



Standard Test Method for Reserve Alkalinity of Engine Coolants and Antirusts¹

This standard is issued under the fixed designation D1121; 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 This test method covers the determination of the reserve alkalinity of new, unused engine coolants, and liquid antirusts as received, of used or unused aqueous dilutions of the concentrated materials, and of aqueous dilutions of solid antirusts.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1123 Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method](#)

[D1176 Practice for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes](#)

[D1287 Test Method for pH of Engine Coolants and Antirusts](#)

3. Terminology

3.1 *Definitions:*

3.1.1 *reserve alkalinity, n*—a term applied to engine coolant concentrates and antirusts to indicate the amount of alkaline inhibitors present in the product.

4. Summary of Test Method

4.1 A 10-mL sample of concentrated coolant, antirust, coolant additive, or an aqueous engine coolant containing these products, is diluted to about 100 mL with water and titrated

potentiometrically with 0.100 *N* hydrochloric acid to a pH of 5.5. The volume of acid used is reported to the nearest 0.1 mL. The concentration of coolant or additive in the coolant solution shall be recorded if required, for calculation of depletion of the reserve alkalinity during performance tests.

5. Significance and Use

5.1 Reserve alkalinity is the number of millilitres, to the nearest 0.1 mL of 0.100 *N* hydrochloric acid (HCl) required for the titration to a pH of 5.5 of a 10-mL sample of an undiluted, unused coolant, antirust, or coolant additive, and unused or used solutions thereof.

5.2 Reserve alkalinity is a term applied to engine coolants and antirusts to indicate the amount of alkaline components present in the product. It is frequently used for quality control during production, and values are often listed in specifications. When applied to used solutions, reserve alkalinity gives an approximate indication of the amount of remaining alkaline components. Unfortunately, the term is sometimes misused in that its numerical value is said to be directly related to coolant quality, the higher the number, the better the coolant. ASTM Committee D15 on Engine Coolants believes there is a need to correct some misconceptions and place the term in its proper perspective.

5.3 Reserve alkalinity (R.A.) as defined in Section 3 of this method is the number of millilitres of 0.1-*N* hydrochloric acid required to titrate 10 mL of concentrated coolant to a pH of 5.5. The term is not a completely accurate description of the property being measured because “alkalinity” usually refers to the pH range above 7.0.

5.4 A review of the origin of the term may be helpful in attempting to understand its proper use. When ethylene glycol was first used as an engine coolant, it was uninhibited. The need for inhibition soon became apparent and triethanolamine was incorporated. When solutions of this inhibited glycol were titrated with dilute hydrochloric acid, it was found that the steepest part of the neutralization curve occurred at a pH of about 5.0. Following the introduction of triethanolamine, other buffers, such as borates and phosphates, have been used. Titration to 5.5 was employed with these buffers which have an end point close to 5.5.

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 Oct. 1, 2011. Published October 2011. Originally approved in 1950. Last previous edition approved in 2007 as D1121 – 07. DOI: 10.1520/D1121-11.

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.

5.5 Generally, most metals in an automotive cooling system corrode less in solutions which are mildly alkaline. The commonly used alkaline buffers, borates and phosphates, help to maintain this desirable alkalinity and a stable pH for substantial additions of acid. A well inhibited coolant contains smaller amounts of other inhibitors (in addition to the buffers), to give broad range corrosion protection for all of the metals found in the cooling system. These additional inhibitors may contribute very little to the titration, but they can provide excellent corrosion protection.

5.6 The alkaline inhibitors provide buffering action and neutralize acids introduced into the coolant by exhaust gas leakage, by residual acid cleaner, or by the oxidation of ethylene glycol and propylene glycol. Some inhibitors which contribute little or no reserve alkalinity may give excellent corrosion protection to certain metals but have little capacity to combat acid contamination. In view of this, the magnitude of the R. A. in a coolant is not always a good criterion in determining its potential protective properties.

5.7 In summary, the precaution against the misuse of reserve alkalinity is that the reserve alkalinity of an engine coolant solution is not a dependable measure of its ability to prevent corrosion, nor can it satisfactorily indicate the additional life of the solution.

6. Apparatus

6.1 The pH meter, glass electrode, and calomel electrode, shall be as specified in the section on Apparatus (Section 5) of Test Method **D1287**.

6.2 It is recognized that many laboratories use a combination electrode system for measuring the reserve alkalinity of engine coolants. It should be noted that results obtained from using a combination electrode system have been found to be statistically different from results obtained when using the calomel and reference electrode system.³

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.⁴ 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 *Purity of Water*—References to water shall be understood to mean distilled water or water of equal purity. Distilled water shall be boiled thoroughly, or purged with carbon dioxide-free air, to remove carbon dioxide, and shall be protected with a soda-lime tube or the equivalent while cooling

and in storage. The pH of the water shall be between 6.2 and 7.2 at 25°C. Take precautions to prevent contamination of the distilled water with traces of the material used for protection against carbon dioxide.

7.3 *Standard Buffer Solution*⁵—The buffer solutions for checking pH assemblies and glass electrodes shall be stored in bottles of chemically resistant glass or polyethylene and shall be prepared from salts sold specifically for use, either singly or in combination, as pH standards. The salts shall be dried for 1 h at 110°C before use.

7.4 *Hydrochloric Acid (0.100 N)*—Prepare and standardize 0.100 N hydrochloric acid (HCl).

7.5 *Phthalate Buffer Solution (0.05 M, pH = 4.01 at 25°C)*—Dissolve 10.21 g of potassium hydrogen phthalate in distilled water and dilute to 1 L.

7.6 *Phosphate Buffer Solution (0.025 M with respect to each phosphate salt, pH = 6.86 at 25°C)*—Dissolve 3.40 g of potassium dihydrogen phosphate (KH₂PO₄) and 3.55 g of anhydrous disodium hydrogen phosphate (Na₂HPO₄) in distilled water and dilute to 1 L.

7.7 *Potassium Chloride Electrolyte*—Prepare a saturated solution of potassium chloride (KCl) in water.

8. Sampling

8.1 Sample the material in accordance with Standard Practice **D1176**.

9. Preparation of Electrode System

9.1 *Maintenance of Electrodes*—Clean the glass electrodes or combination electrode at frequent intervals (not less than once every week during continual use) in accordance with the manufacturer's instructions. Drain the calomel electrodes at least once each week and fill with KCl electrolyte. Keep the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times. When not in use, immerse the lower half of the electrodes in water and do not allow them to be immersed in the titrated solution for any appreciable period of time between titrations. Although the electrodes are not extremely fragile, they should be handled carefully at all times.

9.1.1 A combination electrode system can also be used for this test method.

9.2 *Preparation of Electrodes*—Before and after using, blot the glass electrode or combination electrode thoroughly with a clean cloth, or a soft, absorbent tissue, and rinse with water. Blot the calomel reference electrode with a cloth or tissue; carefully remove the ground-glass sleeve and thoroughly blot both ground-glass surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the ground-glass joint. Wet the ground surfaces thoroughly with electrolyte, set the sleeve firmly in place, and rinse the electrode with water. Prior to each titration, soak the prepared electrode in water for at least 2 min. Immediately before use, touch the tips of the electrodes with a dry cloth or tissue to remove excess water.

³ Refer to ASTM Report RR:D15-1004.

⁴ *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.

⁵ Commercially available buffer tablets or prepared buffer solutions may be used.

10. Electrode System in pH Units

10.1 Turn on the instrument, allow to warm up, and adjust in accordance with the manufacturer's instructions. Allow sufficient time for the temperature of the buffer solution and immersed electrodes to equalize and set the temperature knob at the temperature of the buffer solution. Calibrate the assembly with a minimum of two buffer solutions to check the linearity of the response of the electrode or incorrect temperature compensation. The presence of a faulty electrode is indicated by a failure to obtain a reasonably correct value for pH of the second standard solution when the meter has been standardized with the first. A cracked electrode will often yield pH values that are essentially the same for both standards. Adjust the standardization or asymmetry potential control until the reading of the dial corresponds to the known pH of the standardizing buffer solution.

11. Procedure

11.1 Pipet 10 mL of a thoroughly mixed sample into a 250 mL tall-form spout-less beaker. Allow 1 minute drain time. Add about 90 mL of distilled water (Note 2).

NOTE 1—The amount of water added is not critical; however, it must be sufficient to cover the electrode tips. If the reserve alkalinity is less than 2, the sample size may be increased to 50 mL diluted to 100 mL with water, and the total titration divided by 5 to give the reserve alkalinity as defined.

11.2 Prepare the calomel and glass electrode as described in Section 9. Place the beaker containing the test solution on the titration stand, adjust so that the lower half of each electrode is immersed, start the stirrer, and adjust the rate of the stirring so that there is vigorous stirring without spattering. Fill the 50-mL buret with standardized 0.100 *N* HCl. The normality of the acid used may be in the range from 0.095 to 0.105, but the actual titration will require correction to give the equivalent titration with 0.100 *N* acid. Position the buret tip inside the beaker. Adjust the pH meter temperature compensator to agree with the solution temperature. Record the initial pH and proceed with the titration to a pH of about 7. Use a slow, drop wise titration rate from pH 7 to approach the end point of pH 5.5. Record the volume of acid used, acid normality, and sample size. Switch the pH meter to standby and rinse the electrodes with water and dry with clean absorbent material before the next determination. When the pH meter is not in use, immerse the electrodes in distilled water. When a large number of reserve alkalinity determinations are made during a period of several hours, it is recommended that the meter be recalibrated at various intervals as described in 10.1.

NOTE 2—In the event that the glass electrode becomes coated with an oil, grease, or other film, it is recommended that a 1 to 1 solvent mix of toluene and ethyl acetate be used to remove the film.

12. Calculations Using Reserve Alkalinity Data

12.1 Calculations of percent depletion during simulated or actual coolant service may be obtained by use of the following equation:

$$\text{Percent depletion} = 100 [(RA_1/C_1 - RA_2/C_2)/(RA_1/C_1)] \quad (1)$$

where:

RA_1 = initial reserve alkalinity,

RA_2 = final reserve alkalinity,

C_1 = initial coolant or additive concentration in percent, and

C_2 = final coolant or additive concentration in percent.

NOTE 3—In the case of a coolant solution, if the concentration is unknown, it can be determined by appropriate test methods, such as refractive index, freezing point, or specific gravity, and by reference to available tables. The water content of the coolant solution can be determined by Test Method D1123, and the concentration calculated.

12.2 The percent depletion data allows coolant investigators to compare, on an equivalent basis, the reserve alkalinity data from a number of identical tests on similar coolants.

12.3 In the case of vehicle service tests the percent depletion should be reported on the basis of some unit of mileage, such as 10 000 miles. As implied in 5.2, percent depletion of the reserve alkalinity, although related to coolant durability and the condition or performance of cooling system, is only a part of the coolant evaluation procedure.

13. Report

13.1 Report the sample description and the reserve alkalinity to the nearest 0.1 mL of 0.100 *N* HCl for the standard 10-mL sample. Sample description may vary from a simple identification number to a complete history and analysis, such as that utilized for used coolants from laboratory performance and vehicle service tests.

14. Precision and Bias

14.1 *Repeatability*—Duplicate results by the same operator should not be considered suspect unless they differ by more than ± 0.2 mL.

14.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless the results differ by more than ± 0.2 mL.

15. Keywords

15.1 buffering; engine coolants; RA; reserve alkalinity

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