Designation: D 4952 – 02

An American National Standard

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 D 4952; 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 Department of Defense.

1. Scope *

1.1 This test method 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 acceptable SI units are to be regarded as 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 3227 Test Method for Thiol Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)[3]

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. Reagents and Materials

5.1 *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.[4] 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.

5.2 *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 D 1193.

5.3 *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—Alternate volumes of the solution may be prepared or purchased, provided the final solution concentration is equivalent.

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

6. Procedure

6.1 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 sulfur 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.

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[1] 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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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 05.01.

[4] *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.

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

TABLE 1 Relationship Between Sample and Sulfur

Appearance	Type of Sulfur
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

NOTE 2—It is important to avoid adding more sulfur than will just cover the interface. About 20 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.

7. Interpretation of Results

7.1 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*.

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.

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.

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

7.2 If the doctor test is positive, mercaptan content may be determined using Test Method D 3227.

8. Precision and Bias

8.1 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.

9. Keywords

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

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 4952–97) that may impact the use of this standard.

(1) Deleted reference to Specification D 235 in Scope and Referenced Documents.
(2) Deleted Footnote 2, and renumbered subsequent footnotes.
(3) Added new Note 2.
(4) Added new Note 3, Note 4, and Note 5.
(5) Added new 7.1.1.