



Designation: D2913 – 20

# Standard Test Method for Mercaptan Content of the Atmosphere<sup>1</sup>

This standard is issued under the fixed designation D2913; 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 is for the measurement of mercaptans (organic thiols) in the atmosphere at concentrations below 100 parts per billion (ppb(v) = 195  $\mu\text{g}/\text{m}^3$ ). For concentrations above 100 ppb(v), the sampling period can be reduced or the trapping liquid volume increased either before or after aspirating. (See Practice D1357 for sampling guidance.) The minimum detectable amount of methyl mercaptan is 0.04  $\mu\text{g}/\text{mL}$  (**1**)<sup>2</sup> in a final liquid volume of 25 mL. When sampling air at the maximum recommended rate of 2 L/min for 2 h, the minimum detectable mercaptan concentration is 1.0 ppb(v) (1.95  $\mu\text{g}$  methyl mercaptan/ $\text{m}^3$  at 101.3 kPa (760 mm Hg) and 25°C). This test method determines total mercaptans and does not differentiate among individual mercaptans, although it is most sensitive to the lower molecular weight alkanethiols.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.7, 8.8, and Section 9.

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.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>3</sup>

- D1193 Specification for Reagent Water
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D1357 Practice for Planning the Sampling of the Ambient Atmosphere
- D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres
- D2914 Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)
- D3195 Practice for Rotameter Calibration
- D3249 Practice for General Ambient Air Analyzer Procedures
- D3609 Practice for Calibration Techniques Using Permeation Tubes
- D3631 Test Methods for Measuring Surface Atmospheric Pressure
- E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356.

## 4. Summary of Test Method

4.1 This test method is intended for obtaining an integrated sample over a selected time span (such as 2 h) either manually or in an automatic sequential sampler using 10 mL of absorption liquid in a bubbler.

4.2 The absorption liquid is delivered to the laboratory for colorimetric analysis by reaction between the collected mercaptan and *N,N*-dimethyl-*p*-phenylenediamine.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

## 5. Significance and Use

5.1 Mercaptans are odorous substances offensive at low concentrations and toxic at higher levels. They are emitted from geothermal sources, industrial processes, and food processing facilities. Mercaptans at low concentrations are commonly added to natural gas and LP gases for safety purposes as well.

## 6. Interferences

6.1 The *N,N*-dimethyl-*p*-phenylenediamine reaction is also used in the determination of other sulfur-containing compounds including hydrogen sulfide and dimethyl disulfide (2). The potential for interference from these latter compounds is especially important, since all of these compounds commonly coexist in certain industrial emissions. Appropriate selection of the color formation conditions and measurements of absorbance at the specified wavelength will eliminate the potential interference from hydrogen sulfide.

6.2 Hydrogen sulfide, if present in the sampled air, may cause a turbidity in the sample absorbing solution. This precipitate must be filtered before proceeding with the analysis. One study showed that 100 µg of H<sub>2</sub>S gave a mercaptan color equivalent to 1.5 to 2.0 µg of mercaptan (3). Another study reported no absorption at 500 nm in the presence of 150 µg of hydrogen sulfide (4, 5).

6.3 Approximately equimolar response is obtained from the hydrolysis products of dimethyl disulfide, the molar extinction coefficient for the amine-mercaptan reaction product being  $4.4 \times 10^3$ , and the amine-dimethyl disulfide reaction product being  $5.16 \times 10^3$  (5). The interference due to dimethyl disulfide has been experimentally determined. Dimethyl disulfide concentrations of 0.6 ppm(v) and 1.0 ppm(v) given an equivalent response as 0.4 ppm(v) and 0.8 ppm(v), respectively, of methyl mercaptan.<sup>4</sup>

6.4 Sulfur dioxide up to 250 µg does not influence the color development even when sampling a test atmosphere containing 300 ppm(v) of SO<sub>2</sub>.

6.5 Nitrogen dioxide does not interfere up to 700 µg of NO<sub>2</sub> when sampling a test atmosphere containing 6 ppm mercaptans. Higher concentrations of NO<sub>2</sub> caused a positive interference when mercaptans were present, but no interference in the absence of mercaptans. Such elevated NO<sub>2</sub> concentrations are not commonly encountered in ambient air except in the vicinity of an accidental spillage.

6.6 The supply of mercuric acetate must be free of mercurous ion. If mercurous ion is present, turbidity will result when the chloride ion-containing reagents are added in the last step of the analytical procedure.

<sup>4</sup> Supporting data giving the results of a laboratory examination of this method by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) are available in special report No. 80-07, "A Laboratory Examination of the Use of the ASTM/APHA. Spectrophotometric Method for the Measurement of Methyl Mercaptan in Kraft Mill Workspace Atmospheres," May 1980, NCASI, 260 Madison Ave., New York, NY 10016.

## 7. Apparatus

### 7.1 Sampling Apparatus:

7.1.1 *Absorber*—Midget bubbler with coarse porosity frit.

7.1.2 *Air Sample Probe*—TFE-fluorocarbon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

7.1.3 *Moisture Trap-Glass*, or polypropylene tube with a two port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with 16-mesh activated charcoal to prevent moisture entrainment. The charcoal should be changed at least weekly and more frequently when sampling high humidity air.

7.1.4 *Filter*—Membrane, of 0.8 to 2.0 µm porosity.

7.1.5 *Pump*—Capable of maintaining a vacuum greater than 70 kPa (0.7 atm) at the specified flowrate.

7.1.6 *Flow Control Device*—A needle valve capable of maintaining a constant flow rate ( $\pm 2\%$ ). Protect the needle valve from particulate matter and moisture entrainment.

7.1.7 *Flow meter*, having a range of 0 to 2.5 L/min.

7.1.8 *Thermometers*—Precision digital thermometers based on resistance temperature detectors (RTDs), thermistors, thermocouples, or organic liquid-in-glass thermometers (such as Thermometer S18C in Specification E2251) meeting the requirements of specific applications in this method may be used.

7.1.9 *Barograph or Barometer*—Capable of measuring atmospheric pressure to  $\pm 0.5$  kPa (4 Torr), meeting the requirements of Test Methods D3631.

7.1.10 *Stopwatch or timer*, accurate to  $\pm 1$  s/24 h.

7.1.11 The arrangements of the component parts of sampling is shown in Fig. 1a, Test Methods D2914.

7.2 *Calibration Apparatus*—A means of generating dynamic standard atmospheres using a permeation device. Dilution air and excess dilution flow must be filtered through activated charcoal to prevent recirculating small quantities of mercaptans. See Practice D3609 for details.

7.3 *Colorimeter or Spectrophotometer, (at 500 nm)*—Use 2.5- or 5.0-cm path length to obtain adequate sensitivity.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water conforming to Specification D1193.

8.3 Solutions should be refrigerated when not in use.

<sup>5</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.4 *Amine-Hydrochloric Acid Solution, Stock*—Dissolve 5.0 g of *N,N*-dimethyl- *p*-phenylenediamine hydrochloride (*p*-aminodimethylaniline hydrochloride) in 1 L of concentrated hydrochloric acid (HCl). Refrigerate at approximately 10°C and protect from light. This solution is stable for at least 6 months.

8.5 *Reissner Solution*—Dissolve 67.6 g of ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) in distilled water, dilute to 500 mL, and mix with 500 mL of nitric acid (HNO<sub>3</sub>) solution containing 72 mL of boiled concentrated nitric acid (sp gr 1.42). This solution is stable for at least 3 months.

8.6 *Color-Developing Reagent*—Mix 3 volumes of amine solution and 1 volume of Reissner solution. Prepare this solution freshly for each set of determinations.

8.7 *Absorbing Solution*—Dissolve 50 g of mercuric acetate Hg(CH<sub>3</sub>COO)<sub>2</sub> in 400 mL of distilled water and add 25 mL of glacial acetic acid (CH<sub>3</sub>COOH). Dilute to 1 L. The mercuric acetate must be free of mercurous salts to prevent precipitation of mercurous chloride during color development. Reagent grade mercuric acetate sometimes contains mercurous mercury. Determine the acceptability of each new bottle of mercuric acetate by adding 3 mL of concentrated hydrochloric acid to 3 mL of the 5 % mercuric acetate. If the solution becomes cloudy, the mercuric acetate is not acceptable. (**Warning**—The absorbing solution and mercury salts are toxic. Avoid contact with the skin and especially with the eyes. Avoid generating or breathing dust. Wash hands after use. Keep away from food. Do not ingest.)

8.8 *Lead Methyl Mercaptide*—Bubble tank methyl mercaptan gas (CH<sub>3</sub>SH) into 10 % lead acetate solution Pb(CH<sub>3</sub>COO)<sub>2</sub> in a fume hood (1). Collect the yellow crystals by vacuum filtration, wash with distilled water, and dry overnight in a vacuum oven at 45°C. Store crystals in a vacuum-sealed container in the dark. One mole of this mercaptide is equivalent to two moles of a mercaptan. Lead mercaptide may be purchased from commercial sources, if desired. (**Warning**—Methyl mercaptan gas is extremely toxic. At high levels of exposure, the human olfactory sense may become insensitive to its presence.)

8.9 *Concentrated, Standard Lead Mercaptide Solution*—Weigh out 156.6 mg of the crystalline lead mercaptide and make up to 100 mL with the 5 % mercuric acetate absorbing solution. This solution contains the equivalent of 500 µg of methyl mercaptan/mL.

8.10 *Diluted Mercaptan Solution, Standard*—Dilute 2 mL of the concentrated standard solution to 100 mL with the 5 % mercuric acetate absorbing solution. This solution contains the equivalent of 10 µg CH<sub>3</sub>SH/mL.

8.11 *Methyl Mercaptan Permeation Device*, with a permeation rate appropriate to the dilution flow and concentrations expected. For example, see the table below.

Concentrations	Permeation Rate Required
10 ppb(v) @ 2 L/min	40 ng/min
100 ppm(v) @ 1 L/min	200 ng/min

## 9. Safety Precautions

9.1 *Mercury*—The absorbing solution contains mercury salts, which are toxic. Precautions for its use are described in 8.7.

9.2 Disposal procedures are described in Annex A3, Test Methods D2914.

9.3 *Compressed Gas Cylinders and Permeation Tubes*—Permeation tubes and compressed gas standards should only be handled in well ventilated locations. Improper handling of compressed gas cylinders can result in explosion. Rapid release of inert gases can result in asphyxiation. Compressed air supports combustion.

9.3.1 Compressed gas cylinders may be used in this test method for preparation of reagents or standard atmospheres. Precautions on methyl mercaptan cylinders are described in 8.8.

9.3.2 General safety precautions for handling and storing compressed gas cylinders are described in Practice D3249.

## 10. Sampling

10.1 Sampling procedures are described for 2-h sampling periods. Different sampling rates and sampling times may be selected to suit specific requirements, but sample volume and flow rates must be adjusted to maintain linearity between absorbance and concentration over the dynamic range of the colorimetric procedure.

10.2 Measure the temperature of the atmosphere being sampled before and after sampling.

10.3 Measure the atmospheric pressure during sampling, in accordance with Test Methods D3631.

## 11. Calibration and Standardization

11.1 *Sampling Equipment*—Calibrate the flow meter before and after use in accordance with Practice D3195.

11.1.1 The pressure drop of the flow meter must be maintained the same during sampling as during calibration.

11.2 *Standard Atmospheres*—See Practice D3609 for preparation of standard atmospheres using the calibration apparatus and the permeation device.

11.2.1 Calibrate the components of the calibration apparatus and the permeation device in accordance with Practice D3609 before and after use.

### 11.3 Calibration Curve:

11.3.1 Sample five standard atmospheres in accordance with Section 12.1. The mercaptan content of the standard atmospheres shall be such that the intensities of the color of the resultant analyzed solutions shall be evenly spaced over the dynamic range of the analytic procedure. One of the five standard atmospheres shall be a blank, generated by removing or bypassing the permeation device.

11.3.2 Analyze the solutions according to 12.2.

11.3.3 Prepare a calibration curve of total mass of mercaptan collected versus absorbance of developed color, using the least squares method.