



Designation: D2913 – 14

Standard Test Method for Mercaptan Content of the Atmosphere¹

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 (ϵ) 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**)² 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 μg methyl mercaptan/ 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 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:*³

[D1193](#) Specification for Reagent Water

[D1356](#) Terminology Relating to Sampling and Analysis of Atmospheres

[D1357](#) Practice for Planning the Sampling of the Ambient Atmosphere

¹ 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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² The boldface numbers in parentheses refer to a list of references at the end of this standard.

³ 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.

[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.

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 H₂S 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 4.4×10^3 , and the amine-dimethyl disulfide reaction product being 5.16×10^3 (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.⁴

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 SO₂.

6.5 Nitrogen dioxide does not interfere up to 700 µg of NO₂ when sampling a test atmosphere containing 6 ppm mercaptans. Higher concentrations of NO₂ caused a positive interference when mercaptans were present, but no interference in the absence of mercaptans. Such elevated NO₂ 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.

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 Specifications 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 ± 0.5 kPa (4 Torr), meeting the requirements of Test Methods D3631.

7.1.10 *Stopwatch or timer*, accurate to ± 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.⁵ 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.

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 (FeCl₃·6H₂O) in distilled water, dilute to 500 mL, and mix with 500 mL of nitric acid (HNO₃) 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 (CH₃COO)₂ in 400 mL of distilled water and add 25 mL of

⁴ 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.

⁵ *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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.