



# HYDROGEN SULFIDE, MERCAPTAN SULFUR, AND CARBONYL SULFIDE IN HYDROCARBON GASES BY POTENTIOMETRIC TITRATION

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## UOP Method 212-05

### SCOPE

This method is for determining hydrogen sulfide (H<sub>2</sub>S), mercaptan sulfur (RSH) and carbonyl sulfide (COS) in gaseous hydrocarbons and in typical liquefied petroleum gas (LPG) consisting of C<sub>3</sub> and/or C<sub>4</sub> hydrocarbons. Also covered is the determination of mercaptan sulfur in LPG which may contain a wide range of hydrocarbon types ranging from ethane to such gasoline boiling range hydrocarbons as pentane and hexane. Each sulfur type can be determined from less than 1 to several thousand mass-ppm sulfur (less than 0.1 to several thousand grains per 100 cu ft).

### REFERENCES

- ASTM Method D 1070, "Relative Density of Gaseous Fuels," [www.astm.org](http://www.astm.org)
- ASTM Method D 6667, "Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence," [www.astm.org](http://www.astm.org)
- Bruss, D.B., Wyld, G.E.A., and Peters, E.D., *Anal. Chem.*, **29**, 807 (1957)
- Handbook of Chemistry and Physics*; [www.crcpress.com](http://www.crcpress.com)
- Lykken, L., and Tuemmler, F.D., *Ind. Eng. Chem., Anal. Ed.*, **14**, 67 (1942)
- Tamele, M.W., Ryland, L.B., and Irvine, V.C., *Ind. Eng. Chem., Anal. Ed.*, **13**, 618 (1941)
- UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons," [www.astm.org](http://www.astm.org)
- UOP Method 516, "Sampling and Handling Gasolines, Distillate Fuels, and of C<sub>3</sub>-C<sub>4</sub> Fractions," [www.astm.org](http://www.astm.org)
- UOP Method 948, "Relative Density of Gas Mixtures by Calculation from Composition," [www.astm.org](http://www.astm.org)
- UOP Method 999, "Precision Statements in UOP Methods," [www.astm.org](http://www.astm.org)

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## OUTLINE OF METHOD

The sample, taken either from a sample cylinder or directly from a refinery stream according to the procedures described in UOP Method 516, is scrubbed first through a potassium hydroxide solution and then through a monoethanolamine solution. The potassium hydroxide solution contains chelating agents which inhibits the oxidation of sulfur compounds by chelating heavy metals. A potentiometric titration of the absorbed hydrogen sulfide and mercaptan sulfur in the potassium hydroxide solution follows, using either an aqueous or an alcoholic silver nitrate titrant. The monoethanolamine solution, which contains the absorbed carbonyl sulfide is titrated potentiometrically with alcoholic silver nitrate in an acidic titration solvent. The electrode system for both titrations is a silver/silver sulfide electrode with a glass reference electrode. The concentration of each analyzed component is calculated from the titration curve. Either an automatic (preferred) or a manually-operated titrator may be used.

## APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used if equivalent performance can be obtained.

In addition to the apparatus listed below, all of the sampling-related apparatus specified in UOP Method 516 for C<sub>3</sub>-C<sub>4</sub> fractions is also required for this method.

*Balance*, capable of weighing 5 kg to the nearest 0.5 g

*Balance*, readability 0.1-mg

*Barometer*, Fisher Scientific, Cat. No. 02-406

*Beakers*, electrolytic, 250-mL, Brinkmann Instruments, Cat. No. 020212209, two or more required

*Beaker*, stainless steel, 4000-mL, Fisher Scientific, Cat. No. 02-583G. Drill a hole in the bottom to fit the selected neoprene stopper.

*Cleaning pad*, synthetic, mildly abrasive, Scotch-Brite™, Runco Office Supply, Cat. No. MMM-96

*Electrode*, combination silver/glass titrode, Brinkmann Instruments, Cat. No. 020948507. The electrode should be dedicated to sulfur analysis.

*Flasks*, volumetric, Class A, 250-, 500-, and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5E, -5F, and -5G, respectively

*Flask*, volumetric, Class A, amber, for light sensitive materials, 100-mL, Fisher Scientific, Cat. No. 10-229C

*Funnel*, separatory, 250-mL, Fisher Scientific, Cat. No. 10-437-5C

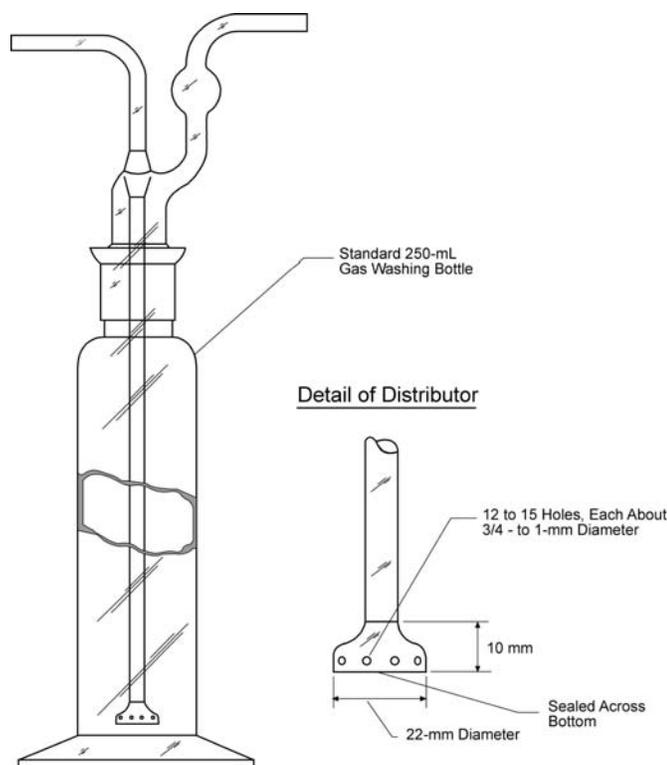
*Gas washing bottle*, 125-mL. The type fitted with sintered glass disk of coarse porosity is suitable and can be obtained commercially, Reliance Glass, Cat. No. LG-3761-100, or, Fisher Scientific, Cat. No. 03-040A. Because light is the most serious factor affecting recovery of carbonyl sulfide, *completely* mask the gas washing bottle with black tape. In order to view the bubbling, a vertical slit, 2-3 mm wide, may be cut in the tape, which can be taped over except when needed.

*Gas washing bottle*, 250-mL, Reliance Glass, Cat. No. LG-3690-110

*Gas washing bottles*, 250-mL. The type fitted with a sintered glass gas-distribution plate of coarse porosity is suitable and this type can be obtained commercially, Reliance Glass, Cat. No. LG-

3762-102, or Fisher Scientific, Cat. No. 03-040B, two required. The maximum gas flow rate for this type of gas washing bottle is about 30 L/hr (1 cu ft/hr).

If no COS scrubber is connected downstream of the caustic scrubbers, an alternative gas washing bottle, suitable for a higher flow rate, may be used. This type is fitted with a perforated disk gas distributor (see Figure 1), and is available on special order from Reliance Glass. The rate with this distributor can be as high as 90 L/hr (3 cu ft/hr), *provided that no COS scrubber is connected downstream from the caustic scrubber*. The scrubbing rate for the COS scrubber *must not exceed 30 L/hr*.



**Figure 1**  
Gas Washing Bottle with  
Perforated Disk Gas Distributor

*Gauge*, pressure, stainless steel, 0 to 2800 kPa gauge (0 to 400 psig) range, Matheson Tri-Gas, Cat. No. 63-2242, with adapter to fit the specific sample cylinders used

*Graduated cylinders*, 5-, 100-, and 1000-mL, Fisher Scientific, Cat. No. 08-550A, -550E, and -550H, respectively

*Laboratory expansion valve*, Swagelok Type SS-3NRS4 (regulating stem 316 stainless steel valve and fittings), Swagelok. Wrap the valve with electrical heating tape and provide a variable transformer to control the temperature of the tape. (See Figure 2 for laboratory expansion valve apparatus arrangement.) To ensure that the valve provides a smooth, regular flow without any blockages, it must be cleaned regularly, by rinsing with water. Additional maintenance requires either a rebuild kit, returning to the manufacturer for repair, or replacement.