



Designation: D5384 – 14

Standard Test Methods for Chlorine in Used Petroleum Products (Field Test Kit Method)¹

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1. Scope*

1.1 These test methods cover the determination of chlorine in used oils, fuels, and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene, all containing <25 % (mass/mass) water.

1.1.1 If the sample contains greater than 25 % water, the sodium metal reacts preferentially with the water rather than with the halogenated organics in the oil.

1.1.2 Bromide and iodide are also titrated and reported on a molar basis as chlorine. The method does not detect fluorine because AgF remains in the solution during the titration, while AgI, AgBr, and AgCl precipitate out and can therefore be detected.

1.1.3 Some of the chlorinated organic compounds that have been shown to be detectable by this method include trichloroethane, dichloroethane, trichlorobenzene, monochlorobenzene, chlorooctadecane, methylene chloride, perchloroethylene, Freon, and polychlorinated biphenyls. These nine compounds represent the major classes of chlorinated compounds that are found in used oils.

1.2 The entire analytical sequence, including sampling, sample pretreatment, chemical reactions, extraction, and quantification, is available in kit form using predispensed and encapsulated reagents. The overall objective is to provide a simple, easy to use procedure, permitting nontechnical personnel to perform a test in or outside of the laboratory environment in under 10 min. The test method also gives information to run the test without a kit.

1.2.1 Test Method A is preset to provide a greater than or less than result at 1000 mg/kg (ppm) total chlorine to meet regulatory requirements for used oils.

1.2.2 Test Method B provides results over a range from 200 to 4000 mg/kg total chlorine.

1.3 For both test methods, positive bias will result from samples that contain greater than 3 % (mass/mass) total sulfur.

While a false negative result will not occur, other analytical methods should be used on high sulfur oils.

1.4 *Test Method B, Lower Limit of Quantitation*—In the round-robin study to develop statistics for this test method, participants were asked to report results to the nearest 100 mg/kg. The lower limit of quantification could therefore only be determined to be in the range from 870 mg/kg⁵ to 1180 mg/kg⁵.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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 safety statements are given in Sections 3, 6, and 7.

2. Referenced Documents

2.1 *ASTM Standards*:²

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

2.2 *Federal Regulation*:

40 CFR 261 Identification and Listing of Hazardous Waste³

3. Summary of Test Methods

3.1 The oil sample (approximately 0.3 g) is dispersed in a hydrocarbon solvent and reacted with a mixture of metallic sodium catalyzed with naphthalene and diglyme at ambient temperature. This process converts organic halogens to their respective sodium halides. Halides in the treated mixture, including those present prior to the reaction, are then extracted into an aqueous buffer, which is then titrated with mercuric nitrate using diphenyl carbazone as the indicator. The end point

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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.

³ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

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

of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.1.1 Preset reagent quantities are used for Test Method A so that the final result is clearly determined to be either above or below 1000 mg/kg total chlorine.

3.1.1.1 Analysis time is approximately ten minutes, and the necessary reagents are all contained in a small test kit. Each kit contains sufficient materials for ten analyses.

3.1.2 A fixed concentration titrant of mercuric nitrate in water is used for Test Method B. A titration is performed on the extracted aqueous sample until the color changes from yellow to blue. At this point, the titration is stopped and the chlorine concentration is determined based on the volume of titrant added. (**Warning**—In case of accidental breakage onto skin or clothing, wash with large amounts of water. All the reagents are poisonous and should not be taken internally.) (**Warning**—The gray ampules contain metallic sodium which is a flammable, water-reactive solid. Reaction with water will generate flammable hydrogen gas.) (**Warning**—In addition to other precautions, do not ship kits on passenger aircraft. Kits contain metallic sodium and mercury salts. Used kits will pass the USEPA Toxic Characteristic Leaching Procedure (TCLP) test. Check with your state environmental enforcement office to see if additional disposal regulations may apply.) (**Warning**—When the sodium ampule in either kit is crushed, oils that contain more than 25 % (m/m) water will cause the sample to turn clear to light gray and will build noticeable pressure. Under these circumstances, the results can be biased excessively low and should be disregarded.) (**Warning**—In addition to other precautions, take care to ensure that fingers are not cut by glass in the kits. All reagents in prepackaged kits are contained in crushable glass ampules inside plastic test tubes. Each ampule should be crushed only once to reduce the risk of glass pieces piercing the sides of the tube. Wear safety glasses and gloves throughout the testing procedure.)

4. Significance and Use

4.1 Chlorinated compounds can lead to corrosion of equipment and poisoning of the catalyst. Chlorinated compounds also present a health hazard when incompletely combusted. Chlorine content of petroleum products is determined prior to their being recycled.

NOTE 1—Federal Regulations mandate that often the chlorine content of used oil must be determined before recycling. EPA regulation 40 CFR 261 bars the sale of used oil for fuel if it is contaminated with halogens measured as chlorine at levels exceeding 1000 mg/kg. Such oil is considered to be a hazardous waste unless it can be proven that the chlorine content is inorganic or that the halogenated organics are not hazardous constituents. The cost of disposing of a hazardous waste is many times higher than the cost of used oil disposal. Therefore it is critical for users, generators, haulers, reproducers, and collectors to test the material they handle in order to comply with regulations, maintain safe operations, and avoid high disposal costs.

4.2 These test methods can be used to determine when a used petroleum product meets or exceeds requirements for total halogens measured as chloride. It is specifically designed for used oils, permitting on-site testing at remote locations by nontechnical personnel to avoid the delays of laboratory testing.

5. Apparatus

5.1 Both the fixed end point test (Test Method A) and the quantitative test (Test Method B) are available as completely self-contained test kits containing all the reagents necessary to complete the test.⁴ Each kit includes a sampling syringe to withdraw a fixed volume of sample for analysis; a first polyethylene test tube into which the sample is introduced for dilution and reaction with metallic sodium; a second polyethylene tube containing a buffered aqueous extractant, the mercuric nitrate titrant (Test Method A only), and diphenyl carbazone indicator; a polypropylene filter funnel; and a 1-mL titration syringe filled with mercuric nitrate titrant (Test Method B only).

5.2 If prepackaged kits are not used, the following materials and reagents will be required.

5.2.1 *Test Tubes*, two test tubes capable of holding 30 mL, sealed with screw caps.

5.2.2 *Filtration Device*, composed of a funnel containing a plug of polypropylene felt (or equivalent) to retain residual hydrocarbons from 5 mL of aqueous solution.

5.2.3 For quantitative Test Method B only, a 1.0-mL polypropylene tuberculin type syringe or equivalent. The syringe is to be marked with divisions at every 0.025 mL.

6. Reagents

6.1 If prepackaged kits are to be used, all necessary reagents and instructions are contained within the kits.

6.2 If not using prepackaged kits, the following must be prepared.

6.2.1 A solution of 10 % (m/m) naphthalene in *bis*-2-methoxy-ethyl ether (diglyme). Dissolve 10 g of naphthalene into 90 g of *bis*-2-methoxy-ethyl ether.

6.2.2 A dispersion of 40 % (m/m) ground sodium in mineral oil.

6.2.3 A 0.15 % (mass/volume) solution of *s*-diphenyl carbazone in ethyl alcohol. Dissolve 0.15 g *s*-diphenyl carbazone powder into 100 mL of ethyl alcohol.

6.2.4 For Test Method A, a 4.75-mmol/L solution of mercuric nitrate. Prepare a mercuric nitrate stock solution by first dissolving 5.14 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**Warning**—**EXTREMELY TOXIC**) in 5 mL of 50 % (vol/vol) nitric acid. After solute has completely dissolved, make up to 150 mL with Type II water. Stock solution = 0.100 mol/L. Prepare 4.75 mmol/L solution by putting 47.5 mL of stock solution into a 1-L volumetric flask and make up to 1 L with Type II water.

6.2.5 For Test Method B, a 13.7-mmol/L solution of mercuric nitrate. Place 137 mL of stock solution (see 6.2.4) into a 1-L volumetric flask and make up to 1 L with Type II water.

6.2.6 An aqueous buffer solution containing 6 % (mass/mass) sodium sulfate, 2.6 % (mass/mass) sodium phosphate and 3.175 % (mass/mass) sulfuric acid (pH 1.5).

⁴The sole source of supply of Clor-D-Tect 1000 (Test Method A) and Clor-D-Tect Q4000 (Test Method B) known to the committee at this time is Dexsil Corp., One Hamden Park Dr., Hamden, CT 06517. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.