Designation: ~~D5305 – 12~~ D5305 – 18

Standard Test Method for Determination of Ethyl Mercaptan in LP-Gas Vapor[1]

This standard is issued under the fixed designation D5305; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method ~~covers~~describes a rapid and simple procedure using ~~length of stain~~ length-of-stain tubes for field measurement of ethyl mercaptan in the vapor phase of LP-gas systems. Although length-of-stain tubes are available to detect ethyl mercaptan concentrations in the range of 0.5 to 120 parts per million ~~volume (ppmv),~~by volume, this test method is specifically applicable to systems containing 5 ~~ppmv~~ ppm by volume or more of ethyl mercaptan in LP-gas vapors.

NOTE 1—A chromatographic technique can be used for more precise, quantitative determination of ethyl mercaptan in LP-gas.

1.2 The values stated in SI ~~(metric)~~ units are to be regarded as ~~the~~ standard. The values given in parentheses ~~are for information only.~~after SI units are provided for information only and are not considered standard.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *NFPA Standard:*[2]

NFPA 58 Standard for the Storage and Handling of Liquefied Petroleum Gases

3. Terminology

3.1 *Abbreviations:*

3.1.1 *EM*—ethyl mercaptan

3.1.2 *LP-Gas, LPG*—liquefied petroleum gas

3.1.3 *PTFE*—polytetrafluoroethylene

3.1.4 *TBM*—*t*-butyl mercaptan

4. Summary of Test Method

4.1 Using a manually-operated vacuum pump, a sample of LP-gas from the vapor space of an LP-gas cylinder, storage tank or other closed containment system is drawn through a detector tube made specifically for detection of ~~mercaptans. The length of stain~~ ethyl mercaptan. The length-of-stain (color change) produced in the detector tube when exposed to a measured volume of sample is directly proportional to the amount of ethyl mercaptan present in the sample being tested. The ~~length of stain~~ length-of-stain produced in the detector tube is converted to concentration, in parts per million ~~volume (ppmv),~~by volume, by comparison with a calibration scale provided by the manufacturer of the stain tube.

5. Significance and Use

5.1 LP-gas is colorless and odorless, and not detectable by normal human senses. To provide an olfactory warning in the event of a leak, LP-gas intended for domestic or commercial fuel use is intentionally odorized so as to be readily detectable well below

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.H0 on Liquefied Petroleum Gas.

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[2] Available from National Fire Protection Association (NFPA), 1 Batterymarch Park, Quincy, MA 02169-7471, http://www.nfpa.org.

***A Summary of Changes section appears at the end of this standard**

flammable or suffocating concentration levels of LP-gas in air. (See Appendix X1.) for important explanations.) The most common odorant for LP-gas is ethyl mercaptan. The field use of this test method will rapidly determine the presence and concentration of ethyl mercaptan in LP-gas vapor without the necessity for complex laboratory equipment.

6. Interferences

6.1 Detector tubes can be subject to interferences from materials other than the target substance. Methyl mercaptan will likely interfere with tubes designed to measure ethyl mercaptan. Because of different detection chemistry by different manufacturers, interferences can vary. Consult the manufacturer's instructions for specific interference information and observe any instructions given.

6.2 Propylene (propene) will cause an interfering (gray) discoloration with some tubes designed for ethyl mercaptan. LP-gas from natural gas sources usually does not contain propylene (propene). However, LP-gas produced in refinery operations often does contain propylene (propene). Detector tubes calibrated for *t*-butyl mercaptan eliminate this interference, and should be used if the presence of propylene (propene) is suspected. Some tubes designed for measurement of *t*-butyl mercaptan are calibrated in milligrams per cubic metre (mg/m^3) and should be converted to ppmv ppm by volume ethyl mercaptan as shown in Annex A1.

6.3 The validity of this test method depends on the ethyl mercaptan in the LP-gas vapor phase being in equilibrium with ethyl mercaptan in the LP-gas liquid phase. If LP-gas vapor has recently been vented, or if a significant volume of vapor relative to the total volume of the vapor phase is vented during this test procedure, the concentration of ethyl mercaptan in the vapor phase sample can be lower than the equilibrium concentration.

7. Apparatus

7.1 *Pump*—A manually-operated vacuum pump, capable of drawing 100 mL per stroke of sample through the detector tube with an accuracy of ±2.0 mL. ±2.0 mL.

7.2 *Detector Tubes*—Sealed tubes, made of glass with break-off tips sized to fit the orifice of the pump used (tubes and pumps from different manufacturers shall not be interchanged). The tube used shall be appropriate for the determination of ethyl mercaptan and shall produce a distinct color change when exposed to a sample of LP-gas containing ethyl mercaptan. Any substance known to interfere shall be listed in instructions accompanying the tubes (see tubes. 5.2). A calibration scale or other markings referenced to a scale shall be etched directly on the tube to allow direct interpretation of ethyl mercaptan concentration. See Note 2.

NOTE 2—Detector tubes based on the palladium sulfate detection principle are usually calibrated for ethyl mercaptan; detector tubes using mercuric chloride detection chemistry are usually calibrated for *t*-butyl mercaptan.

7.2.1 Detector tubes should be calibrated for a tube temperature of approximately 20°C20 °C and normal atmospheric pressure. Shelf life of the detector tubes shall be a minimum of two years when stored according to the manufacturer's recommendations.

7.2.2 Detector tubes and pumps form an integrally designed unit, that are to be used as a unit. Each manufacturer calibrates detector tubes to match the flow characteristics of its pump, and the use of one brand of tube with another brand of pump will give unreliable results.

7.3 *Gas Sampling Chamber*—Any container of a material that is not reactive with mercaptan and that provides for access of the detector tube into a uniform flow of sample gas at atmospheric pressure and isolated from the surrounding atmosphere. The size of the gas sampling chamber shall be large enough that operation of the pump (6.1) does not draw so much vapor through the detector tube (6.2) relative to the flow of sample vapor that atmospheric air is sucked into the sample chamber, diluting the sample being tested (see 8.1.3.2).

7.3.1 A suitable container may be devised from a half-litre0.5 L polyethylene bottle (see Fig. 1). A 6 mm 6 mm outside diameter polyethylene tubing sealed into the bottle and discharging near the bottom of the bottle provides for flow into the sampling container. A 12 mm 12 mm hole cut into the cap of the bottle provides both access for the detector tube and a vent for the excess gas flow.

7.3.2 Other possible inert materials for the gas sampling chamber and tubing are nylon, polytetrafluoroethylene (PTFE), chlorinated or fluorinated polyethylene and chlorosulfonated polyethylene.

7.4 *Needle Valve and Tubing*—A stainless steel needle valve that can be adjusted to control the flow of gas into the gas sampling chamber. Although a stainless steel needle valve is preferred, a pressure regulator may be used in lieu of a needle valve to control the flow of gas into the gas sampling chamber. Polyethylene or PTFE-fluorocarbon tubing may be used to connect the needle valve or pressure regulator to the gas sampling chamber.

8. Sampling the LP-Gas Vapor Phase

8.1 Select a sampling point that provides access to a representative sample of LP-gas vapor from the container to be sampled. (**Warning—**When selecting a sample point, consider the safety aspects of the release of LPGLP-gas vapor.)

8.1.1 Open the source valve (Valve A in Fig. 1) and briefly blow down vigorously to clear foreign material from the source valve and connecting nipple. Close the source valve.

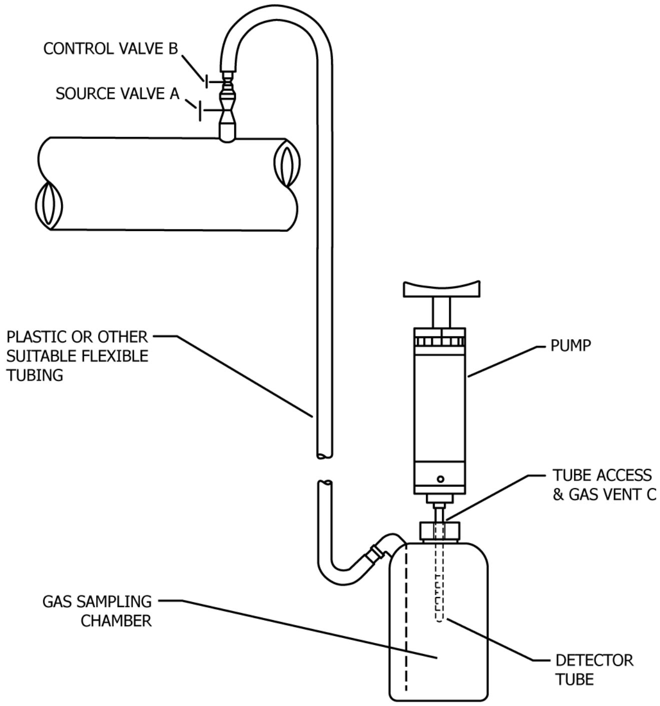

FIG. 1 Half Litre Polyethylene or Other Inert Bottle

8.1.1.1 Excess venting can result in a lower concentration of ethyl mercaptan in the vapor phase.

8.1.2 Install the control valve (Valve B in Fig. 1) or pressure regulator on the outlet of the source valve. Connect outlet of the control valve to the gas sampling chamber using the shortest length practicable of suitable tubing.

8.1.3 Open the source valve and then the control valve to obtain a slight positive flow through the gas sampling chamber, venting to atmosphere through the tube access and vent (Vent C in Fig. 1).

8.1.3.1 Purged gas shall be vented at a suitable rate so that pressure does not build up in the sampling chamber and increase the flow rate through the detector tube.

8.1.3.2 Conversely, the positive flow of ~~LP gas~~ LP-gas vapor shall be sufficient so that operation of the detector tube pump does not pull ambient air into the gas sampling chamber which would dilute the LP-gas vapor.

8.1.4 Purge the gas sampling chamber for at least ~~3 min~~ 3 min to displace air.

8.1.5 Maintain flow of LP-gas during the test procedure in Section ~~9~~10.

9. Preparation of Apparatus

9.1 Before sampling, all sampling equipment should be thoroughly clean and dry.

9.2 Immediately before each series of tests, test the pump for leak-free operation in accordance with manufacturer's instructions. A loss in vacuum on the pump within ~~60 s~~ 60 s indicates a leak. If a leak occurs, follow the pump manufacturer's instructions for resealing the pump and retest. If the pump vacuum cannot be maintained, do not use the pump for testing.

10. Procedure

10.1 Select the tube range that includes the expected concentration of ethyl mercaptan present in the sample. Reading accuracy is improved when the stain extends at least one-half of the tube length. Consider multiple strokes or a lower range tube, or both, to achieve this length of stain.

10.2 Break off both tips of the glass stain tube and insert the outlet of the tube (indicated by arrow in direction of flow) snugly into the pump head. Temperature of tube shall be maintained in the ~~0~~0 °C to ~~40°C~~40 °C range throughout the test.

10.3 Insert the detector tube well into the gas sampling chamber through the tube access and vent (Vent C).

10.4 Operate the pump to draw a measured amount of sample through the detector tube. Within any limits set by the manufacturer's instructions, use multiple strokes to achieve a stain extending to approximately one-half the tube length.

10.5 Remove the tube from the pump and follow the manufacturer's instructions if further handling of the tube is necessary.

10.6 Within ~~30 seconds,~~ 30 s, read the concentration of ethyl mercaptan from graduations on the tube or from charts supplied with the tube. The scale reading nearest the end of the stain is taken as the appropriate scale reading.

11. Interpretation of Results

11.1 If the number of pump strokes used is different from the number specified by the manufacturer, apply a correction as follows:

~~corrected ethyl mercaptan concentration = scale reading ×(specified strokes/actual strokes)~~ (1)

corrected ethyl mercaptan concentration =scale reading×(specified strokes/actual strokes) (1)

11.2 Some detector tubes that may be used in this test method may be calibrated for other mercaptans in milligrams per cubic metre (mg/m^3). Perform the conversion from mg/m^3 of *t*-butyl mercaptan to ~~ppmv~~ ppm by volume of ethyl mercaptan as documented in Annex A1.

11.3 Correct the reading for barometric pressure, especially at high altitudes. For details of this correction, see Annex A1.

11.4 Readings of concentrations below ~~5 ppmv~~ 5 ppm by volume may not be reliable, and may warrant further investigation. (See Appendix X2.)

NOTE 3—This test method is a direct measure of the concentration of ethyl mercaptan in the vapor phase of LP-gas. If the temperature of the system is known, results can be used to obtain an approximation of the concentration of ethyl mercaptan in the liquid phase. (See Appendix X1.)

12. Report

12.1 Report the observed tube reading and corrected concentration of ethyl mercaptan in parts per million by volume ~~(ppmv)~~ to the nearest 0.5 ~~ppmv.~~ppm by volume, and reference this test method.

13. Precision and Bias

13.1 *Precision:*

13.1.1 The precision of this test method as determined by statistical analysis of interlaboratory test results is as follows:

13.1.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty: from ~~5 to 20 ppmv,~~ 5 ppm to 20 ppm by volume, the larger of ~~1 ppm~~ 1 ppm or ±15 % of the ~~mean~~average of the two results; above ~~20 ppmv,~~ 20 ppm by volume, ±20 % of the ~~mean~~average of the two results.

13.1.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the normal and correct operation of the test method, exceed the following value only in one case in twenty: the larger of ~~1.5 ppmv~~ 1.5 ppm by volume or ±20 % of the ~~mean~~average of the two results.

NOTE 4—The preceding repeatability and reproducibility were obtained from statistical analysis of results submitted by twelve testers who cooperatively tested five samples of propane with ethyl mercaptan concentrations ranging from ~~3.3 to 32 ppmv~~ 3.3 ppm to 32 ppm by volume in the vapor phase.

13.2 *Bias*—~~Within the precision limits defined in~~Since there are no suitable standard ~~12.1.1.1 and~~reference materials, ~~12.1.1.2, this test method has no bias.~~no statement on bias can be made.

14. Keywords

14.1 ethyl mercaptan; liquefied petroleum gases; ~~odorant~~odorant; stain tube