



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

This standard is issued under the fixed designation D 2913; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

### 1. Scope

1.1 This test method covers measurement of the concentration 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) level, the sampling period can be reduced or the liquid volume increased either before or after aspirating. 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 the 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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.7, 8.8, and Section 9.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1193 Specification for Reagent Water<sup>3</sup>
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere<sup>4</sup>
- D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres<sup>4</sup>
- D 2914 Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)<sup>4</sup>
- D 3195 Practice for Rotameter Calibration<sup>4</sup>
- D 3249 Practice for General Ambient Air Analyzer Procedures<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres 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 the list of references at the end of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.03.

D 3609 Practice for Calibration Techniques Using Permeation Tubes<sup>4</sup>

D 3631 Test Methods for Measuring Surface Atmospheric Pressure<sup>4</sup>

E 1 Specification for ASTM Thermometers<sup>5</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1356.

### 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.

### 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.

### 6. Interferences

6.1 The *N,N*-dimethyl-*p*-phenylenediamine reaction is also suitable for 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  $\mu\text{g}$  of  $\text{H}_2\text{S}$  gave a mercaptan color equivalent to 1.5 to 2.0  $\mu\text{g}$  of mercaptan (**3**). Another study reported no absorption at 500 nm in the presence of 150  $\mu\text{g}$  of hydrogen sulfide (**4**, **5**).

6.3 Approximately equimolar response is obtained from the hydrolysis products of dimethyl disulfide, the molar extinction

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.03.

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>6</sup>

6.4 Sulfur dioxide up to 250  $\mu\text{g}$  does not influence the color development even when sampling a test atmosphere containing 300 ppm(v) of  $\text{SO}_2$ .

6.5 Nitrogen dioxide does not interfere up to 700  $\mu\text{g}$  of  $\text{NO}_2$  when sampling a test atmosphere containing 6 ppm. Higher concentrations of  $\text{NO}_2$  caused a positive interference when mercaptans were present, but no interference in the absence of mercaptans. Such elevated  $\text{NO}_2$  concentrations are unrealistic and would not be encountered in the 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.

## 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 weekly.

7.1.4 *Filter*—Membrane, of 0.8 to 2.0  $\mu\text{m}$  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*—ASTM Thermometer 33C, meeting the requirements of Specification E 1, will be suitable for most applications of this test method.

7.1.9 *Barograph or Barometer*—Capable of measuring atmospheric pressure to  $\pm 0.5$  kPa (4 Torr), meeting the requirements of Test Methods D 3631.

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 D 2914.

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 D 3609 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>7</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 D 1193.

8.3 Solutions should be refrigerated when not in use.

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 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 ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in distilled water, dilute to 500 mL, and mix with 500 mL of nitric acid ( $\text{HNO}_3$ ) solution containing 72 mL of boiled concentrated nitric acid (sp gr 1.42). This solution is stable.

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  $\text{Hg}(\text{CH}_3\text{COO})_2$  in 400 mL of distilled water and add 25 mL of glacial acetic acid ( $\text{CH}_3\text{COOH}$ ). 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 very poisonous. 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 ( $\text{CH}_3\text{SH}$ ) into 10% lead acetate solution  $\text{Pb}(\text{CH}_3\text{COO})_2$  in an adequate 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

<sup>6</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.

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, 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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

desired.<sup>8</sup> (**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.<sup>9</sup> For example, see 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. Precautions for its use are described in 8.7.

9.2 Disposal procedures are described in Annex A3, Test Methods D 2914.

9.3 *Compressed Gas Cylinders*.

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 D 3249.

## 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 D 3631.

## 11. Calibration and Standardization

11.1 *Sampling Equipment*—Calibrate the flow meter before and after use in accordance with Practice D 3195.

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 D 3609 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 D 3609 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.

11.4 Spot checks or audit samples are prepared by analyzing the diluted standard Mercaptan solutions prepared in 8.10. A minimum of two audit samples shall be analyzed for each ten atmospheric samples.

11.4.1 Pipet appropriate aliquots of the diluted standard lead mercaptide into a series of 25-mL volumetric flasks, diluting each to 15 mL with 5 % mercuric acetate absorbing solution and developing the color in the same manner as the samples. A reference blank is prepared in the same manner with the exception that no lead mercaptide is added. Determine the absorbance at 500 nm against the mercaptan-free reference blank.

## 12. Procedure

12.1 *Collection of Sample*—Collect the sample by bubbling the air through 10 mL of absorbing solution in a bubbler at a measured rate between 0.6 to 2.0 L/min for a selected period up to 2-h duration.

12.2 *Analysis*—Quantitatively transfer the sample from the bubbler to a 25-mL volumetric flask and dilute to approximately 22 mL with distilled water that has been used to rinse the frit and bubbler flask. Add 2 mL of freshly prepared color developing reagent, dilute to volume with distilled water, and mix well. Prepare a reference blank in the same manner using 15 mL of unspirated 5 % mercuric acetate and 2 mL of color-developing reagent diluted to 25 mL. After 30 min, measure the absorbance at 500 nm with a spectrophotometer against the mercaptan-free reference blank.

## 13. Calculation

13.1 Calculate the volume of the atmosphere sampled at standard conditions of 25°C and 101.3 kPa (1 atm) as follows:

$$V_r = Q \times t \times \frac{P}{101.3} \times \frac{298.15}{T} \quad (1)$$

where:

- $V_r$  = Volume of air at standard conditions, L,
- $Q$  = average flow, L/min,
- $t$  = sampling time, min,
- $P$  = average atmospheric pressure, kPa,
- $T$  = average temperature of air sample, K,
- 101.3 = pressure of standard atmosphere, kPa, and
- 298.15 = temperature of standard atmosphere, K.

13.2 Calculate the concentration of total mercaptan in the atmosphere as follows:

$$\text{Mercaptan, } \mu\text{g/m}^3 = A \times 1000/V_r \quad (2)$$

<sup>8</sup> Lead mercaptide is available from Eastman Organic Chemicals, Rochester, NY.

<sup>9</sup> Methyl mercaptan permeation tube is available from Metronics Associates Inc., Santa Clara, CA, or PolyScience Corp., Evanston, IL.

where:

$A$  = mass of mercaptan read from calibration curve,  $\mu\text{g}$ ,  
and

1000 = conversion factor, L/m.

13.3 See Practice D 1914 for a method to convert  $\mu\text{m}/\text{m}^3$  to ppm(v).

#### 14. Precision and Bias

14.1 The relative standard deviation for four mercaptans for

methyl to hexyl mercaptan ranged from 0.0 to 2.6 % (1). The relative standard deviation increased with increasing molecular weight of the mercaptans.

#### 15. Keywords

15.1 ambient atmospheres; analysis; mercaptans; sampling

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- (5) Bamesberger, W. L., and Adams, D. F., unpublished information, 1968.

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