

HYDROGEN SULFIDE IN GASES BY THE TUTWILER METHOD

UOP Method 9-85

SCOPE

This method is for determining hydrogen sulfide in gas mixtures. Mercaptan sulfur and carbonyl sulfide, if present, are determined as hydrogen sulfide. The accuracy of this method is not sufficient to obtain reliable results below 5 grains of H₂S per 100 cu ft (115 mg/m³). This method is intended primarily as a field test. UOP Method 212, "Hydrogen Sulfide, Mercaptan Sulfur and Carbonyl Sulfide in Hydrocarbon Gases by Potentiometric Titration" is recommended for more accurate laboratory determinations.

OUTLINE OF METHOD

A known constant volume of sample is drawn into a Tutwiler buret, replacing a starch solution. A volume of starch solution, retained in the buret, is titrated with standard iodine solution until the starch solution assumes a faint permanent blue color. The concentration of hydrogen sulfide is calculated from the volume of iodine solution used and its known molarity.

APPARATUS

Balance, readability, 0.1-mg

Flask, volumetric, one-liter

Tubing, neoprene, 6.4-mm ID, 11.1-mm OD, Sargent-Welch Scientific Co., Cat. No. S-73655-KD, or equivalent

Tutwiler hydrogen sulfide apparatus (see Figure), Curtin Matheson Scientific, Cat. No. 123-265 (complete), or equivalent, consisting of:

Bottle, leveling, 250-mL

Buret, Tutwiler, 100- and 110-mL graduations with attached 10-mL graduated cylinder having 0.1-mL divisions

Support, with clamps

Tubing, neoprene

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).

© COPYRIGHT 1959, 1985 UOP LLC
ALL RIGHTS RESERVED

UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

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.

Iodine, resublimed crystals, Sargent-Welch Scientific Co., Cat. No. SC 12837, or equivalent

Mercuric iodide, powder, Sargent-Welch Scientific Co., Cat. No. SC 13473, or equivalent

Potassium iodide, granular, Sargent-Welch Scientific Co., Cat. No. SC 17240, or equivalent

Starch, soluble, Sargent-Welch Scientific Co., Cat. No. SC 15034, or equivalent

PREPARATION OF SOLUTIONS

Mix 4 g of soluble starch with 10 mL of water and 10 mg of mercuric iodide and mix into a thin paste. Add the mixture to one liter of boiling water, stir, allow to stand until cold, and decant the clear solution for use. Prepare a fresh solution at 3-day intervals. When low concentrations are being determined using the 0.0005-*M* iodine solution, renew the starch solution in the leveling bottle after a maximum of 3 analyses.

Three standard iodine solutions are usually sufficient for determining the hydrogen sulfide content of most petroleum refinery gas streams. These solutions are made to specific molarities for analytical convenience.

Solution A is used for the determination of hydrogen sulfide when present in concentrations less than 1000 grains per 100 cu ft of gas (23 g/m^3), but more than 25 grains per 100 cu ft of gas (0.57 g/m^3). The specified molarity is 0.00673, so that one milliliter of solution is equivalent to 100 grains per 100 cu ft of gas (2.3 g/m^3) when a 100-mL gas sample is analyzed. To prepare this solution, weigh $1.7076 \text{ g} \pm 0.1 \text{ mg}$ of iodine crystals into a one-liter volumetric flask containing approximately 15 g of potassium iodide. Dissolve in water and dilute to volume.

Solution B is used for the determination of hydrogen sulfide when present in concentrations greater than 1000 grains per 100 cu ft of gas (23 g/m^3). The specified molarity is 0.01345, so that one milliliter of solution is equivalent to 200 grains of hydrogen sulfide per 100 cu ft of gas (4.6 g/m^3) when a 100-mL gas sample is analyzed. To prepare this solution, weigh $3.4152 \text{ g} \pm 0.1 \text{ mg}$ of iodine crystals into a one-liter volumetric flask containing approximately 15 g of potassium iodide. Dissolve in water and dilute to volume.

Solution C is used for the determination of hydrogen sulfide when present in concentrations less than 25 grains per 100 cu ft of gas (0.575 g/m^3). The specified molarity is 0.0005, so that one milliliter of solution is equivalent to 7.4 grains of hydrogen sulfide per 100 cu ft of gas (0.17 g/m^3) when a 100-mL gas sample is analyzed. To prepare this solution, weigh $0.1269 \text{ g} \pm 0.1 \text{ mg}$ of iodine crystals into a one-liter volumetric flask containing approximately 15 g of potassium iodide. Dissolve in water and dilute to volume.

PROCEDURE

Fill the leveling bottle with starch solution and connect it to the bottom of the buret (see Figure). Open the bottom stopcock and then turn the stopcock at the top of the buret to connect the buret with the gas inlet tube. Raise the leveling bottle until the buret and inlet tube are filled with starch solution. Close the

stopcock at the bottom of the buret. Flush the line from the gas source and attach it to the gas inlet tube with neoprene tubing (see *PRECAUTIONS*). Open the stopcock at the bottom of the buret and lower the leveling bottle, drawing in gas until the level of the starch solution just passes the 100-mL mark on the buret. Close both stopcocks and disconnect the gas sample tubing. Open the bottom stopcock and raise the starch solution to the 100-mL mark by raising the leveling bottle. Close the stopcock. With the gas slightly compressed, briefly open the top stopcock to the air to bring the gas to atmospheric pressure and then close it. Open the bottom stopcock and lower the starch solution level to the 110-mL mark to place the gas under reduced pressure. Close the bottom stopcock and disconnect the leveling bottle from the buret.

Fill the graduated cylinder at the top of the buret with one of the standard iodine solutions and record the reading. Turn the top stopcock to admit small amounts of iodine solution into the buret and shake well after each addition. Continue the additions until the starch solution assumes a faint, but permanent, blue color. Record the reading on the graduated cylinder and subtract it from the initial reading to find the mL of iodine used during the analysis.

Run a blank analysis daily for each iodine solution used to determine the amount required to give the starch solution a faint, but permanent, blue color in the absence of hydrogen sulfide. Determine a blank in the same manner as described above, except that a hydrogen sulfide-free gas or air is used. The volume of iodine solution required to establish the proper endpoint for a specific starch solution is subtracted from the volume of iodine solution consumed in a sample determination.

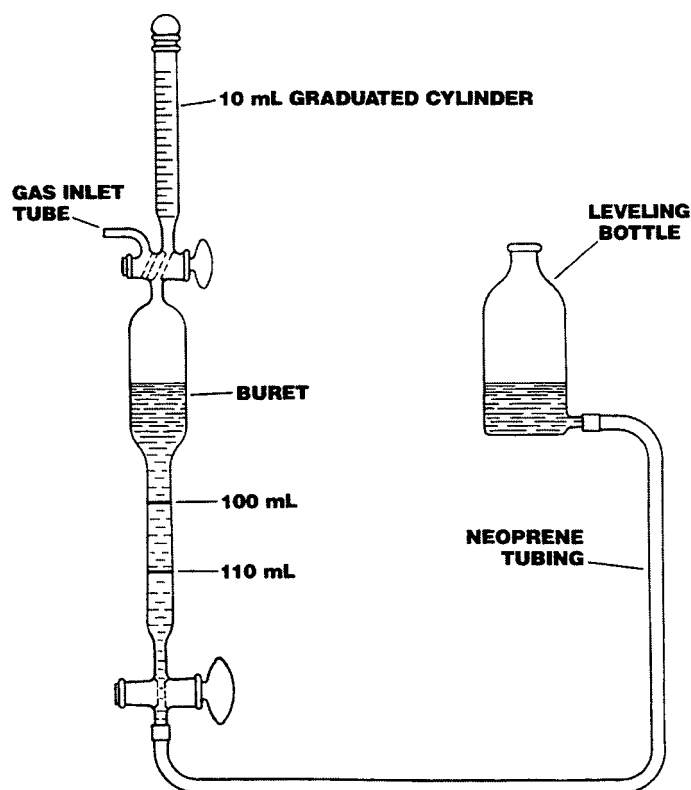


Figure
Tutwiler Hydrogen Sulfide Apparatus

CALCULATIONS

Calculate the amount of hydrogen sulfide as follows:

$$\text{H}_2\text{S, grains/100 cu ft} = (\text{A} - \text{B})\text{C}$$

where:

A = iodine solution required to titrate sample, mL

B = iodine solution required to titrate blank, mL

C = 100 (Solution A)
200 (Solution B) or
7.4 (Solution C)

$$\text{H}_2\text{S, g/m}^3 = (\text{A} - \text{B})\text{D}$$

where:

A and B = previously defined

D = 2.3 (Solution A)
4.6 (Solution B) or
0.17 (Solution C)

To report the hydrogen sulfide content in volume percent, divide grains/100 cu ft by 636.4.

PRECAUTIONS

It is recommended that gases to be analyzed for hydrogen sulfide content be sampled directly from the plant stream into the buret. If the sample is to be transported, it should be done in a dry glass or stainless steel container.

Do not confuse the blue color of the iodine-starch complex with the opalescent milky appearance resulting from the separation of free sulfur.

If the gas contains tarry vapors, pass it through cotton before admitting it to the buret.

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 and labor requirement for an analysis, without preparation of solutions, are identical, 0.5 hour.

REFERENCES

American Gas Chemists Handbook, 3rd., 462, Chemical Publishing Co., New York (1929)
Tutwiler, C.C., *J. Am. Chem. Soc.*, **23**, 173 (1901)
UOP Method 212

SUGGESTED SUPPLIERS

Curtin Matheson Scientific, 1850 Greenleaf Ave., Elk Grove Village, IL 60007
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077