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## Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosene, Aviation Turbine, and Distillate Fuels (Potentiometric Method)<sup>1</sup>

This standard is issued under the fixed designation D 3227; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope \*

1.1 This test method covers the determination of mercaptan sulfur in gasolines, kerosenes, aviation turbine fuels, and distillate fuels containing from 0.0003 to 0.01 mass % of mercaptan sulfur. Organic sulfur compounds such as sulfides, disulfides, and thiophene, do not interfere. Elemental sulfur in amounts less than 0.0005 mass % does not interfere. Hydrogen sulfide will interfere if not removed, as described in 9.2.

1.2 The values in acceptable SI 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.* For specific hazard statements, see Sections 6, 8, and 9.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1193 Specification for Reagent Water<sup>2</sup>
- D 1250 Guide for Petroleum Measurement Tables<sup>3</sup>
- D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method<sup>3</sup>
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>4</sup>
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>4</sup>
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance<sup>5</sup>

### 3. Summary of Test Method

3.1 The hydrogen sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate solution, using as an indicator the potential between a glass reference electrode and a silver/silver-sulfide indicating electrode. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide and the end point of the titration is shown by a large change in cell potential.

### 4. Significance and Use

4.1 Mercaptan sulfur has an objectionable odor, an adverse effect on fuel system elastomers, and is corrosive to fuel system components.

### 5. Apparatus

5.1 As described in 5.2-5.5; alternatively, any automatic titration system may be used that, using the same electrode pair described in 5.3, is capable of performing the titration as described in Section 9 and selecting the endpoint specified in 11.1 with a precision that meets or is better than that given in Section 13.

5.2 *Meter*—An electronic voltmeter, operating on an input of less than  $9 \times 10^{-12}$  A and having a sensitivity of  $\pm 2$  mV over a range of at least  $\pm 1$  V. The meter shall be electrostatically shielded, and the shield shall be connected to the ground.<sup>6</sup>

5.3 *Cell System*, consisting of a reference and indicating electrode. The reference electrode should be a sturdy, pencil-type glass electrode, having a shielded lead connected to ground. The indicating electrode shall be made from a silver wire, 2 mm (0.08 in.) in diameter or larger, mounted in an insulated support. Silver billet electrodes can also be used.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 05.03.

<sup>6</sup> Any apparatus that will give equal or better precision will be acceptable.

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

5.4 *Buret*, 10-mL capacity, graduated in 0.05-mL intervals, with a tip that extends approximately 120 mm (5 in.) below the stopcock.

5.5 *Titration Stand*, preferably built as an integral part of the meter housing and provided with supports for the electrodes and electrical stirrer, all connected to ground. No permanent change in meter reading should be noticeable upon connecting or disconnecting the stirring motor.

## 6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that 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.

6.1.1 Commercially available solutions may be used in place of prepared laboratory solutions, when they are certified to meet the required concentrations.

6.1.2 Alternate volumes of solutions and solvents may be prepared, when an equivalent concentration is maintained.

6.2 *Water*—Reagent grade, Type I, Specification D 1193.

6.3 *Cadmium Sulfate, Acid Solution* (150 g/L)—Dissolve 150 g of cadmium sulfate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) in water. (**Warning**—Poison. May be fatal if swallowed or inhaled. A known carcinogen (animal positive).) Add 10 mL of dilute  $\text{H}_2\text{SO}_4$ . (**Warning**—Poison. Causes severe burns. Harmful or fatal if swallowed or inhaled) and dilute to 1 L with water.

6.4 *Potassium Iodide, Standard Solution* (approximately 0.1 mol/L)—Dissolve 17 g of KI (weigh to 0.01 g) in 100 mL of water in a 1-L volumetric flask and dilute to 1 L. Calculate the exact molarity.

6.5 *Propan-2-ol*—(**Warning**—Flammable. **Warning**—Unless inhibited against it, peroxides can form in Propan-2-ol when stored in the same container that is exposed to air. When this happens and the Propan-2-ol evaporates to dryness, an explosion can occur. When peroxides are suspected, they may be removed by percolation through an activated alumina column.)

6.6 *Silver Nitrate, Standard Alcoholic Solution* (0.1 mol/L)—Dissolve 17 g of  $\text{AgNO}_3$  in 100 mL of water in a 1-L volumetric flask and dilute to 1 L with Propan-2-ol (99 %) (see Note 1). Store in a dark bottle and standardize at intervals frequent enough to detect a change of 0.0005 or greater in molarity.

NOTE 1—It is important to pass the Propan-2-ol through a column of activated alumina to remove peroxides that may have formed on storage; failure to remove peroxides will lead to low results. It is not necessary to perform this step if the alcohol is tested and found free of peroxides.

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

6.6.1 *Standardization*—Add six drops of concentrated  $\text{HNO}_3$  (relative density 1.42) (**Warning**—Poison. Causes severe burns. Harmful or fatal if swallowed or inhaled) to 100 mL of water in a 300-mL tall-form beaker. Remove oxides of nitrogen by boiling for 5 min. Cool to ambient temperature. Pipet 5 mL of 0.1 mol/L KI solution into the beaker and titrate with the  $\text{AgNO}_3$  solution choosing the end point at the inflection of the titration curve.

6.7 *Silver Nitrate, Standard Alcoholic Solution* (0.010 mol/L)—Prepare daily when the test is being performed by dilution of the 0.1 N standard. Pipet 100 mL of the 0.1 mol/L standard into a 1-L volumetric flask and dilute to volume with Propan-2-ol. Calculate the exact molarity.

6.8 *Sodium Sulfide Solution* (10 g/L)—Dissolve 10 g of  $\text{Na}_2\text{S}$  in water and dilute to 1 L with water. Prepare fresh as needed.

6.9 *Sulfuric Acid*, dilute. Cautiously dilute five volumes of water with one volume of sulfuric acid (relative density 1.84). (**Warning**—Adding the acid will generate heat: mix well. If water begins to boil, cool before adding more acid.) Note that only limited volumes are required because only 10 mL are needed for each litre of cadmium sulfate solution.

6.10 *Titration Solvent*—Low molecular weight mercaptans, as usually found in gasoline, are readily lost from the titration solution if an acidic titration solvent is used. For the determination of the higher molecular weight mercaptan as normally encountered in kerosenes, aviation turbine fuels, and distillate fuels, the acidic titration solvent is used to achieve more rapid equilibrium between successive additions of the titrant.

6.10.1 *Alkaline Titration Solvent*—Dissolve 2.7 g of sodium acetate trihydrate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ) or 1.6 g of anhydrous sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ ) in 25 mL of water free of dissolved oxygen and pour into 975 mL of Propan-2-ol (99 %) (Note 1). When necessary, remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use; keep protected from the atmosphere. To minimize oxygen from dissolving in the solution during storage, an option exists to nitrogen blanket the solution prior to sealing the solvent container.

6.10.2 *Acidic Titration Solvent*—Dissolve 2.7 g of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  or 1.6 g of  $\text{NaC}_2\text{H}_3\text{O}_2$  in 20 mL of water free of dissolved oxygen and pour into 975 mL of Propan-2-ol (99 %) (Note 1) and add 4.6 mL of glacial acetic acid. When necessary, remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use; keep protected from the atmosphere. To minimize oxygen from dissolving in the solution during storage, an option exists to nitrogen blanket the solution prior to sealing the solvent container.

6.11 *Polishing Paper or Cloth*, 6–20  $\mu\text{m}$  average particle size abrasive.

## 7. Sampling

7.1 Take the sample in accordance with Practice D 4057 or Practice D 4177.

7.2 Methanethiol (methyl mercaptan) has a boiling point of  $6.2^\circ\text{C}$  and may be expected to be present in light untreated gasolines. Therefore, when the presence of this low boiling

thiol (mercaptan) is known or expected, specimen to be tested shall be kept below 4°C to prevent the loss of mercaptan from such samples.

## 8. Preparation of Apparatus

8.1 *Glass Electrode*—After each manual titration, or batch of titrations, in the case of automatic titration systems, wipe the electrode with a soft, clean tissue and rinse with water. Clean the electrode at frequent intervals (at least once a week) by stirring in cold chromic acid solution (**Warning**—Causes severe burns. A recognized carcinogen. Strong oxidizer—contact with other material may cause fire. Hygroscopic. An equivalent, chromium-free cleaning solution may be used) for a few seconds (10 s maximum). When not in use, keep lower half of the electrode immersed in water.

8.2 *Silver/Silver-Sulfide Electrode*—Each day prior to use, or as triggered by the analysis of a quality control (QC) sample (see Section 12), prepare a fresh silver sulfide coating on the electrode by the following method:

8.2.1 Burnish electrode with polishing paper or cloth until a clean, polished silver surface shows.

8.2.2 Place electrode in operating position and immerse it in 100 mL of titration solvent containing 8 mL of Na<sub>2</sub>S solution.

8.2.3 Add slowly from a buret, with stirring, 10 mL of 0.1 mol/L AgNO<sub>3</sub> solution over a period from 10 to 15 min.

8.2.4 Remove electrode from solution, wash with water, and wipe with a soft, clean tissue.

8.2.5 Between manual titrations, or batches of titrations in the case of automatic titration systems, store the electrode a minimum of 5 min in 100 mL of titration solvent containing 0.5 mL of the 0.1 mol/L AgNO<sub>3</sub> solution.

## 9. Procedure

9.1 *Determination of Density*—If the sample is to be measured volumetrically, determine the density by Test Method D 1298 or Test Method D 4052 at the temperature at which the test portion will be taken, either directly or from the density determined at a reference temperature and converted to the transfer temperature by use of the Petroleum Measurement Tables (Guide D 1250).

9.2 *Removal of Hydrogen Sulfide*—Test the sample qualitatively for hydrogen sulfide (H<sub>2</sub>S) by mixing 5 mL of the sample with 5 mL of the acid CdSO<sub>4</sub> solution. If no precipitate appears, proceed with the analysis of the sample as described in 9.3. If a yellow precipitate appears, remove the H<sub>2</sub>S in the following manner: Place a quantity of the sample, three to four times that required for the analysis, in a separatory funnel containing a volume of the acid CdSO<sub>4</sub> solution equal to one half that of the sample and shake vigorously. Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with another portion of the CdSO<sub>4</sub> solution. Again draw off the aqueous phase, and wash the sample with three 25 to 30-mL portions of water, withdrawing the water after each washing. Filter the hydrocarbon through a rapid paper. Test a small portion of the washed sample, such as in a test tube or vial, with a few millilitres of the CdSO<sub>4</sub> solution as described previously. If no further precipitate is formed, proceed as directed in 9.3. If a precipitate appears, repeat the extraction with the CdSO<sub>4</sub> solution until all of the

H<sub>2</sub>S has been removed. (**Warning**—Certain straight run gasolines can contain significant amounts of both low molecular weight mercaptans and dissolved elemental sulfur, which, when heated under total reflux conditions, may produce H<sub>2</sub>S by the inter-reaction of both. This phenomenon is particularly noticed in straight run gasolines produced from some natural gas condensates. Therefore, it is advisable that during the removal of H<sub>2</sub>S (and after all H<sub>2</sub>S has been extracted), that no heat should be applied to the sample.)

9.2.1 When the test results obtained are not for referee purposes and Quality Assurance/Quality Control (QA/QC) protocol permits, an alternative test for, and a procedure for the removal of, hydrogen sulfide can be used. This process uses lead acetate paper and sodium hydrogen carbonate and is described in Appendix X1.

9.2.2 There are available automated instruments that eliminate the necessity to remove H<sub>2</sub>S when present, prior to performing the analysis, since the H<sub>2</sub>S titration curve does not interfere with the titration curve of the thiol or mercaptan determination. Such equipment may be used when the test is not for referee purposes. The precision statement does not include data obtained from this alternate procedure.

9.2.3 For referee purposes, the protocol, as detailed in 9.2, shall be used. A possible non-referee situation may be the instance of routine refinery control.

9.3 Measure with a pipet (or other suitable transfer device) or weigh 20 to 50 mL of the original or treated sample into an appropriately sized beaker (for example, a 200, 250, or 300 mL size beaker is typically large enough) containing 100 mL of the appropriate titration solvent. Place the beaker on the titration stand or on the auto-sampler of an automatic titration system. If an automatic titration system is used, set up the system to reproduce the experimental conditions specified in 9.3.1, 9.3.2, and 9.3.3. Adjust the position of the titration stand so that the electrodes are about half immersed. Fill the buret with 0.01 mol/L alcoholic AgNO<sub>3</sub> solution and position it in the titration assembly so that the tip extends approximately 25 mm (1 in.) below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring without spattering.

9.3.1 Record the initial buret and cell potential readings. The usual meter readings for mercaptan presence are in the -250 mV to -350 mV range. Add suitable small portions of 0.01 mol/L AgNO<sub>3</sub> solution and, after waiting until a constant potential has been established, record the buret and meter readings. Consider the potential constant if it changes less than 6 mV/min.

NOTE 2—If potential readings obtained with freshly prepared electrodes are erratic, it is possible that the electrodes are not properly conditioned. This difficulty usually disappears in succeeding titrations.

NOTE 3—When analyzing samples with a relatively high mercaptan concentration, the use of a 20 to 50 mL sample size can require an unreasonably long titration time and a large quantity of the titrant. For such samples, a smaller sample size may be used or the original sample may be diluted with a suitable solvent that is miscible with the sample and free of mercaptans into the 20 to 50 mL sample size range prior to titrating the sample. The precision of samples using <20 mL sample sizes or samples that have been diluted have not been determined in an interlaboratory study.

NOTE 4—With certain instruments, the algebraic sign of the potentials may appear reversed.

9.3.2 When the potential change is small for each increment of AgNO<sub>3</sub> solution, add volumes as large as 0.5 mL. When the change of potential becomes greater than 6 mV/0.1 mL, use 0.05-mL increments of 0.01 mol/L AgNO<sub>3</sub> solution. Near the end point of the titration, 5 or 10 min may elapse before a constant potential is obtained. Although it is important to wait for equilibrium conditions, it is also important that the duration of the titration be as short as possible to avoid oxidation of the sulfur compounds by atmospheric oxygen. Once started, a titration must never be interrupted and resumed later.

9.3.3 Continue the titration until the meter reading change of the cell potential per 0.1 mL of 0.01 M AgNO<sub>3</sub> solution has become relatively constant. Consider the potential constant if it changes less than 6 mV/min. Remove the titrated solution, rinse the electrodes with alcohol, and wipe with a dry tissue. If an automatic titration system is used, rinse the electrodes well with alcohol, allow the excess alcohol to drain off the electrode and then proceed with the next sample. Between successive determinations (or batches of determinations in the case of automatic titration systems) on the same day, store the electrodes in accordance with 8.1 and 8.2.5.

9.4 As often as is required and preferably, at least daily, when the test equipment is being used, perform a blank titration following 9.3-9.3.3 without adding a test sample.

## 10. Calculation

10.1 Calculate the mercaptan sulfur content of the sample as follows:

$$\text{Mercaptan sulfur, mass \%} = (DM(A_1 - A_0) \times 3.206)/W \quad (1)$$

or

$$\text{Mercaptan sulfur, mass \%} = (DM(A_1 - A_0) \times 3.206)/(d \times V) \quad (2)$$

$$D = (W + I)/W \quad (3)$$

$$D = (V + J)/V \quad (4)$$

where:

- $A_1$  = millilitres of AgNO<sub>3</sub> solution required to reach the end point in the vicinity of +300 mV (see Fig. 1), when a sample is being titrated,
- $A_0$  = mL of AgNO<sub>3</sub> solution required to reach the end point in the vicinity of +300mV (see Fig. 1), when only the blank is titrated. (Note, there are no other changes to the factors in the equation).
- $d$  = density of sample at transfer temperature, g/mL,
- $D$  = dilution factor (if necessary, see Note 3),
- $I$  = grams of diluent used,
- $J$  = mL of diluent used,
- $M$  = molarity of the AgNO<sub>3</sub> solution,
- $W$  = grams of sample used,
- 3.206 = 100 × g meq weight S in mercaptan, and
- $V$  = mL of sample used.

## 11. Interpretation of Results

11.1 *Treatment of Data*—Plot the cumulative volumes of 0.01 M AgNO<sub>3</sub> solution added against the corresponding cell potentials. Select the end point at the inflection point of the steepest portion of each “break” in the titration curve as shown

in Fig. 1. The shape of the titration curve may change with different instruments. However, the above interpretation of the end point should be followed.

11.1.1 *Mercaptans Only*—If mercaptans alone are present in the sample, the titration produces a curve of the first type shown in Fig. 1, having an initial plateau at a potential equal to or more negative than –250 mV, and an end point when a potential change of less than 6 mV/min is reached and the change in mV/min of titrant is reduced with each incremental addition.

11.1.2 *Mercaptans and Elemental Sulfur*—When elemental sulfur and mercaptans are both present in the sample, a chemical interaction occurs which, in the titration solvent used, precipitates silver sulfide (Ag<sub>2</sub>S) during the titration.

11.1.3 When mercaptans are present in excess, the end of the Ag<sub>2</sub>S precipitation occurs at about –550 to –350 mV, and is followed by the precipitation of the silver mercaptide to the +300-mV end point. This situation is shown in the middle curve of Fig. 1. Since all of the Ag<sub>2</sub>S originates from an equivalent amount of mercaptan, the total titration to the mercaptide end point must be used to calculate the amount of mercaptan sulfur.

11.1.4 When elemental sulfur is present in excess, the end of the Ag<sub>2</sub>S precipitation is taken in the same region (+300 mV) as in the case of silver mercaptide, and is calculated as mercaptan sulfur.

11.1.5 When samples of light gasolines containing methanethiol (methyl mercaptan) or heavier thiols (mercaptans) appear to give erratic results, it may be necessary to cool and maintain the test apparatus below 4°C prior to proceeding, as detailed in 9.2-9.4 inclusive. For these samples, this step may be necessary for more reproducible test results.

## 12. Quality Assurance/Quality Control

12.1 Confirm the performance of the instrument and the test procedure by analyzing a control (QC) sample.

12.1.1 When QA/QC protocols are already established in the testing facility, these may be used when they confirm the reliability of test result.

12.1.2 When there is no QA/QC protocol established in the testing facility, Appendix X2 may be used as the QA/QC system.

12.2 Users of this test method are advised that in contractual agreements, one or more of the contracting parties can and may make Appendix X2 a mandatory practice.

## 13. Precision and Bias

13.1 *Precision*—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

13.1.1 *Repeatability*—The difference between two successive test results, obtained by the same operator with 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:

$$\text{Repeatability} = 0.00007 + 0.027x \text{ (see Note 5)}$$