Standard Test Method for Chlorine in New and Used Petroleum Products (High Pressure Decomposition Device Method)[1]

This standard is issued under the fixed designation D808; 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 the determination of chlorine in lubricating oils and greases, including new and used lubricating oils and greases containing additives, and in additive concentrates. Its range of applicability is 0.1 m% to 50 m% chlorine. The procedure assumes that compounds containing halogens other than chlorine will not be present.

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

1.2.1 The preferred units are mass percent.

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.* Attention is called to specific warning statements incorporated in the test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Summary of Test Method

3.1 The sample is oxidized by combustion in a high pressure decomposition device containing oxygen under pressure. (**Warning**—Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the high pressure decomposition device, or a blow-out, provided the high pressure decomposition device is of proper design and construction and in good mechanical condition. It is desirable, however, that the high pressure decomposition device be enclosed in a shield of steel plate at least 13 mm (½ in.) thick, or equivalent protection be provided against unforeseeable contingencies.) The chlorine compounds thus liberated are absorbed in a sodium carbonate solution and the amount of chlorine present is determined gravimetrically by precipitation as silver chloride.

4. Significance and Use

4.1 This test method may be used to measure the level of chlorine-containing compounds in petroleum products. This knowledge can be used to predict performance or handling characteristics of the product in question.

4.2 This test method can also serve as a qualitative tool for the presence or non-detection of chlorine in petroleum products. In light of the efforts in the industry to prepare chlorine free products, this test method would provide information regarding the chlorine levels, if any, in such products.

5. Apparatus

5.1 *High Pressure Decomposition Device,* having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the high pressure decomposition device may be readily achieved. The inner surface of the high pressure decomposition device may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the high pressure decomposition device assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction that will affect the chlorine content of the liquid in the high pressure decomposition device.

5.2 *Sample Cup,* platinum, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 g to 11 g.

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[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**

5.3 *Firing Wire,* platinum, No. 26 B & S gage 0.41 (16 thou), 27 SWG or equivalent.

5.4 *Ignition Circuit,* capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

5.4.1 The switch in the ignition circuit shall be of a type that remains open, except when held in closed position by the operator.

5.5 *Nylon Sewing Thread, or Cotton Wicking,* white.

5.6 *Filter Crucible,* fritted-glass, 30 mL capacity, medium porosity.

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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 Type II or III of Specification D1193.

6.3 *Nitric Acid* (1 + 1)—Mix equal volumes of concentrated nitric acid (HNO_3, sp gr 1.42) and water.

6.4 *Oxygen,* free of combustible material and halogen compounds, available at a pressure of 41 kgf/cm^2 (40 atmos). (**Warning—**Oxygen vigorously accelerates combustion.)

6.5 *Silver Nitrate Solution* (50 g $AgNO_3$/L)—Dissolve 50 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

6.6 *Sodium Carbonate Solution* (50 g Na_2CO_3/L)—Dissolve 50 g of anhydrous Na_2CO_3, 58.5 g of $Na_2CO_3 \cdot H_2O$, or 135 g of $Na_2CO_3 \cdot 10\ H_2O$ in water and dilute to 1 L.

6.7 *White Oil,* refined.

6.8 *Quality Control (QC) Samples,* preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 10.

6.9 *Methyl Red Indicator Solution*—Dissolve 0.1 g of methyl red indicator solid in 100 mL of water.

7. Sampling

7.1 Take samples in accordance with the instructions in Practices D4057 or D4177.

7.2 Take care that the sample is thoroughly representative of the material to be tested and that the portion of the sample used for the test is thoroughly representative of the whole sample.

TABLE 1 Quantities of Sample and White Oil

Chlorine Content, m%	Weight of Sample, g	Weight of White Oil, g
2 and under	0.8	0.0
Above 2 to 5, incl.	0.4	0.4
Above 5 to 10, incl.	0.2	0.6
Above 10 to 20, incl.	0.1	0.7
Above 20 to 50, incl.	0.05	0.7

8. Procedure

8.1 *Preparation of High Pressure Decomposition Device and Sample*—Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (about 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert into the coil a nylon thread, or wisp of cotton, of such length that one end will extend into the sample cup. Place about 5 mL of Na_2CO_3 solution in the high pressure decomposition device and by means of a rubber policeman, wet the interior surface of the high pressure decomposition device, including the head, as thoroughly as possible. Introduce into the sample cup the quantities of sample and white oil (Note 1). (**Warning—**Do not use more than 1 g total of sample and white oil or other chlorine free combustible material) specified in Table 1. Do not add oxygen or ignite the sample if the high pressure decomposition device has been jarred, dropped, or tilted), weighing the sample to the nearest 0.2 mg.) When white oil is used, stir the mixture with a short length of quartz rod and allow the rod to remain in the sample cup during the combustion.

8.1.1 After repeated use of the high pressure decomposition device for chlorine determination, a film may be noticed on the inner surface. This dullness can be removed by periodic polishing of the high pressure decomposition device. A satisfactory method for doing this is to rotate the high pressure decomposition device in a lathe at about 300 r/min and polish the inside with Grit No. 2/0 or equivalent paper coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[4] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the high pressure decomposition device wash it with soap and water to remove oil or paste left from the polishing operation. high pressure decomposition devices with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

8.1.2 When the sample is not readily miscible with white oil, some other nonvolatile, chlorine-free combustible diluent may be employed in place of white oil. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble, but may be satisfactorily burned when covered with a layer of white oil. (**Warning—**Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material.)

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[3] *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 *Annual 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.

[4] The sole source of supply of the chromic oxide known to the committee at this time is J. T. Baker & Co., Phillipsburg, NJ 08865. 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.

TABLE 2 Gage Pressures

Capacity of High Pressure Decomposition Device, mL	Minimum Gage Pressure,[A] kgf/cm^2 (atm)	Maximum Gage Pressure,[A] kgf/cm^2 (atm)
300 to 350	39 (38)	41 (40)
350 to 400	36 (35)	38 (37)
400 to 450	31 (30)	33 (32)
450 to 500	28 (27)	30 (29)

[A] The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the *maximum pressures represent a safety requirement.*

NOTE 1—The practice of running alternately high and low samples in chlorine content shall be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the high pressure decomposition device and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample shall be repeated and one or both of the low values thus obtained can be considered suspect if they do not agree within the limits of repeatability of this test method.

8.2 *Addition of Oxygen*—Place the sample cup in position and arrange the nylon thread, or wisp of cotton, so that the end dips into the sample. Assemble the high pressure decomposition device and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 2. (**Warning—**Do not add oxygen or ignite the sample if the high pressure decomposition device has been jarred, dropped, or tilted.)

8.3 *Combustion*—Immerse the high pressure decomposition device in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the high pressure decomposition device from the bath after immersion for at least 10 min. Release the pressure at a slow, uniform rate such that the operation requires not less than 1 min. Open the high pressure decomposition device and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the high pressure decomposition device before again putting it in use (8.1.1).

8.4 *Collection of Chlorine Solution*—Rinse the interior of the high pressure decomposition device, the sample cup, and the inner surface of the high pressure decomposition device cover with a fine jet of water, and collect the washings in a 600 mL beaker. Scrub the interior of the high pressure decomposition device and the inner surface of the high pressure decomposition device cover with a rubber policeman. Wash the base of the terminals until the washings are neutral to the indicator methyl red. (The volume of the washings is normally in excess of 300 mL.) Take special care not to lose any wash water.

8.5 *Determination of Chlorine*—Acidify the solution by adding HNO_3 (1 + 1) drop by drop until acid to methyl red. Add an excess of 2 mL of the HNO_3 solution. Filter through a qualitative paper (if the solution is cloudy, the presence of lead chloride ($PbCl_2$) is indicated and the solution should be brought to a boil before filtering) and collect in a second 600 mL beaker. Heat the solution to about 60 °C (140 °F) and, while protecting the solution from strong light, add gradually, while stirring, 5 mL of $AgNO_3$ solution. Heat to incipient boiling and retain at this temperature until the supernatant liquid becomes clear. Test to ensure complete precipitation by adding a few drops of the $AgNO_3$ solution. If more precipitation takes place, repeat the above steps which have involved heating, stirring, and addition of $AgNO_3$, as often as necessary, until the additional drops of $AgNO_3$ produce no turbidity in the clear, supernatant liquid. Allow the beaker and contents to stand in a dark place for at least an hour. Filter the precipitate by suction on a weighed fritted-glass filter crucible. Wash the precipitate with water containing 2 mL of HNO_3 (1 + 1)/L. Dry the crucible and precipitate at 110 °C for 1 h. Cool in a desiccator, and weigh.

NOTE 2—If no precipitate is visible at this stage after addition of silver nitrate, this may be taken as an indication of non-detectable quantities of chlorine in the test sample above this test method's detection limit (0.1 m%). The test can be considered as completed at this stage.

8.6 *Blank*—Make a blank determination with 0.7 g to 0.8 g of white oil by following the normal procedure but omitting the sample (Note 3). Repeat this blank whenever new batches of reagents or white oil are used. The blank must not exceed 0.03 m% chlorine based upon the weight of the white oil.

NOTE 3—This procedure measures chlorine in the white oil and in the reagents used, as well as that introduced from contamination.

9. Calculation

9.1 Calculate the chlorine content of the sample as follows:

$$\text{Chlorine, mass\%} = \left[(P - B) \times 24.74\right]/W \quad (1)$$

where:

P = grams of AgCl obtained from the sample,
B = grams of AgCl obtained from the blank, and
W = grams of sample used.

10. Quality Control

10.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 6.8).

10.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

10.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

11. Report

11.1 Report the results to the nearest 0.1 m%.

11.2 If there is absence of a visible precipitate in 8.5, report the results as non-detectable above the detection limits (0.1 m%) of this test method.

12. Precision and Bias

12.1 The precision of this test method is not known to have been obtained in accordance with currently accepted guidelines (for example, in Committee D02 Research Report RR:D02-1007, Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants).

12.2 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.2.1 *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, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Chlorine, m%	Repeatability
0.1 to 1.9	0.07
2.0 to 5.0	0.15
Above 5.0	3 % of amount present

12.2.2 *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, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Chlorine, m%	Reproducibility
0.1 to 1.9	0.10
2.0 to 5.0	0.30
Above 5.0	5 % of the amount present

12.3 *Bias:*

12.3.1 Cooperative data indicate that deviations of test results from the true chlorine content are of the same order of magnitude as the reproducibility.

12.3.2 It is not practicable to specify the bias of this test method for measuring chlorine because the responsible subcommittee, after diligent search, was unable to attract volunteers for an interlaboratory study.

13. Keywords

13.1 chlorine; high pressure decomposition device

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL 7).[5]

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D6299 and MNL 7).[5] Any out-of-control data should trigger investigation for root cause(s).

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice D6299 and MNL 7[5] for further guidance on QC and Control Charting techniques.

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[5] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D808 – 11) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Added Practice D4177 to Referenced Documents; revised subsection 7.1 to include the additional sampling procedure.

(2) Added new subsection 6.9 for a new reagent.

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