Designation: D 3634 – 99$^{\epsilon 1}$

Standard Test Method for Trace Chloride Ion in Engine Coolants[1]

This standard is issued under the fixed designation D 3634; 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.

ϵ^1 NOTE—Editorial changes were made in November 2001.

---

1. Scope

1.1 This test method covers the determination of chloride ion in engine coolants in the range from 5 to 200 ppm in the presence of up to 0.6 weight % mercaptobenzothiazole.

1.2 Other materials that react with silver ion will interfere.

1.3 Chloride in engine coolants containing an aryltriazole instead of mercaptobenzothiazole can be determined directly by this test method without pretreatment with hydrogen peroxide.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *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 hazards statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1176 Test Method for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes[2]

D 1193 Specification for Reagent Water[3]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[2]

2.2 *Manufacturing Chemists Association Document:*[4]

MCA Chemical Safety Data Sheet SD-53

3. Summary of Test Method

3.1 The sample is first treated at a pH of 12 to 13 with aqueous hydrogen peroxide to oxidize the mercaptobenzothiazole to soluble, noninterfering sulfonate. The treated sample is dissolved in glacial acetic acid and titrated potentiometrically with dilute standard silver nitrate solution. Since the solubility of silver chloride in this system is sufficient to prevent obtaining a suitable inflection at the very low limit of the test method, some chloride is deliberately added to the glacial acetic acid solvent and then corrected for by a blank titration.

4. Significance and Use

4.1 This test method permits the determination of very low levels of chloride ion in engine coolants containing the common corrosion inhibitor, mercaptobenzothiazole, or related mercaptans, which would normally interfere with the titration by also forming insoluble silver salts with silver nitrate.

5. Apparatus

5.1 *Manual Titrations*:

5.1.1 *pH Meter* — An expanded scale pH meter which can be read to 1 or 2 mV is desirable but not required. A silver billet indicator electrode[5] and glass reference electrode[6] are used for the chloride titration. The silver electrode should be polished occasionally with fine steel wool or scouring powder and thoroughly rinsed.

5.1.2 *Buret*, 10-mL, micro, Class A, calibrated in 0.02-mL divisions.

5.1.3 *Beakers*, electrolytic, 250-mL tall form.

5.2 *Automatic Titrators* are satisfactory for this test method, provided they exhibit resolution and accuracy equivalent to that specified for manual titrations.

5.3 *Pipets*, 10, 20, and 100-mL, Class A.

5.4 *Flask, Erlenmeyer*, 250 mL, with a 24/40 standard taper, female ground glass joint.

---

[1] This test method is under the jurisidiction of ASTM Committee D15 on Engine Coolants and is the direct responsibility of Subcommittee D15.04 on Chemical Properties.

Current edition approved May 10, 1999. Published August 1999. Originally published as D 3634 – 77. Last previous edition D 3634 – 93.

[2] *Annual Book of ASTM Standards,* Vol 15.05.

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

[4] Available from the Manufacturing Chemists Association, 1825 Connecticut Ave., Washington, DC 20009.

[5] The 1993–1994 Fisher Scientific Company Catalog number for the Silver Billet Electrode is: 13-620-122 and it is available from 10700 Rockley Road, P.O. Box 1307, Houston, TX 77251.

[6] The 1993-1994 Fisher Scientific Company Catalog number for the reference electrode is 13-620-216 and it is available from 10700 Rockley Road, P.O. Box 1307, Houston, TX 77251.

5.5 *Condenser*—The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket approximately 200 mm in length. The bottom end of the condenser shall have a 24/40 male ground glass joint to match the Erlenmeyer flask.

5.6 *Flask*, volumetric, 200 mL, Class A.

NOTE 1—All glassware should be thoroughly cleaned and reserved for use in this test method. Great care must be exercised to avoid contamination. Glassware should be cleaned with chromic acid (**Warning**—See 7.1.) cleaning solution, then thoroughly rinsed with water, then with acetone (**Warning**—See 7.2.), and dried.

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.[7] 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*— References to water shall be understood to mean Type IV reagent water conforming to Specification D 1193: total particulate and dissolved matter, 2.0 mg/L maximum; pH at 25°C, 5.0 to 8.0; electrical conductivity at 25°C, 5.0 µmho/cm maximum; minimum color retention time of potassium permanganate, 10 min.

6.3 *Acetic Acid, Glacial* (**Warning**—See 7.3.).

6.4 *Hydrogen Peroxide Solution* (**Warning**—See 7.4)—Use 30 mass % hydrogen peroxide (H_2O_2), reagent grade. Aged or contaminated H_2O_2 can undergo considerable decomposition and cause incomplete oxidation of the sulfur compounds with subsequent high apparent chloride values; therefore, fresh reagent should be used.

6.5 *Potassium Chloride Solution*— Dissolve 0.20 ± 0.02 g of potassium chloride (KCl) in 100 mL of water. The solution will contain 1 mg of chloride per mL solution.

6.6 *Silver Nitrate Solution* (**Warning**—See 7.5)—Prepare a standard 0.01 *N* silver nitrate ($AgNO_3$) solution weekly by diluting 10 mL of standard 0.1 *N* aqueous $AgNO_3$ solution to 100 mL with water. The 0.1 *N* standard $AgNO_3$ solution should be prepared and standardized in accordance with Sections 44 to 48 of Practice E 200.

6.7 *Sodium Hydroxide Solution* (**Warning**—See 7.6)—Prepare a 20 mass % sodium hydroxide (NaOH) solution in water.

7. Hazards

7.1 *Chromic Acid*— Highly toxic; cancer suspect agent; corrosive; avoid skin contact.

7.2 *Acetone*—Extremely flammable; harmful if swallowed or inhaled; causes irritation.

7.3 *Acetic Acid, Glacial*—Poison, causes severe burns; combustible; harmful if swallowed or inhaled.

7.4 *Hydrogen Peroxide Solution*—Strong oxidizer; contact with other material may cause fire; causes severe burns. Do not tightly stopper containers. For further details, see MCA Chemical Safety Data Sheet SD-53.

7.5 *Silver Nitrate*— May be fatal if swallowed; causes severe burns.

7.6 *Sodium Hydroxide Solution*—Causes severe burns to skin and eyes.

8. Sampling

8.1 Sampling of engine coolant should be carried out in accordance with Method D 1176.

9. Preparation of Titration Solvent

9.1 Determine a titration blank on a full 5-lb (2.3-kg) bottle of glacial acetic acid by titrating 100 mL potentiometrically with 0.01 *N* $AgNO_3$ solution. If the blank is more than 0.2 mL of 0.01 *N* $AgNO_3$ solution, reject the bottle. If the blank is less than 0.05 mL of titrant, add an amount of the KCl solution (1 mL maximum) to the glacial acetic acid remaining in the bottle (about 2300 mL) to give an approximately 0.1-mL titration for 100 mL of the acetic acid. Determine the blank on exactly 100 mL of this titration solvent in duplicate. The values should not differ by more than 0.02 mL. Reserve the supply of solvent for this test method and recheck the blank occasionally.

10. Procedure

10.1 To a 250-mL Erlenmeyer flask add 50 ± 0.1 g of engine coolant and approximately 30 mL of water. Make the solution strongly alkaline by the addition of 5 mL of 20 mass % aqueous NaOH solution. Add 5 mL of 30 mass % aqueous H_2O_2 with stirring, then connect the flask to a reflux condenser and reflux for 30 min. Cool the solution to room temperature

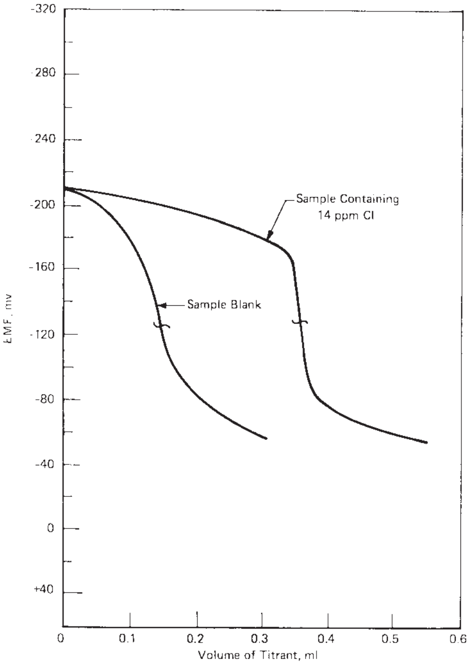

FIG. 1 Titration Curves for Trace Chloride in Engine Antifreezes

---

[7] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

and transfer the contents quantitatively to a 200-mL volumetric flask and dilute to volume with water.

10.2 In a 200-mL volumetric flask, prepare a blank by adding 5 mL of 30 mass % aqueous H_2O_2 and the same amount of 20 mass % aqueous NaOH solution used in 10.1 and dilute to 200 mL with water.

10.3 Pipet 100 mL of the glacial acetic acid titration solvent into each of two beakers. Accurately pipet 20 mL of the treated engine coolant sample into one beaker and 20 mL of the blank (10.2) into the second beaker and allow to dissolve. Titrate the contents of each beaker potentiometrically with 0.01 *N* $AgNO_2$ solution while stirring slowly with a magnetic stirrer. The equilibration of electrode potentials is slow in the vicinity of the end point; therefore, the titrant should be added in 0.02-mL increments in this region and sufficient time allowed for stable readings to be obtained.

11. Calculation

11.1 *Chloride Content*:

11.1.1 Prepare a titration curve by plotting potential readings, using 2 mV per division, against the corresponding volume of titrant added, using 0.02 mL per division. The end point is selected at the middle of the steepest portion of the curve (see Fig. 1).

11.1.2 Calculate ppm of the chloride ion in the original engine coolant sample as follows:

$$\text{Chloride, ppm} = \frac{(V - B)\,(N)\,(35.5)\,(200)\,(10^6)}{(20)\,(50)\,(1000)} = (V - B)(N)(7100)$$

where:

V = titrant used, mL, in the engine coolant sample,
B = titrant used, mL, in the blank sample, and
N = normality of titrant.

12. Report

12.1 Report the chloride content of the engine coolant to the nearest unit.

13. Precision and Bias

13.1 The reproducibility of the chloride ion determination by this test method is 5 ppm in the range from 5 to 200 ppm.

13.2 The bias for this test method has not been determined.

14. Keywords

14.1 engine coolants; trace chloride