Designation: D4952 – 12 (Reapproved 2017)

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

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)

2.2 *Energy Institute Standards:*[3]

IP 30 Detection of Mercaptans, Hydrogen Sulfide, Elemental Sulfur, and Peroxides – Doctor Test Method

3. Summary of Test Method

3.1 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.

4. Significance and Use

4.1 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.

5. Interferences

5.1 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]

5.2 To check if peroxides are present in sufficient concentration to invalidate the test, shake 10 mL ± 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 5.4.

5.3 Alternatively, one may choose to perform a preliminary Doctor Test. If a brown precipitate slowly forms, peroxide is probably present. Proceed in accordance with 5.2 to confirm presence of peroxides at sufficient quantity to invalidate the test.

5.4 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

[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.

Current edition approved May 1, 2017. Published June 2017. Originally approved in 1989. Last previous edition approved in 2012 as D4952 – 12. DOI: 10.1520/D4952-12R17.

[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.

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

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

prescribed in 7.1. None of the normal refinery units or blending processes producing spark ignition motor fuels are known to create peroxides under normal operating conditions.

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 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.

6.2 *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.

6.3 *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.

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

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

6.5 *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.

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

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

7. Sampling and Handling of Test Samples

7.1 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 headspace air volume and time of exposure.[6] It has been reported that peroxides can interfere with the Doctor Test—see 5.1.

7.2 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.

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

8. Procedure

8.1 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.

9. Interpretation of Results

9.1 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 5.2.

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 solution these spots will be difficult to detect.

NOTE 4—Strictly speaking, the test will not reject the sample on the basis of mercaptans only. The primary criterion for rejection is the appearance of the sulfur layer after shaking, and small amounts of mercaptans will only discolor the sulfur. However, samples which contain mercaptans will also normally contain small amounts of sulfur in other forms which will discolor the layers at the interface. The addition of pure, sublimed flowers of sulfur is required to indicate that a reaction of mercaptan and sodium plumbite has occurred.

NOTE 5—When the sample contains appreciable amounts of hydrogen sulfide, a heavy black precipitate may be formed during the initial shaking and before the addition of the sulfur. If such a precipitate is noted, the test may be stopped at that point and the sample reported as "Does not pass." However, if this observation is at all doubtful, the test should be continued. If the sample darkens before the addition of sulfur is made, this indicates that the sample contains mercaptans and an excess of elemental sulfur that is needed to drive the sample reaction with sodium plumbite.

9.1.1 The relationship between the appearance of the sample and the type of sulfur is shown in Table 1.

9.2 If the doctor test is positive, mercaptan content may be determined using Test Method D3227.

10. Precision and Bias

10.1 No justifiable values of repeatability, reproducibility, or bias for this test method can be stated here because the test detects only the presence or absence of active sulfur species, such as hydrogen sulfide or mercaptan.

[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.

[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.

TABLE 1 Relationship Between Sample and Sulfur

Appearance	Type of Sulfur
Formation of a brown precipitate before addition of sulfur	Peroxide is probably present; proceed in accordance with 5.2
Darkening of the sample before addition of sulfur	Mercaptans and elemental sulfur present in sample
Black precipitate before addition of sulfur	Appreciable amounts of hydrogen sulfide
Black color of sulfur after shaking	Traces of hydrogen sulfide
Spots of discoloration in the sulfur layer, plus darkening of the sample	Hydrogen sulfide absent; mercaptans or elemental sulfur, or both, present
Clear yellow Doctor solution; no discoloration of sulfur	Hydrogen sulfide and elemental sulfur absent; traces of mercaptans present

11. Keywords

11.1 doctor test; hydrogen sulfide; kerosine; mercaptans; motor fuel; sulfur