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 a rapid and simple procedure using 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), this test method is specifically applicable to systems containing 5 ppmv 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 in parentheses are for information only.

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.*

2. Referenced Documents

2.1 *NFPA Standard:*[2]

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

3. Summary of Test Method

3.1 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 (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 produced in the detector tube is converted to concentration, in parts per million volume (ppmv), by comparison with a calibration scale provided by the manufacturer of the stain tube.

4. Significance and Use

4.1 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 flammable or suffocating concentration levels of LP-gas in air. (See Appendix X1.) 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.

5. Interferences

5.1 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.

5.2 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 ethyl mercaptan as shown in Annex A1.

5.3 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.

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[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**

6. Apparatus

6.1 *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.

6.2 *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 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.[3]

6.2.1 Detector tubes should be calibrated for a tube temperature of approximately 20°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.

6.2.2 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.

6.3 *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.

6.3.1 A suitable container may be devised from a half-litre polyethylene bottle (see Fig. 1). A 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 hole cut into the cap of the bottle provides both access for the detector tube and a vent for the excess gas flow.

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

6.4 *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.

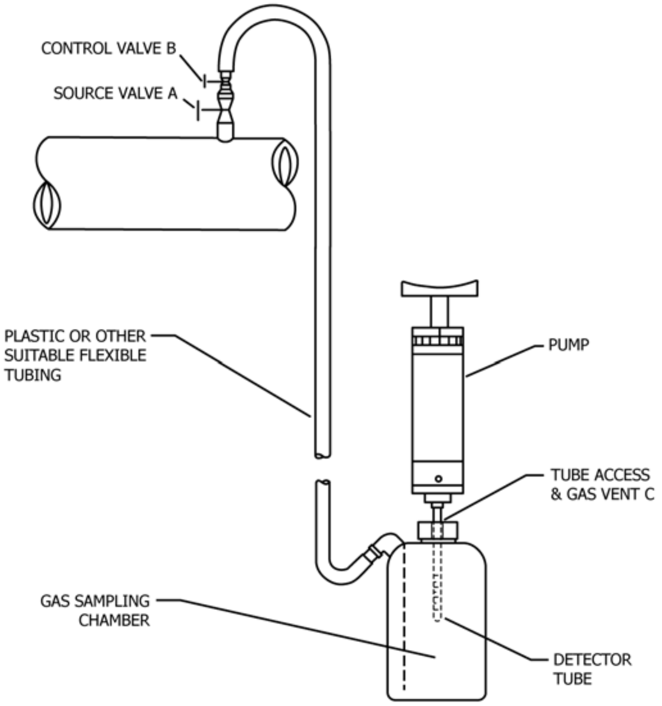

FIG. 1 Half Litre Polyethylene or Other Inert Bottle

7. Sampling the LP-Gas Vapor Phase

7.1 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 LPG vapor.)

7.1.1 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.

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

7.1.2 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.

7.1.3 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).

7.1.3.1 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.

7.1.3.2 Conversely, the positive flow of 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.

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

7.1.5 Maintain flow of LP-gas during the test procedure in Section 9.

8. Preparation of Apparatus

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

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[3] Detector tube No. 72, manufactured by Gastec Corporation, based on the palladium sulfate detection principle, is calibrated for ethyl mercaptan; Gastec detector tubes No. 75 and 75L, using mercuric chloride detection chemistry, are calibrated for *t*-butyl mercaptan. Other manufacturer's tubes may be based on other detection chemistry.

8.2 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 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.

9. Procedure

9.1 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.

9.2 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 to 40°C range throughout the test.

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

9.4 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.

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

9.6 Within 30 seconds, 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.

10. Interpretation of Results

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

$$\text{corrected ethyl mercaptan concentration} = \text{scale reading} \times (\text{specified strokes/actual strokes}) \quad (1)$$

10.2 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 of ethyl mercaptan as documented in Annex A1.

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

10.4 Readings of concentrations below 5 ppmv may not be reliable, and may warrant further investigation. (See Appendix X2.)

NOTE 2—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.)

11. Report

11.1 Report the observed tube reading and corrected concentration of ethyl mercaptan in parts per million by volume (ppmv) to the nearest 0.5 ppmv.

12. Precision and Bias

12.1 *Precision:*

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

12.1.1.1 *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, the larger of 1 ppm or ±15 % of the mean of the two results; above 20 ppmv, ±20 % of the mean of the two results.

12.1.1.2 *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 or ±20 % of the mean of the two results.

NOTE 3—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 in the vapor phase.

12.2 *Bias*—Within the precision limits defined in 12.1.1.1 and 12.1.1.2, this test method has no bias.

13. Keywords

13.1 ethyl mercaptan; liquefied petroleum gases; odorant-stain tube

ANNEX

(Mandatory Information)

A1. CONVERSION AND CORRECTION INFORMATION

A1.1 Conversion of mg/m^3 *t*-butyl mercaptan (TBM) to mg/m^3 ethyl mercaptan (EM):

$$\text{mg/m}^3\ \text{EM} = \text{mg/m}^3\ \text{TBM} \times (\text{mol weight EM/mol weight TBM}) \tag{A1.1}$$

Therefore:

$$1\ \text{mg/m}^3\ \text{TBM} = 1 \times (62.14/90.19) = 0.689\ \text{mg/m}^3\ \text{EM} \tag{A1.2}$$

A1.2 Conversion of mg/m^3 EM to ppmv EM at approximately 25°C:

$$\text{ppmv} = ((\text{mg/m}^3) \times (24.45))/(\text{mol weight EM}) \tag{A1.3}$$

Therefore:

$$1\ \text{mg/m}^3\ \text{EM} = ((1)\times(24.45)/(62.14) = 0.393\ \text{ppmv EM} \tag{A1.4}$$

NOTE A1.1—1 g mol = 22.4 *L* at 0° = 24.45 *L* at 25°C.

A1.3 A convenient tabulation of conversions:

mg/m^3 TBM	mg/m^3 × 0.689 = EM × 0.393 =	ppmv EM
2.5	1.72	0.68
5.0	3.45	1.36
10	6.89	2.71
15	10.34	4.06
20	13.78	5.42
25	17.23	6.77
30	20.67	8.12

A1.4 Correction for barometric pressure:

$$\text{ppmv (corrected)} = \text{ppmv} \times (760\ \text{mm Hg/barometric pressure, mm Hg}) \tag{A1.5}$$

Atmospheric Pressure, kPa (mm Hg)	Elevation in metres (feet)	ppm Reading	ppm Corrected
101.325 (760)	0 (0)	10	10.0
97.709 (733)	305 (1000)	10	10.4
93.977 (705)	610 (2000)	10	10.8
90.644 (680)	915 (3000)	10	11.2
87.312 (655)	1220 (4000)	10	11.6
84.246 (632)	1524 (5000)	10	12.0
81.313 (610)	1829 (6000)	10	12.5

APPENDIXES

(Nonmandatory Information)

X1. RELATIONSHIP OF VAPOR-LIQUID CONCENTRATIONS

X1.1 Published data on vapor-liquid equilibria (k-ratios) of the ethyl mercaptan/propane system are as follows:

Temperature, °C	−30	−20	−10	0	10	20	30
Temperature, °F	−22	−4	14	32	50	68	86
K-ratio[4]	0.12	0.15	0.18	0.21	0.24	0.27	0.31

NOTE X1.1—The K-ratios given herein are for a pure propane/ethyl mercaptan system and can vary for commercial propane/ethyl mercaptan systems.

X1.2 Assuming system equilibrium and accurate data on the temperature of the system, the liquid-phase concentration of ethyl mercaptan can be approximated, based on the following relationship:

$$\text{liquid-phase concentration, ppmv} = \frac{\text{vapor-phase concentration, ppmv}}{\text{K-ratio (at system temperature)}} \tag{X1.1}$$

X1.3 Concentration of Ethyl Mercaptan in Liquid-Phase and Vapor-Phase of Propane / LPG – Interpretation of Liquid Phase and Vapor Phase Results

X1.3.1 Under most circumstances, when a propane container is relatively full, the concentration of ethyl mercaptan odorant in vapor phase samples of LPG will be lower than the concentration of ethyl mercaptan in the liquid phase. So, for example, if LPG were odorized at 1 lb / 10 000 USG (the minimum required dose rate in fuel LPG), a liquid phase sample of LPG should show 1 lb/10 000 USG, or 16.7 mL/m^3 (stain tube reading, ppm v/v). However, a sample of LPG vapor collected from the top of a tank or cylinder containing this odorized LPG would show considerably less ethyl mercaptan depending on the temperature: at -30 °C (-22 °F), only 2 mL/m^3; at 20 °C (68 °F), 4.5 mL/m^3.

X1.3.2 The reason for this difference is that ethyl mercaptan has a lower vapor pressure than propane. The LP Gas Code Handbook (NFPA 58) indicates that ethyl mercaptan has a higher boiling point [35 °C (95 °F)] than propane [-42 °C (-44 °F)]. So there is relatively less ethyl mercaptan in the vapor phase space of an LPG container than in the liquid phase. As

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[4] Heng-Joo, Ng and Robinson, Donald B., "Vapor Liquid Equilibrium in Propane Odorant Systems," Gas Processors Assoc. Research Report, No. 113, 1989,. Available from Gas Processors Assoc., 6526 E. 60th St., Tulsa, OK 74145.

shown in X1.1, the vapor-liquid equilibrium ratio (K-ratio) of ethyl mercaptan in propane is only 0.12 at -30 °C (-22 °F) – meaning that the concentration of ethyl mercaptan in the vapor phase is only 12% of the concentration of the liquid phase. The concentration of ethyl mercaptan in LPG vapor in an LPG container does increase with temperature, so at 30 °C (86 °F), with a K-ratio of 0.31, the ethyl mercaptan concentration in the LPG vapor will be 31% of the concentration in the LPG liquid.

X1.3.3 This ASTM Test Method D5305 is a stain tube test for ethyl mercaptan in the LPG vapor phase. Until an LPG container is almost empty, the ethyl mercaptan concentration in the vapor phase of the container will be much lower than the concentration in the liquid phase LPG. This test method can show how much ethyl mercaptan would be in LPG vapor if there were a leak in an LPG vapor line. Note that the odorization requirement is to be detectable at 1/5th the lower limit of flammability – so LPG vapors must contain sufficient odorant to be detectable, which is usually in the parts per billion range.

X1.3.4 The Canadian stain tube test method for LPG odorant, CAN/CGSB-3.0, No. 18.5, Test Method for Ethyl Mercaptan Odorant in Propane, Field Method, is specifically designed to measure ethyl mercaptan in LPG liquid. So results by CAN/CGSB 3.0 No. 18.5 should be much higher than results by Test Method D5305. In fact, Test Method D5305 results will be smaller than CAN/CGSB 3.0 No. 18.5 results by the factor of the K-ratio in X1.1 for the appropriate temperature: at 20 °C (68 °F), Test Method D5305 should give results only 25% of those given by CAN/CGSB 3.0 No. 18.5 – and that assumes that the LPG vapor tested by Test Method D5305 is actually in equilibrium with the liquid phase. If the ethyl mercaptan in the vapor phase has not reached equilibrium with the liquid phase, Test Method D5305 can give even lower results.

X1.3.5 Note that while CAN/CGSB 3.0 No. 18.5 determines the ethyl mercaptan concentration in liquid phase LPG, it does this by totally evaporating a small liquid sample of LPG and testing the vapor. This vapor, because it is totally vaporized LPG, is representative of the liquid phase and is different from the vapor phase in an LPG container, where the vapor phase is NOT representative of the liquid phase, but in equilibrium with it, based on K-ratios for different components.

X1.3.6 LPG in the form of butane and propane-butane mixtures is used in warm and hot climates. The difference between ethyl mercaptan concentration in the vapor space versus the concentration in the liquid phase is expected to be less in butane and butane mixtures because there is less difference between the vapor pressure of ethyl mercaptan and butane.

X2. ODORIZATION REQUIREMENTS IN THE U.S.A.

X2.1 NFPA 58 is the basis for most regulatory requirements for odorization of LP-gas in the U.S.A. This standard stipulates, in part:

“1-4.1.1 All LP-gases shall be odorized prior to the delivery to a distributing plant by the addition of a warning agent of such character that they are detectable, by a distinct odor, down to a concentration in air of not over ⅕ the lower limit of flammability.

“Exception: Odorization, however, is not required if harmful in the use or further processing of LP-gas, or if such odorization will serve no useful purpose as a warning agent in such further use or processing.

“1-4.4.2 If odorization is required, the presence of such odorants shall be determined by sniff testing or other means and the results documented:

a) whenever LP-gas is delivered to a distributing plant, and

b) when shipments of LP-gas by-pass the distributing plant.”

X2.2 An informational appendix to NFPA 58 states the following:

“A-1-4.1.1 It is recognized that no odorant will be completely effective as a warning agent in every circumstance.

“It is recommended that odorants be qualified as to compliance with 1-4.1.1 by tests or experience. Where qualifying is by tests, such tests should be certified by an approved laboratory not associated with the odorant manufacturer. Experience has shown that ethyl mercaptan in the ratio of 1.0 lb (0.45 kg)/10 000 gallons (37.9 m^3) of liquid LP-gas has been recognized as an effective odorant.”

SUMMARY OF CHANGES

Subcommittee D02.H0 has identified the location of selected changes to this standard since the last issue (D5305–97(2007)) that may impact the use of this standard.

(1) Minor editorial changes were made throughout the standard to comply with Form & Style.
(2) Changed "gas sample container" to "gas sampling chamber" throughout for consistency.
(3) Clarified 3.1 to show that the sample is a vapor-phase sample.
(4) Added 5.3 to identify another potential interference in obtaining a valid result.
(5) Revised 6.3 and 6.3.1 for clarity.
(6) Added 7.1.1.1 as a warning about excess venting.
(7) Added 7.1.3.2 to provide guidance on the appropriate gas flow rate.
(8) Added X1.3 to clarify the difference between ethyl mercaptan concentrations in liquid phase and vapor phase samples.

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