



# Standard Test Method for Mercaptans in Natural Gas Using Length-of-Stain Detector Tubes<sup>1</sup>

This standard is issued under the fixed designation D 1988; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers a rapid and simple field determination of mercaptans in natural gas pipelines. Available detector tubes provide a total measuring range of 0.5 to 160 ppm by volume of mercaptans, although the majority of applications will be on the lower end of this range (that is, under 20 ppm). Besides total mercaptans, detector tubes are also available for methyl mercaptan (0.5 to 100 ppm), ethyl mercaptan (0.5 to 120 ppm), and butyl mercaptan (0.5 to 30 mg/M<sup>3</sup> or 0.1 to 8 ppm).

NOTE 1—Certain detector tubes are calibrated in terms of milligrams per cubic metre (mg/M<sup>3</sup>) instead of parts per million by volume. The conversion is as follows for 25°C (77°F) and 760 mm Hg.

$$\text{mg/M}^3 = \frac{\text{ppm} \times \text{molecular weight}}{24.45} \quad (1)$$

1.2 Detector tubes are usually subject to interferences from gases and vapors other than the target substance. Such interferences may vary among brands because of the use of different detection principles. Many detector tubes will have a pre-cleanse layer designed to remove interferences up to some maximum level. Consult manufacturer's instructions for specific interference information. Hydrogen sulfide and other mercaptans are usually interferences on mercaptan detector tubes. See Section 5 for interferences of various methods of detection.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 7.3.

## 2. Referenced Documents

### 2.1 Gas Processors Association Standard:

GPA Standard 2188 Tentative Method for the Determination of Ethyl Mercaptan in LP Gas Using Length-of-Stain Detector Tubes, Appendix B, Test for Ethyl Mercaptan Odourant in Propane, Field Method, 1988<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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<sup>2</sup> Available from Gas Processors Association, 6526 E. 60th St., Tulsa, OK 74145.

## 3. Summary of Test Method

3.1 The sample is passed through a detector tube filled with a specially prepared chemical. Any mercaptan present in the sample reacts with the chemical to produce a color change, or stain. The length of the stain produced in the detector tube, when exposed to a measured volume of sample, is directly proportional to the amount of mercaptan present in the sample. A hand-operated piston or bellows-type pump is used to draw a measured volume of sample through the tube at a controlled rate of flow. The length of stain produced is converted to parts per million (ppm) by volume mercaptan by comparison to a calibration scale supplied by the manufacturer for each box of detection tubes. The system is direct reading, easily portable, and completely suited to making rapid spot checks for mercaptans under field conditions (see Note 1).

## 4. Significance and Use

4.1 The measurement of mercaptans in natural gas is important, because mercaptans are often added as odorants to natural gas to provide a warning property. The odor provided by the mercaptan serves to warn consumers (for example, residential use) of natural gas leaks at levels that are well below the flammable or suffocating concentration levels of natural gas in air. Field determinations of mercaptans in natural gas are important because of the tendency of the mercaptan concentration to fade over time.

4.2 This test method provides inexpensive field screening of mercaptans. The system design is such that it may be used by nontechnical personnel, with a minimum of proper training.

## 5. Interferences

5.1 Interference from hydrogen sulfide gas (H<sub>2</sub>S) is a common problem with mercaptan detector tubes and its extent should be understood to make use of tube readings. There are at least three detection principles used in mercaptan detector tubes and each is summarized below.

5.1.1 Palladium sulfate is used by at least one manufacturer. It has a positive interference from H<sub>2</sub>S, but H<sub>2</sub>S may be removed in a preconditioning layer at the front of the tube. If this is the case, the manufacturer will state some finite level of H<sub>2</sub>S at which interference initiates (for example, greater than 500-ppm H<sub>2</sub>S causes a positive error). Consult manufacturers' instruction sheets for this information. Propylene and hydrocarbons of five or more carbon atoms will cause interfering

discolorations making the palladium sulfate detection principle ineffective for liquefied petroleum gas (LPG). (Palladium chloride is used by at least one manufacturer, and it exhibits similar H<sub>2</sub>S interference as with the palladium sulfate detection principle. Palladium chloride may also exhibit the hydrocarbon interference described for the palladium sulfate detection principle. Contact the manufacturer for specific interference information.)

5.1.2 Mercuric chloride is used by at least one manufacturer. It has a positive interference from H<sub>2</sub>S but does not have the hydrocarbon interference described above for palladium sulfate. This detection principle is preferred for LPG applications. H<sub>2</sub>S will produce a stain on mercuric chloride tubes even if mercaptans are not present. The approximate H<sub>2</sub>S sensitivity ratio is as follows: One part per million H<sub>2</sub>S will produce a reading of 0.4- to 0.7-ppm mercaptans. Consult manufacturers for exact information if it does not appear in tube instruction sheets.

5.1.3 A two-stage copper salt/sulfur reaction is used by at least one manufacturer. This detection principle has a positive interference from H<sub>2</sub>S with H<sub>2</sub>S being twice as sensitive (that is, 10-ppm H<sub>2</sub>S will appear as 20-ppm mercaptan). Ammonia or amines also interfere with this principle producing a second color.

## 6. Apparatus

6.1 *Length-of-Stain Detector Tube*—A sealed glass tube with breakoff tips sized to fit the tube holder of the pump. The reagent layer inside the tube, typically a silica gel substrate coated with the active chemicals, must be specific to mercaptans and produce a distinct color change when exposed to a sample of gas containing mercaptans. Any substances known to interfere must be listed in the instructions accompanying the tubes. A calibration scale printed on the glass tube shall correlate mercaptan concentration to the length of the color stain. A separate calibration scale supplied with the tubes shall be acceptable. Shelf life of the detector tubes must be a minimum of two years from date of manufacturer, when stored according to manufacturer's recommendations.

6.2 *Detector Tube Pump*—A hand-operated pump of a piston or bellows type. It must be capable of drawing 100 mL per stroke of sample through the detector tube with a volume tolerance of ±5 mL.<sup>3</sup> It must be specifically designed for use with detector tubes.

NOTE 2—A detector tube and pump together form a unit and must be used as such. Each manufacturer calibrates detector tubes to match the flow characteristics of their specific pump. Crossing brands of pumps and tubes is not permitted, as considerable loss of system accuracy is likely to occur.<sup>3</sup>

6.3 *Gas Sampling Chamber*—Any container that provides for access of the detector tube into a uniform flow of sample gas at atmospheric pressure and isolates the sample from the surrounding atmosphere. A stainless steel needle valve (or pressure regulator) is placed between the source valve and the sampling chamber for the purpose of throttling the sample

flow. Flow rate should approximate one to two volume changes per minute or, at minimum, provide a positive exit gas flow throughout the detector tube sampling period.

NOTE 3—A suitable sampling chamber may be devised from a polyethylene wash bottle of nominal 500-mL or 1-L size. The wash bottle's internal delivery tube provides for delivery of sample gas to the bottom of the bottle. A ½-in. (13-mm) hole cut in the bottle's cap provides access for the detector tube and vent for the purge gas (see Fig. 1). Purge gas must be vented at a sufficient rate so that pressure does not build up within the sampling chamber and increase the flow rate through the detector tube. (An alternative flow-through sampler may be fashioned using a 1-gal zipper-type food storage bag. The flexible line enters one corner of the bag's open end and extends to the bottom of the bag. The opposite corner of the open end is used for tube access and sample vent. The remainder of the bag's top is sealed shut. The basic procedure for the sampler in Fig. 1 applies.)

NOTE 4—An alternative sampling container is a collection bag made of a material suitable for the collection of natural gas (for example, polyester film). The sampling bag should have a minimum capacity of 2 L.

## 7. Procedure

7.1 Select a sampling point that will provide access to a representative sample of the gas to be tested (source valve on the main line). The sample point should be on top of the pipeline and equipped with a stainless steel sample probe extending into the middle third of the pipeline. Open the source valve momentarily to clear the valve and connecting nipple of foreign materials.

7.2 Install needle valve (or pressure regulator) at the source valve outlet. Connect sampling chamber using the shortest length of flexible tubing possible (see Fig. 1). Avoid using tubing that reacts with or absorbs mercaptans, such as copper or natural rubber. Use materials such as TFE-fluorocarbon, vinyl, polyethylene, or stainless steel.

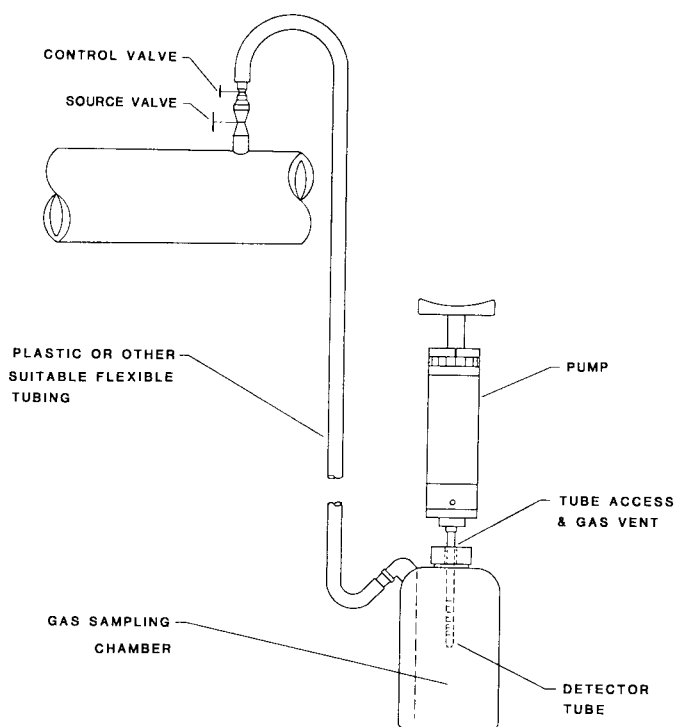


FIG. 1 Apparatus Schematic

<sup>3</sup> *Direct Reading Colorimetric Indicator Tubes Manual*, American Industrial Hygiene Association, Akron, OH, 1976.

7.3 Open source valve. Open needle valve enough to obtain positive flow of gas through the chamber, in accordance with 6.3. Purge the container for at least 3 min (see Fig. 1). (**Warning**—Take precautions to vent the gas away from persons collecting the sample such that the exposure to the gas is minimal. Escaping gases will produce flammable mixtures in air. Keep sources of heat, spark, or flame away from the sampler.)

NOTE 5—If a collection bag is used instead of a sampling chamber, follow 7.1 and 7.2, substituting the bag for the chamber. Follow 7.3, disconnecting the bag when filled. Deflate the bag to provide a purge and fill a second time to provide a sample. The bag must be flattened completely before each filling (Note 4).

7.4 Before each series of measurements, test the pump for leaks by operating it with an unbroken tube in place. Consult manufacturer's instructions for leak check procedure details and for maintenance instruction, if leaks are detected. The leak check typically takes 1 min. A leaking pump used in field testing will bias sample results low.

7.5 Select the tube range that best encompasses mercaptan concentration. Reading accuracy is improved when the stain length extends into the upper half of the calibration scale. Consult manufacturer guidelines for using multiple strokes to achieve a lower range on a given tube.

7.6 Break off the tube tips and insert the tube into the pump, observing the flow direction indication on the tube. Place the detector tube into the sampling chamber through the access hole, such that the tube inlet is near the chamber center (see Fig. 1).

NOTE 6—Detector tubes have temperature limits from 0 to 40°C (32 to 104°F), and sample gases must remain in that range throughout the test. Cooling probes are available for sample temperatures exceeding 40°C.

7.7 Operate the pump to draw the measured sample volume through the detector tube. Observe tube instructions when applying multiple strokes. Ensure that a positive flow is maintained throughout the sample duration at the sampling chamber gas exit vent. Observe tube instructions for proper sampling time per pump stroke. The tube inlet must remain in position inside the sampling chamber until the sample is completed. Many detector tube pumps will have stroke finish indicators that eliminate the need to time the sample. (**Warning**—It is very important to ensure that ambient air is not being drawn into the sample. Intrusion of ambient air into the sample will tend to bias the mercaptan readings low.)

NOTE 7—If a collection bag is used, the sample is drawn from the bag by way of a flexible tubing connection. Do not squeeze the bag during sampling. Allow the bag to collapse under pump vacuum, so that the pump's flow characteristics are not altered.

7.8 Remove the tube from the pump and immediately read the mercaptan concentration from the tube's calibration scale or from the charts provided in the box of tubes. Read the tube at the maximum point of the stain. If channeling has occurred (nonuniform stain length), read the maximum and minimum stain lengths and average the two.

NOTE 8—If the calibration scale is not printed directly on the detector tube, be sure that any separate calibration chart is the proper match for the tube in use.

7.9 If the number of strokes used differs from the number of strokes specified for the calibration scale, correct the reading, as follows:

$$A = (B \times C/D) \quad (2)$$

where:

$A$  = ppm (corrected),  
 $B$  = ppm (reading),  
 $C$  = specified strokes, and  
 $D$  = actual strokes.

7.10 Record the reading immediately, along with the gas temperature and the barometric pressure. Observe any temperature corrections supplied in the tube instruction. Altitude corrections become significant at elevations above 2000 ft. Correct for barometric pressure, as follows:

$$A = (B \times E/F) \quad (3)$$

where:

$E$  = barometric pressure, 760 mm Hg, and  
 $F$  = ambient barometric pressure, mm Hg.

NOTE 9—Even though the amount of chemicals contained in detector tubes is very small, the tubes should not be disposed of carelessly. A general disposal method includes soaking the opened tubes in water before tube disposal. The water should be pH neutralized before its disposal. Observe all local, state, and federal regulations for small-scale chemical disposal.

## 8. Precision and Bias

8.1 The accuracy of detector tube systems is generally considered to be  $\pm 25\%$  of reading. This is based mainly on programs conducted by the National Institute of Occupational Safety and Health (NIOSH) in certifying detector tubes for low-level contaminants in air, adapted to worker exposure monitoring.<sup>4</sup> NIOSH tested tubes at  $\frac{1}{2}$ , 1, 2, and 5 times the threshold limit value (TLV), requiring  $\pm 25\%$  accuracy at the three higher levels, and  $\pm 35\%$  at the  $\frac{1}{2}$ -TLV level. (For example, H<sub>2</sub>S with a TLV of 10 ppm was tested at levels of 5, 10, 20, and 50 ppm.) The higher tolerance allowed at the low level was due to the loss of accuracy for shorter stain lengths.<sup>3</sup> NIOSH discontinued this program in 1983, and it was picked up by the Safety Equipment Institute (SEI) in 1986.

8.2 The Gas Processors Association reported a precision of  $\pm 15\%$  for determination of ethyl mercaptan in propane using detector tubes (see GPA 2188).

## 9. Keywords

9.1 gaseous fuels; natural gas

<sup>4</sup> "NIOSH Certification Requirements for Gas Detector Tube Units," NIOSH/TC/A-012, National Institute of Occupational Safety and Health, July 1978.

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