Designation: D 1123 – 99

Standard Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method[1]

This standard is issued under the fixed designation D 1123; 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.

1. Scope

1.1 These test methods cover the determination of the water present in new or unused glycol-based coolant concentrates using a manual (Test Method A) or an automatic (Test Method B) coulometric titrator procedure.

1.2 Many carbonyl compounds react slowly with the Fischer reagent, causing a fading end point and leading to high results. A modified Fischer reagent procedure is included that minimizes these undesirable and interfering reactions.

1.3 *This standard does not purport to address all of the safety problems, 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.* For specific hazards statements see Sections 8 and 16.

2. Referenced Documents

2.1 *ASTM Standards:*

D 156 Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)[2]

D 1176 Test Method for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes[3]

D 1193 Specification for Reagent Water[4]

E 203 Test Method for Water Using Karl Fischer Reagent[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *color end point*—that point during the titration when the color change from yellow to orange-red is sharp and easily repeated. The orange-red color must persist for at least 30 s in order to indicate an end point.

3.1.1.1 *Discussion*—View the color by transmitted daylight or by transmitted light from an artificial daylight lamp, such as one that complies with the specification given in Test Method D 156.

3.1.2 *instrument end point*—for the purpose of these tests, that point in the titration when two small platinum electrodes, upon which a potential of 20 to 50 mV has been impressed, are depolarized by the addition of 0.05 mL of Fischer reagent (6 mg of water/mL), causing a change of current flow of 10 to 20 μA that persists for at least 30 s.

3.1.2.1 *Discussion*—This end point is sometimes incorrectly called the "dead stop," which is the reverse of the above.

4. Summary of Test Methods

4.1 These test methods are based essentially on the reduction of iodine by sulfur dioxide in the presence of water. This reaction can be used quantitatively only when pyridine and an alcohol are present to react as follows:

$$I_2 + SO_2 + H_2O \rightarrow SO_3 + 2HI \quad (1)$$

4.2 In order to determine water, Karl Fischer reagent is added to a solution of the sample in anhydrous high-purity methanol until all water present has been consumed. This is evidenced by the persistence of the orange-red end point color, or alternatively by an indication on a galvanometer or similar current-indicating device that records the depolarization of a pair of noble metal electrodes. The reagent is standardized by the titration of water.

NOTE 1—It is believed that these methods give all the information required for determining the water in coolant formulations. Should additional information on water determinations be needed, reference should be made to Test Method E 203.

5. Significance and Use

5.1 The total apparent water in engine coolant concentrate as determined by Karl Fischer titrations consists of the following: (*1*) water present in the original glycol base; (*2*) water added (for example, inhibitor solutions); (*3*) water of hydration of inhibitors (for example, $Na_2B_4O_7 \cdot 5H_2O$); (*4*) water formed in the chemical reaction between borate and ethylene glycol,

[1] These test methods are under the jurisdiction of ASTM Committee D-15 on Engine Coolants and are the direct responsibility of Subcommittee D15.04 on Chemical Properties.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

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

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

producing boratediol condensate and water; and (*5*) quantitative interference by the reaction of the reagent with inhibitors such as tetraborate or sodium hydroxide.

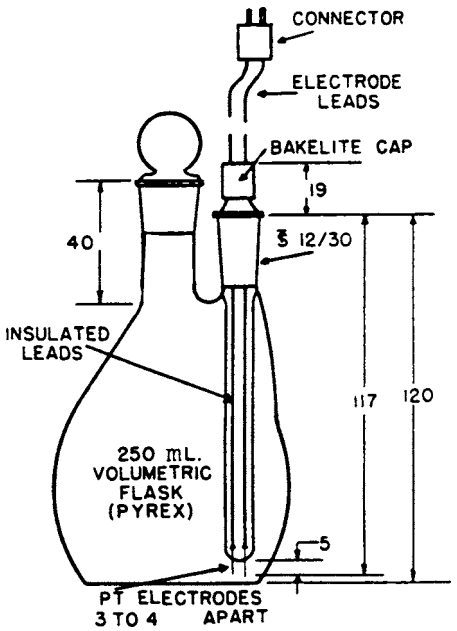
TEST METHOD A—MANUAL TITRATION

6. Apparatus

6.1 *Titration Vessel*— For color end point titrations, use a 100 or 250-mL volumetric flask, which need not be calibrated. For instrument end point, a 250-mL flask fitted with interchangeable electrodes (Fig. 1)[5] may be used. This is particularly good for titrations of coolant concentrate that is deeply colored from dye or any other cause. For permanently mounted assemblies, the vessel should have a capacity about equal to that of a 300-mL tall-form beaker and should be provided with a tight-fitting closure to protect the sample and reagent from atmospheric moisture, a stirrer, and a means of adding sample and reagents and removing spent reaction mixture. It is desirable to have a means for cooling the titration vessel to ice temperature.

6.2 *Instrument Electrodes*, platinum with a surface equivalent to two No. 26 wires, 4.76-mm long. The wires should be 3 to 8 mm apart and so inserted in the vessel that the liquid will cover them.

6.3 *Instrument Depolarization Indicator*, having an internal resistance of less than 5000 Ω and consisting of a means of impressing and showing a voltage of 20 to 50 mV across the electrodes and capable of indicating a current flow of 10 to 20 µA by means of a galvanometer or radio tuning eye circuit.[6]



NOTE 1—All dimensions in millimetres.

FIG. 1 Titration Flask Assembly

6.4 *Buret Assembly* for Fischer reagent, consisting of a 25 or 50-mL buret connected by means of glass (not rubber) connectors to a source of reagent; several types of automatic dispensing burets[7] may be used. Since the reagent loses strength when exposed to moist air, all vents must be protected against atmospheric moisture by adequate drying tubes containing anhydrous calcium sulfate.[8] All stopcocks and joints should be lubricated with a lubricant not particularly reactive[9] with the reagent.

6.5 *Weighing Bottle*, of the Lunge or Grethen type, or equivalent.

6.6 Some laboratory equipment suppliers offer a Karl Fischer apparatus. The noted model or its equivalent has been found to be suitable.[10]

7. Reagents

7.1 *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.[11] 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.

7.2 Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

7.3 *Karl Fischer Reagent*, equivalent to 5 mg of water/mL.[12]

7.4 *Methanol* (**Caution:** See 8.1.)—Anhydrous, high purity.

8. Hazards

8.1 *Methanol*—Poison; flammable; may be fatal or cause blindness if swallowed; cannot be made non-poisonous; harmful if inhaled.

9. Sampling

9.1 A representative sample of the contents of the original container shall be obtained as directed in Test Method D 1176; even if two phases are present, the water-insoluble phase should not be separated.

[5] Flasks made by Rankin Glass Blowing Co., 3920 Franklin Canyon Rd., Martinez, CA have been found satisfactory for this purpose.

[6] A type similar to the Precision Scientific Co. "Aquatrator" or Fisher Scientific Co. "Fisher Titrimeter," is suitable for the measurement of the instrument end point.

[7] A type similar to Catalog No. J-821 of Scientific Glass Apparatus Co., Bloomfield, NJ, or Catalog No. 750 of Eck and Krebs, New York, NY, has been specifically designed for this purpose and presents the minimum contact of reagent with stopcock lubricant.

[8] Indicating Drierite has been found satisfactory for this purpose.

[9] Suitable lubricants include Apiezon N. (James G. Biddle and Co., Philadelphia, PA); High Vacuum Silicone Grease (Dow Corning Co., Midland, MI); Sisco 300 (Swedish Iron and Steel Co., New York, NY).

[10] Metrohm Herisau, Karl Fischer Titrator Type E-452 available from Brinkmann Instruments, Inc., Cantaigue Road, Westbury, NY 11590.

[11] *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.

[12] Reagents, as the pyridine-free hydranal reagent, available from Fisher Scientific, Pittsburgh, PA 15219.