



Standard Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method¹

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 Purposes³

D 1193 Specification for Reagent Water⁴

E 203 Test Method for Water Using Karl Fischer Reagent³

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.

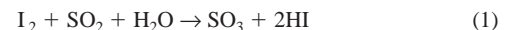
3.1.1.1 *Discussion*—View the color by transmitted daylight or by transmitted light from an artificial daylight lamp, such as one that complies with the specification given in Test Method D 156.

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 μ A 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:



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 D15 on Engine Coolants and are the direct responsibility of Subcommittee D15.04 on Chemical Properties.

Current edition approved May 10, 1999. Published August 1999. Originally published as D 1123 – 50. Last previous edition D 1123 – 93.

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

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 burets⁷ 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 reactive⁹ 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

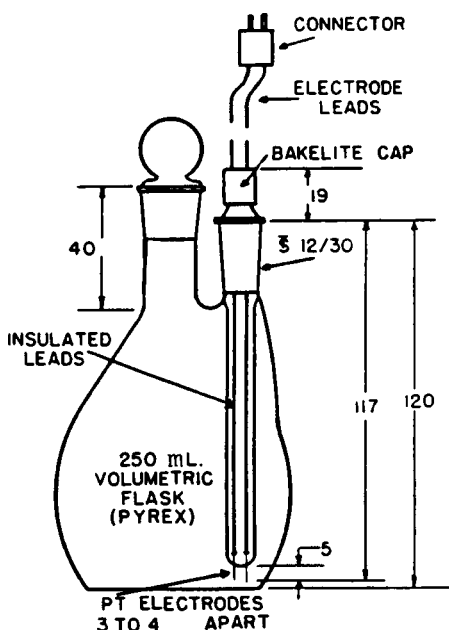
7.4 *Methanol (Warning—See 8.1.)*—Anhydrous, high purity.

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.



NOTE 1—All dimensions in millimetres.

FIG. 1 Titration Flask Assembly

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. "Aquatator" 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

10. Standardization of Reagent

10.1 Standardize the Fischer reagent at least once, prior to use, each day the procedure is used, by either the color or instrument end point (see Section 3) method, using the procedure as used for titrating the sample (Section 11).

10.1.1 Add to each 250 mL flask 25 mL of anhydrous, high purity methanol. Stir rapidly. Titrate with Karl Fischer reagent according to 11.2. Add to the solution 0.15 to 0.18 g of water (to ± 0.1 mg) by use of an accurately sized syringe. Titrate again and record the volume of titrant used. Repeat standardization two more times.

10.1.2 Calculate the equivalency factor of the reagent in terms of water content per millilitre as follows:

$$\text{Equivalency factor, } F, \text{ mg of water/mL} = A/B \quad (2)$$

where:

A = mg of water used in the standardization, and
 B = Karl Fischer reagent required, mL.

11. Procedure

11.1 Introduce 30 to 50 mL of the anhydrous high-purity methanol into a 250 mL Erlenmeyer flask, making sure, if an instrument end point apparatus is used, that the electrodes are covered by this amount of methanol. If the color end point is to be determined, make up a second flask as well.

11.2 Adjust the stirrer, if any, to provide adequate mixing without splashing. Titrate the mixture to the instrument end point (3.1.2), or the color end point (3.1.1), with Karl Fischer reagent. If the color end point is to be observed, titrate one flask to match the first. Set aside the first flask as a comparison standard for titrating the sample.

11.3 To the titration mixture thus prepared, add an amount of sample as indicated in Table 1. Exercise care when the sample is transferred so that water is not absorbed from the air, particularly under conditions of high humidity. Again, titrate the mixture with Karl Fischer reagent to the same instrument or color end point previously employed. Record the amount of reagent used to titrate the water in the sample.

NOTE 2—When using the volumetric flask-type titration vessel in humid climate, place a piece of thin paraffin wax over the mouth of the vessel. Provide a small hole for introducing the buret tip. In less humid climates it is sufficient to lower the tip of the buret deeply into the long neck of the titration flask.

NOTE 3—In titrating with the volumetric flask-type titration vessel, avoid wetting the stopper and upper end of the flask with either the reagent or the sample solvent. Each time the titration is interrupted, touch the buret tip to the neck of the flask to remove droplets which, if not removed, would absorb moisture from the atmosphere. When the flask is removed

TABLE 1 Recommended Sample Sizes

Water Content, weight %	Sample Size, g	Sample Method
2.5 to 10	0.3	Introduce samples by using weigh bottles or disposable, accurate syringes. Obtain sample weight by difference.
0.5 to 2.5	3	
Below 0.5	20	

from under the buret tip, wipe the tip with a clean dry cloth in a downward motion.

12. Calculation

12.1 Calculate the total water content (free plus apparent) of the sample as follows:

$$\text{Water, weight \%} = VF/10M \quad (3)$$

where:

V = mL of Karl Fischer reagent required by the sample,
 F = equivalency factor for Karl Fischer reagent, mg of water per mL of reagent, and
 M = sample used, g.

13. Precision and Bias

13.1 *Precision*—The following data should be used for judging the acceptability of results (95 % probability):

13.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amount:

Repeatability	0.5 mL of titrant
---------------	-------------------

13.1.2 *Reproducibility*—The result submitted by one laboratory should not be considered suspect unless it differs from that of another laboratory by more than the following amount:

Water Content, %	Reproducibility, % of mean
0.1 to 1.0	15
1.0 to 10	5

13.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias has not been determined.

TEST METHOD B—COULOMETRIC TITRATION

14. Apparatus

14.1 *Coulometric Titrator*^{13,14}—A complete control unit with titration chamber and clamp, platinum sensing electrodes, generator, magnetic stirrer, and meeting requirements 14.2 and 18.1.

14.2 The instrument used for determining water in liquids is designed and calibrated to deliver a known number of milliamperes of current which generates sufficient iodine to neutralize a known number of micrograms of water per minute.

14.3 In order to determine the water content of engine coolants, this method requires a two-part titration solution that is brought to zero dryness by iodine produced by the generator when the instrument is powered up. The sample is added and the water content is read directly in micrograms.

14.4 *Glass Syringe*, 50-mL, for removing excess solution from the titration chamber.

14.5 *Syringe*, 25- μ L, fitted with a 11.5-cm hypodermic needle for introduction of samples into the titration chamber.

¹³ This procedure is patented by the Photovolt Corp. under U. S. Patent 3,726,778 and has been included in the standard under Paragraph 11.2 of the Regulations Governing ASTM Technical Committees. Procedure A is a non-patented alternative method.

¹⁴ A detailed drawing is available from ASTM Headquarters. Request Adjunct No. 12-415330-00.

14.6 *Syringe*, 1- μ L, fitted with a 11.5-cm hypodermic needle for standardization of instrument.

14.7 *Fluorocarbon Sealing Grease*,¹⁵ to seal the titration chamber against atmospheric moisture.

14.8 *Septums*, to seal sample port but allow introduction of samples by a needle with a minimum of moisture contamination. Septum caps should be replaced as required to prevent air leakage as indicated by instrument drift.

15. Reagents¹⁶

15.1 *Generator Solution*—(**Warning**—see 16.1)—Provides iodine in the reaction mixture.

15.2 *Titration Solutions*, supplied in two parts, Part A and Part B. The two parts are mixed prior to adding to the titration chamber.

15.3 *Neutralizing Solution*—Methanol—(**Warning**—see 16.2)—Anhydrous, high purity methanol containing approximately 20 mg H₂O/mL.

16. Hazards

16.1 *Generator Solution*—Refer to the manufacturer's material safety data sheet for precautions and hazards.

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

17. Preparation of Apparatus

17.1 Clean, thoroughly dry, and assemble the titration chamber using sealing grease. Connect the titration chamber to the titrator.

17.2 Pour Part B of the titration solution into Part A, close, thoroughly mix by shaking, and allow to cool to room temperature.

17.3 Remove the septum from the sample port and pour the mixture of Parts A and B, made in 17.2, through a dry funnel into the titration chamber. Immediately replace the septum cap.

17.4 Add approximately 6 mL of the generator solution into the generator cartridge. The surface of the generator solution should be below the level of the surface of the titrating solution to prevent backflow contamination of the titrating solution.

17.5 Attach the 11.5-cm hypodermic needle to a 20-mL syringe. Withdraw about 15 mL of neutralizing solution. Insert the needle through the sample port septum and lower it until the tip of the needle is below the surface of the titration solution.

17.6 Slowly inject the neutralizing reagent into the titration solution until it changes color from brown to red. This indicates the end point is near. Continue the addition *very slowly*. The total volume required will range between 5 and 15 mL depending on the residual moisture in the system.

17.7 All liquid samples to be tested should be at room temperature for analyses.

¹⁵ A suitable sealing grease can be obtained from Halocarbon Products, 8 Burlews Court, Hackensack, NJ 07601.

¹⁶ Reagents are available from the apparatus manufacturer and laboratory supply houses.

18. Verification of System by Direct Titration of Water

18.1 To determine if the titration system is functioning properly, fill a 1- μ L syringe with distilled water to the 1- μ L mark. Weigh the filled syringe. Insert the needle through the sample port septum and lower it until the tip of the needle is below the surface of the titrating solution. Depress the START key and immediately inject the water into the titration solution. Remove the syringe and reweigh. The titration is complete when the result is displayed with the symbol "mcg." The weight of the water injected in micrograms should approximate the instrument reading.

19. Sample Sizes

19.1 The sample size is governed by the expected range of moisture content:

Expected Moisture Content	Range of Sample Size
1000 ppm (0.1 %)	0.1 to 3 g
1 %	10 to 300 mg
10 %	1 to 30 mg
100 %	0.1 to 3 mg

20. Procedure

20.1 Using an appropriate dry syringe and needle (see 19.1), draw the sample liquid to be tested into the syringe and discharge the contents into a waste container. Withdraw the sample into the syringe until above the desired calibration mark. Remove the needle from the sample container and force the extra liquid from the syringe to exactly the calibration mark. Wipe the tip of the needle with a clean tissue or towel.

NOTE 4—For most determinations, the volumetric addition of the sample is adequate. However, better accuracy may be obtained by weighing the syringe before and after the addition of the sample.

20.2 The instrument should be left on stand-by when not in use. If the instrument is turned off, it is necessary to allow the titration solution to stabilize or to replace the solution.

21. Calculation

21.1 Calculate the amount of water present in the sample as follows:

$$\text{Water content (ppm)} = \frac{\mu\text{g water (readout number)}}{\text{mass of sample, g}} \quad (4)$$

(The instrument can perform this computation automatically. Consult the operating instructions.)

22. Precision and Bias

22.1 Precision:

22.1.1 *Repeatability*—Duplicate results by the same operator should not differ by more than 3 ppm, 95 % of the time.

22.1.2 *Reproducibility*—The results submitted by one laboratory should not differ from that of another laboratory by more than 10 ppm, 95 % of the time.

22.2 *Bias*—Since there is no accepted reference material for the procedure in this test method, bias has not been determined.

23. Keywords

23.1 engine coolants; Karl Fischer; water content

ANNEX

(Mandatory Information)

A1. NOTES ON INTERFERENCES

A1.1 Some inhibitors react directly with the Karl Fischer reagent by means of condensation or oxidation reactions during the titration and indicate more water than is actually present.¹⁷ Knowledge of the specific interference factors is useful for calculating the true free water content of a sample. Without complete compositional data, it is impossible for the analyst to determine the true free water content. However, in many cases the total apparent water (free water plus apparent water) is determined and is satisfactorily used for qualification or production quality control purposes.

A1.2 Many ethylene glycol-type engine coolant concentrates contain sodium tetraborate. In the titration, some of the Karl Fischer reagent reacts with this borate either directly or with the water formed by the borate-ethylene glycol condensation reaction. The borate-ethylene glycol molecule does not

react; when it is formed, one molecule of water is also formed and this, of course, does react. The borate that is not combined chemically with glycol reacts directly with the Karl Fischer reagent with the same stoichiometry as the above. Therefore, 1 mol of sodium tetraborate appears in the titration as 7 mol of water by either mechanism. In the case of 1 g of sodium tetraborate decahydrate, 0.33 g of water are indicated by the titration; for 1 g of the pentahydrate, the result is 0.43 g of water indicated; and for 1 g of anhydrous sodium tetraborate the Karl Fischer titration indicates 0.63 g water.

A1.3 Monovalent metal hydroxide such as sodium hydroxide reacts with the Karl Fischer reagent to give 1 mol of apparent water per mol of hydroxide.

A1.4 Other inhibitors such as nitrites react stoichiometrically with constituents of the Karl Fischer reagent. For example, 1 mol of sodium nitrite gives 0.5 mol of apparent water. In this case, however, the reaction is slow and the interference can be ignored when the titration is rapid.

¹⁷ Jordan, C. B., "Use of Karl Fischer Reagent for the Determination of Water in Condensates of Sodium Tetraborate and Diols," *Analytical Chemistry*, Vol 36, February 1964, p. 424.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).