Designation: D3634 – 21

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

This standard is issued under the fixed designation D3634; 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 chloride ion in engine coolants in the range from 5 ppm 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 standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 7.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1176 Practice for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes

D1193 Specification for Reagent Water

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

2.2 *Manufacturing Chemists' Association Document:*[3]

MCA Chemical Safety Data Sheet SD-53 Properties and Essential Information for Safe Handling and Use of Hydrogen Peroxide

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 mV or 2 mV is desirable but not required. A silver billet indicator electrode[4] and glass reference electrode[5] are used for the chloride titration. The silver electrode should be

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

Current edition approved Nov. 1, 2021. Published November 2021. Originally approved in 1977. Last previous edition approved in 2015 as D3634 – 99(2015). DOI: 10.1520/D3634-21.

[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 American Chemistry Council (ACC), 700 Second Street, NE, Washington, DC 20002, https://www.americanchemistry.com.

[4] The sole source of supply of the Silver Billet Electrode known to the committee at this time is Fisher Scientific (www.fishersci.com, Catalog No. 13-620-122). 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.

[5] The sole source of supply of the reference electrode known to the committee at this time is Fisher Scientific (www.fishersci.com, Catalog No. 13-620-216). 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.

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 mL, 20 mL, and 100 mL, Class A.

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

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 for use in this test method. Great care must be exercised to avoid contamination.

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.[6] 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 D1193: 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 7.2.).

6.4 *Hydrogen Peroxide Solution*—(**Warning—**See 7.3.) 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 g ± 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 7.4.) 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 E200.

6.7 *Sodium Hydroxide Solution*—(**Warning—**See 7.5.) Prepare a 20 mass % sodium hydroxide (NaOH) solution in water.

7. Hazards

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

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

7.3 *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.

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

7.5 *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 Practice D1176.

9. Preparation of Titration Solvent

9.1 Determine a titration blank on a full 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

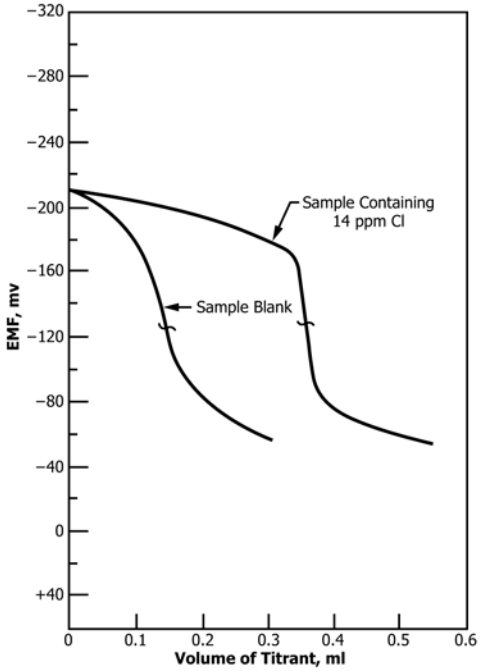

FIG. 1 Titration Curves for Trace Chloride in Engine Antifreezes

[6] *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.