are consumed rather slowly, run a reagent blank along with each set of analyses. The mercuric thiocyanate, as mentioned above under REAGENTS, deteriorates slowly in the dark and more rapidly in the presence of light. The absorbance of the reagent blank (20 ml of water, plus 2 ml of ferric ammonium sulfate solution, plus 2 ml of alcoholic mercuric thiocyanate, diluted to 25 ml with water) using water as reference and a 40-mm cuvette, usually is 0.14 to 0.16 absorbance units with fresh reagents. As the thiocyanate ages, the reagent blank increases. Prepare fresh reagents when the blank exceeds 0.18 absorbance units using a 40-mm cuvette.

CALCULATIONS

A. For Compressed Hydrogen

Subtract the absorbance of the reagent blank at 460 mμ from that of the sample to obtain a net absorbance per 25 ml of colored solution. From the calibration curve obtain the milligrams of chloride per 25 ml. Calculate the chlorine content of the gas sample from the following equation:

$$\text{Chlorine as Cl}_2, \text{ mol - ppm} = \frac{A \times 29.5}{V \times F}$$

where:

- A** = weight of chloride per 25 ml of colored solution, mg (obtained from the calibration curve)
V = volume of metered gas sample, cu ft
F = gas volume correction factor taken from the attached charts, or calculated from the following equation:

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

where:

- t** = temperature, °F
P = barometric pressure, mm Hg
P_w = vapor pressure of water at t °F, mm Hg

B. For Recycle Gases

Subtract the absorbance of the reagent blank at 460 mμ from that of the sample and use this net absorbance to obtain the milligram of chloride per 25 ml from the calibration curve. Then calculate the HCl content of the gas sample from the following equation:

$$\text{HCl, mol - ppm} = \frac{A \times 57.3}{V \times F}$$

where:

A, **V** and **F** are as previously defined.

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 suggested that recycle gas samples scrubbed for HCl 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 from the mean by more than 10% for the 0.1 to 1 mol-ppm range.

TIME FOR ANALYSIS

The elapsed time required for one analysis is about 2 hours; the estimated labor requirement is 1 man-hour.

REFERENCE

Bergmann, J. G., and Sanik, J. Jr., *Anal. Chem.* **29**, 241 (1957)