



Designation: D4952 – 23

Standard Test Method for Qualitative Analysis for Active Sulfur Species in Fuels and Solvents (Doctor Test)¹

This standard is issued under the fixed designation D4952; 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 (ϵ) indicates an editorial change since the last revision or reappraisal.

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

1. Scope*

1.1 This test method covers and is intended primarily for the detection of mercaptans in motor fuel, kerosine, and similar petroleum products. This method may also provide information on hydrogen sulfide and elemental sulfur that may be present in these sample types.

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.* For specific warning statements, see 7.3.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1193 Specification for Reagent Water](#)

[D3227 Test Method for \(Thiol Mercaptan\) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels \(Potentiometric Method\)](#)

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

2.2 *Energy Institute Standards:*³

[IP 30 Detection of Mercaptans, Hydrogen Sulfide, Elemental Sulfur, and Peroxides – Doctor Test Method](#)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *flowers of sulfur, n*—a purified form of sulfur that is prepared by sublimation, as opposed to precipitation.

3.2.2 *sour, adj*—describing material having a detectable quantity of hydrogen sulfide or mercaptan.

3.2.3 *sweet, adj*—describing material having a nondetectable quantity of hydrogen sulfide or mercaptan.

3.3 *Acronyms:*

3.3.1 *UV, adj*—ultraviolet, the spectrum of electromagnetic radiation commonly defined as having a wavelength between 100 and 400 nanometers.

3.3.1.1 *Discussion*—In the context of this test method, the term of UV is expanded to include wavelengths up to 550 nm for the reason discussed in [8.1](#).

4. Summary of Test Method

4.1 The sample is shaken with sodium plumbite solution, a small quantity of powdered sulfur added, and the mixture shaken again. The presence of mercaptans or hydrogen sulfide or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases.

5. Significance and Use

5.1 Sulfur present as mercaptans or as hydrogen sulfide in distillate fuels and solvents can attack many metallic and non-metallic materials in fuel and other distribution systems. A negative result in the doctor test ensures that the concentration of these compounds is insufficient to cause such problems in normal use.

³ Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., <http://www.energyinst.org>.

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 D02.03 on Elemental Analysis.

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² 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.

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

6. Interferences

6.1 This test cannot be used if there are more than trace amounts of peroxides in the test sample. Peroxides can give a false positive results where mercaptans are at low level or not even present.⁴

6.2 To check if peroxides are present in sufficient concentration to invalidate the test, shake 10 mL \pm 0.5 mL of a fresh portion of the sample with approximately 2 mL of the potassium iodide solution, add two drops of the acetic acid solution, and two drops of the starch solution. If the aqueous layer turns a blue color, this confirms the presence of peroxides in sufficient quantity to invalidate the test, and the test on this sample should be discontinued. Proceed in accordance with 6.4.

6.3 Alternatively, one may choose to perform a preliminary Doctor Test. If a brown precipitate slowly forms, peroxide is probably present. Proceed in accordance with 6.2 to confirm presence of peroxides at sufficient quantity to invalidate the test.

6.4 If interference from peroxides is confirmed, proceed to re-sample and retest. Ensure that sampling and handling procedures for the new sample prevent UV light exposures as prescribed in 8.1. None of the normal refinery units or blending processes producing spark ignition motor fuels are known to create peroxides under normal operating conditions.

7. Reagents and Materials

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

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types II or III of Specification D1193.

7.3 *Doctor (Sodium Plumbite) Solution*—(**Warning**—Poisonous and suspect carcinogen.) Dissolve approximately 125 g of sodium hydroxide (NaOH) in 1 L of reagent water. Add 60 g of lead monoxide (PbO) and shake vigorously for 15 min, or let stand with occasional shakings for at least one day. Allow to settle and decant or siphon off the clear liquid. If the solution does not settle clear, filter it through filter paper. Keep the solution in a tightly sealed bottle and refilter before use if not perfectly clear. As an alternative, the lab may use a commercially prepared solution that meets the requirements of the laboratory preparation.

⁴ Brooks, B. T., "Sodium Plumbite or Doctor Test of Gasolines," *Industrial and Engineering Chemistry*, Vol 16, No. 6, June 1924, p. 588.

⁵ *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.

NOTE 1—Alternative volumes of the solution may be prepared or purchased, provided the final solution concentration is equivalent.

7.4 *Sulfur*—Pure, sublimed, stored in a closed container.

7.5 *Potassium Iodide, approximately 100 g/L Solution*—Dissolve approximately 1 g of potassium iodide in approximately 10 mL of water. Prepare fresh for each test.

7.6 *Acetic Acid, approximately 100 g/L Solution*—Add approximately 10 mL of glacial acetic acid to approximately 100 mL water.

7.7 *Starch Indicator, approximately 5 g/L Indicator Solution*—Prepare fresh each time of testing.

8. Sampling and Handling of Test Samples

8.1 Improper choice of clear glass sample bottles followed by exposure to sunlight or fluorescent lighting emitting UV wavelengths shorter than 550 nm in the laboratory can generate peroxides in cracked gasolines as well as finished batches of gasolines. Peroxides are generated in proportion to the head-space air volume and time of exposure.⁶ It has been reported that peroxides can interfere with the Doctor Test—see 6.1.

8.2 It is preferable to collect the field samples using dark brown/amber bottles or metal cans, or if using clear glass bottles to wrap them in foil or place in a light-tight box to prevent UV light exposure.

8.3 The samples should be tested without delay upon receipt in the laboratory before further chemical interactions take place.

9. Procedure

9.1 Shake vigorously together in a test tube 10 mL of the sample being tested and 5 mL of sodium plumbite solution for about 15 s. Add a small amount of pure, sublimed flowers of sulfur so that practically all of it floats on the interface between the sample and the sodium plumbite solution after shaking. Shake again for 15 s. Allow to settle and observe within 2 min.

NOTE 2—It is important to avoid adding more sulfur than will just cover the interface. About 20 mg to 25 mg is the proper quantity, which can be estimated with a little practice. If too much sulfur is added, any possible discoloration will be masked by the excess of sulfur.

10. Interpretation of Results

10.1 If the solution is discolored or if the yellow color of the sulfur film is noticeably masked, report the test as positive and consider the sample as *sour*. If the sample remains unchanged in color and the sulfur film is bright yellow or only slightly discolored with gray or flecked with black, report the test as negative and consider the sample as *sweet*. If a brown precipitate slowly forms, peroxide is probably present. Proceed in accordance with 6.2.

NOTE 3—This examination must be made with extreme care. Sometimes the sulfur layer will be only flecked with spots of gray or black, and if there is any change in the color of either the sample or the Doctor

⁶ Supporting data (Jennings, R., and Kohler, D., "Sunlight and Air Exposure Effects on Octane Number or Cetane Number of Petroleum Product Samples," April 2001) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1502. Contact ASTM Customer Service at service@astm.org.