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An American National Standard

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

This standard is issued under the fixed designation D 5384; 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.

ϵ^1 NOTE—Warning notes were made part of the text in April 2000.

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 Bromide and iodide are also titrated and reported on a molar basis as chlorine.

1.2 The entire analytical sequence, including sampling, sample pretreatment, chefru mical 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 non-technical 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 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 Method B provides results over a range from 200 to 4000 mg/kg total chlorine.

1.3 For both 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 *Method B Lower Limit of Quantitation*—In the roundrobin study to develop statistics for this 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 to 1180 mg/kg[5].

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 and 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[2]

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

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

3.1.2 A fixed concentration titrant of mercuric nitrate in water is used for 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

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[1] These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.02.

to other precautions, take care to ensure that fingers are not cut by glass in the kits. All reagents in pre-packaged 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.

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 (Method A) and the quantitative test (Method B) are available as completely self-contained test kits containing all the reagents necessary to complete the test.[3] 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 (Method A only), and diphenyl carbazone indicator; a polypropylene filter funnel; and a 1- mL titration syringe filled with mercuric nitrate titrant (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 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 Method A, a 4.75-mmol/L solution of mercuric nitrate. Prepare a mercuric nitrate stock solution by first dissolving 5.14 g $Hg(NO_3)_2 \cdot H_2O$ (**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 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).

7. Sampling

7.1 Take samples in accordance with the instructions in Practice D 4057.

7.2 Free water, as a second phase, is to be removed. However, this second phase can be analyzed separately for chloride content by using a method suitable for materials with high water content (**Warning**—The gray ampules contain metallic sodium which is a flammable, water-reactive solid. Reaction with water will generate flammable hydrogen gas.) (**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.).

8. Procedure (Methods A and B)

NOTE 2—Perform the test in a dry area with an ambient temperature greater than 15°C (60°F) and adequate light. In cold weather, a truck cab is sufficient.

8.1 Using a volumetric pipette, place 0.40 ± 0.02 mL of sample into one of the polyethylene tubes.

8.2 Using a volumetric pipette, add 1.5 mL of naphthalene/*bis*-2-methoxyethyl ether solution. Shake well.

8.3 Add 200 mg of metallic sodium dispersion (80 mg Na) and shake well for 1 min.

8.4 Add 7 mL of aqueous buffer solution to the mixture. Cap and shake well. Vent the tube so that the resulting pressure is released.

8.5 Allow the aqueous and hydrocarbon phases to separate for 2 min. Decant off the aqueous phase and pass 5 mL through the polypropylene filter into a second polyethylene tube.

8.6 *Method A (Qualitative at 1000 mg/kg)*—Add 0.75 mL of 4.75 mmol/L mercuric nitrate solution to the 5 mL of aqueous filtrate. Shake well.

8.6.1 Add approximately 0.5 mL of diphenylcarbazone indicator solution. Shake well.

8.6.2 Observe color. A violet solution means the original oil sample contains less than 1000 mg/kg total chlorine. A yellow or colorless solution means the oil sample contains greater than

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[3] Clor-D-Tect 1000 (Method A) and Clor-D-Tect Q4000 (Method B), available from Dexsil Corp., One Hamden Park Dr., Hamden, CT 06517, have been found satisfactory for this purpose.

1000 mg/kg total chlorine.

8.7 *Method B (Quantitative to 4000 mg/kg)*—Fill the 1 cc tuberculin syringe with 13.7 mmol/L of mercuric nitrate solution to a volume of 1.0 mL by placing the tip of the syringe in the mercuric nitrate solution and withdrawing the plunger slowly until the syringe is full. If a burette is used instead of a syringe, fill the burette with the mercuric nitrate solution and dispense solution until the meniscus is at the zero point.

8.7.1 Add approximately 0.5 mL of diphenylcarbazone solution to the 5 mL of aqueous filtrate and mix well.

8.7.2 Place the filled tuberculin syringe in the polyethylene tube containing the aqueous filtrate and indicator reagent, and slowly depress the syringe so that the mercuric nitrate titrant is dispensed drop by drop. If the burette is used, add titrant drop by drop. Gently shake the solution between each drop. Stop titrating when a persistent violet color remains throughout the solution.

8.7.3 Examine the titrating syringe and determine where the tip of the plunger is in relation to the scale marked on the outside of the syringe barrel. Determine the amount of titrant (to the nearest 0.025 mL) that has been used.

9. Interpretation of Results

9.1 Calculations are not required when prepackaged kits are used.

9.2 For Method A, report results as either greater than or less than 1000 mg/kg (ppm).

9.3 For Method B, calculate the concentration (mg/kg) of total chlorine in the original oil sample by the following equation:

$$\text{Chlorine (mg/kg)} = \frac{(V - 0.05)(c)(35.45)(F)}{m} \tag{1}$$

where:

V = volume of mercuric nitrate titrant used, mL,
0.05 = volume of excess titrant required for color formation, mL,
c = concentration of mercuric nitrate solution, meq/L, for example, 27.4,
35.45 = average atomic weight of chlorine,
F = dilution factor due to adding 7 mL of buffer solution and extracting only 5 mL for analysis, for example, 1.4, and
m = mass of oil sample used, for example, 0.34 g for a volume of 0.4 mL motor oil, g.

10. Quality Control

10.1 Test each sample two times. For Method A, if the results do not agree, a third test must be performed. Report the results of the two that agree. For Method B, the two results should be within 20 % or 300 mg/kg (whichever is larger) of each other. If they are not, perform a third test and report the results of the two tests that agree.

11. Precision and Bias

11.1 For Method A, no formal statement is made about either the precision or bias of the test method because the result merely states whether there is conformance to the criteria for success specified in the procedure, that is, a blue or yellow color in the final solution. In a collaborative study,[4] ten laboratories analyzed seven used oil samples and one unused motor oil sample using prepackaged test kits. Each laboratory ran each sample in duplicate. Out of the eighty samples that were run, one laboratory's results disagreed with the rest of the laboratories' results on one sample. All 79 other tests were in agreement with their duplicates and with other laboratories' results. These data indicate that all participants get results of <1000 for all samples containing less than 870 mg/kg Cl, 9 out of 10 get >1000 on a sample at 1180 mg/kg, and all participants get >1000 at and above 1272 mg/kg. These data indicate that this test method makes correct predictions for samples containing <870 or >1272 mg/kg and probably correct predictions for samples between 870 and 1272 mg/kg Cl. See Table 1.

11.2 *Precision and Bias Statement for Method B.*

11.2.1 *Precision*—The following criteria should be used for judging the acceptability of results.

11.2.2 *Repeatability*—The difference between 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, and in the normal and correct operation of this test method, exceed the stated values only in one case in twenty.

$$\text{Repeatability} = 46.1\,X^{0.25} \tag{2}$$

where:

X = method result, mg/kg.

11.2.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of this test method, exceed the stated values only in one case in twenty.

$$\text{Reproducibility} = 84.44\,X^{0.25} \tag{3}$$

where:

X = method result, mg/kg.

11.2.4 In a collaborative study,[4] using prepackaged kits, ten laboratories analyzed seven used oil samples and one unused motor oil sample.

11.2.5 *Bias*—No bias statement is made for this test method because results obtained for total chlorine were determined only by the test method itself.

12. Keywords

12.1 chlorine; field test; halogen; on-site testing; test kit; used oil

TABLE 1 Repeatability and Reproducibility

mg/kg Cl (ppm)	Repeatability 46.1X$^{0.25}$	Reproducibility 84.44X$^{0.25}$
100	146	267
500	218	399
1000	259	474
1500	287	525
2000	308	565
2500	326	597
3000	341	625
4000	367	672

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[4] Data supporting this study is available from ASTM Headquarters. Request RR:D02-1368.

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