Designation: D4548 – 11

Standard Test Method for
Anion-Cation Balance of Mixed Bed Ion-Exchange Resins [1]

This standard is issued under the fixed designation D4548; 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.

1. Scope

1.1 This test method determines the ratio between the equivalents of anion-exchange capacity and the equivalents of cation-exchange capacity present in a physical mixture of salt-splitting anion-exchange material and salt-splitting cation-exchange material.

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 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2187 Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *anion-exchange material, n*—an ion-exchange material capable of the reversible exchange of negatively charged ions.

3.2.2 *cation-exchange material, n*—an ion-exchange material capable of the reversible exchange of positively charged ions.

3.2.3 *ion-exchange material, n*—an insoluble material that has the ability to exchange reversibly certain ions in its structure or attached to its surface as functional groups with ions in a surrounding medium.

3.2.4 *ion-exchange resin, n*—a synthetic organic ion-exchange material.

3.2.5 *mixed bed, n*—a physical mixture of anion-exchange material and cation-exchange material.

3.2.6 *salt-splitting, adj*—the ability of anion-exchange or cation-exchange materials to exchange hydroxide or hydrogen ions respectively for the ions in neutral salts.

4. Summary of Test Method

4.1 This test method consists of simultaneous conversion of the cation-exchange component to the hydrogen form and the anion-exchange component to the chloride form with hydrochloric acid. After rinsing to remove the excess acid, the hydrogen ion from the cation resin and the chloride ion from the anion resin are simultaneously eluted with neutral sodium nitrate, and the amount eluted is determined by titration of the effluent for both ions.

5. Significance and Use

5.1 This test method is applicable to the analysis of new materials that are sold as mixtures and to samples taken from regenerable units containing mixtures of anion-exchanging and cation-exchanging materials. It is used to determine the ratio of the components without separating them from each other.

5.2 This test method is intended for mixtures of ion-exchange materials that have salt-splitting capacity as measured by Test Method E of Test Methods D2187 for cation-exchange resins, and Test Method H for anion-exchange resins. In the case of cation-exchange resins, these are styrene-based polymers with sulfonic acid functional groups. The anion-exchanging materials in this class are styrene-based materials with quaternary ammonium functional groups. The test method will determine the amount of anion-exchange material of any functionality present in the mixture. However, when anionic groups that are not salt-splitting are present, the values for cationic groups will be high due to the acidic character of the anion effluent. Cationic groups that do not split salts are not measured.

5.3 Samples are analyzed in this test method as received. It is not necessary that the cation-exchanging resin be in the

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.08 on Membranes and Ion Exchange Materials.

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[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.

hydrogen form and the anion-exchanging resin be in the hydroxide form for this test method.

5.4 This test method may be used to determine if new materials are balanced to meet their specification values. In operating regenerable units, it may be used to determine if the components are separating properly or remixing properly. It may also be used to check for improper balance in bedding or for loss of a component during operation.

5.5 This test method begins with the conversion to the hydrogen and chloride forms. However, it may be combined with the determination of the residual chloride and sulfate sites by elution with sodium nitrate as described in Test Methods J and L in Test Methods D2187. In such cases the hydrogen ion as well as the chloride ion is determined in the second sodium nitrate elution described in Test Method I of Test Methods D2187, and the calculations given herein are made using the titration values so determined.

6. Apparatus

6.1 *Test Apparatus,* as shown in Fig. 1, shall consist of a filter tube of at least 30 mL in capacity having a diameter of at least 20 mm, containing a sintered glass plate of coarse (A) porosity, a 1-L separatory funnel, and a 1-L volumetric flask.

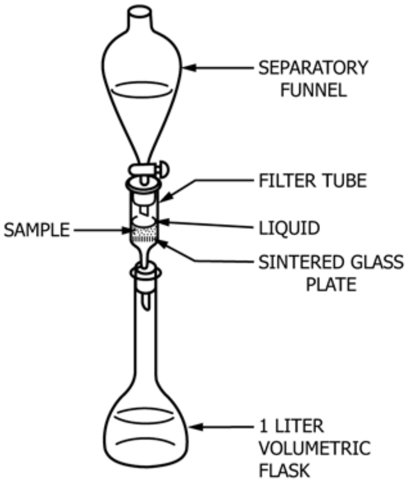

FIG. 1 Typical Arrangement of Apparatus for Salt-Splitting Capacity

7. Reagents and Materials

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.[3] 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*—Unless otherwise indicated, reference to water shall be understood to mean reagent water, conforming to Specification D1193, Type IV.

7.3 *Ammonium Hydroxide* (1 + 9)—Pour 1 vol of ammonium hydroxide (sp gr 0.90) into 9 vol of water and mix well.

7.4 *Hydrochloric Acid* (1 + 9)—Carefully pour 100 mL of hydrochloric acid (sp gr 1.19) into 500 mL of water, stirring constantly. Cool to 25 ± 5°C and dilute to 1 L.

7.5 *Isopropyl Alcohol,* neutral.

7.6 *Methyl Orange Indicator Solution* (0.5 g/L)—Dissolve 0.05 g of methyl orange in water and dilute to 100 mL with water.

7.7 *Nitric Acid* (1 + 9)—Pour 1 vol of nitric acid (sp gr 1.42) into 9 vol of water and mix thoroughly.

7.8 *Phenolphthalein Indicator Solution* (5.0 g/L)—Dissolve 0.5 g of phenolphthalein in 50 mL of 95 % ethanol (see Note 1). Transfer to a volumetric flask and dilute to 100 mL with water.

NOTE 1—Isopropyl alcohol or specially denatured ethyl alcohol conforming to Formula 3A or 30 of the US Bureau of Internal Revenue may be substituted for 95 % alcohol.

7.9 *Potassium Chromate Solution* (50 g/L)—Dissolve 5.0 g of potassium chromate in 50 mL of water. Dilute to 100 mL with water.

7.10 *Silver Nitrate Solution, Standard* (0.10*N)*—Dry crystalline silver nitrate at 105°C for 1 h and cool in a desiccator. Weigh out 17± 0.05 g of $AgNO_3$. Transfer to a 1-L volumetric flask with water. Dissolve in 500 mL of water. Dilute to 1-L with water at 25 ± 5°C and mix well. Store the solution in a tightly stoppered amber glass bottle.

7.10.1 To standardize, dry approximately 5 g of sodium chloride in a glass container at 105°C for 2 h. Cool in a desiccator. Weigh accurately three 0.25 ± 0.01 g portions of the dried NaCl and transfer to separate 250 mL conical flasks. Add 100 mL of water and dissolve the NaCl. Add 1 mL of K_2CrO_4 solution (50 g/L) and titrate with the 0.1 *N* $AgNO_3$ standard solution with vigorous swirling until the color change of the solution from yellow to red-orange persists for 30 s.

7.10.2 Calculate the normality of the $AgNO_3$ standard solution as follows:

$$N_s = A/(0.05845 \times B)$$

where:

N_s = normality of the $AgNO_3$ standard solution,
A = actual grams of NaCl used, and
B = $AgNO_3$ standard solution required for the titration, mL.

7.11 *Sodium Hydroxide Solution*, 50 %—Prepare a 50 % solution by dissolving 162 g of sodium hydroxide pellets in 150 mL of freshly boiled and cooled water. Cool to 25 ± 5°C and decant the clear liquid. Store in a plastic bottle.

7.12 *Sodium Hydroxide Solution, Standard* (0.10*N)*—Measure 5.45 mL or 8.0 g 50 % sodium hydroxide solution in a 10 mL graduated cylinder, calibrated to contain. Rinse the

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[3] *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.

solution into a 1-L volumetric flask with freshly boiled water at 25 ± 5°C, dilute to 1 L, and mix well. Standardize monthly.

7.12.1 To standardize, dry approximately 10 g of primary standard grade potassium hydrogen phthalate in a glass container at 120°C for 2 h. Cool in a desiccator. Weigh accurately three 1.00 g samples of the dried potassium hydrogen phthalate and transfer to separate 250 mL conical flasks. Add 100 mL of freshly boiled and cooled water and dissolve the sample. Titrate with the 0.1 *N* NaOH solution electrometrically to a pH of 8.6 or add two drops of phenolphthalein indicator solution and titrate to the first pink that persists for 15 s with swirling.

7.12.2 Calculate the normality of the NaOH solution as follows:

$$N_B = C/(0.20423 \times D)$$

where:

N_B = normality of the NaOH solution,
C = actual grams of $KHC_8H_4O_4$ used, and
D = NaOH used in the titration, mL.

7.13 *Sodium Nitrate Solution* (20 g/L)—Dissolve 20 g of sodium nitrate in 500 mL of water. Dilute to 1 L and mix well.

8. Procedure

8.1 Weigh accurately into separate 100 mL beakers three 20.0 g representative portions of the material.

8.2 Quantitatively rinse the weighed samples into the filter tubes with water. Fill three separatory funnels with 1 L each of HCl (1 + 9). Fill the filter tubes with acid and tap to remove air bubbles. Attach the stems of the funnels to the filter tubes with rubber stoppers of suitable size. Pass the acid through the samples at a rate of 20 to 25 mL/min, keeping the samples covered with acid at all times. Drain the liquid to the sample level. Discard the effluent.

8.3 Rinse the separatory funnels thoroughly with water and then with three 10 mL portions of isopropyl alcohol. Run isopropyl alcohol through the acid-treated samples at the rate of 20 to 25 mL/min until a 10 mL portion of the effluent, mixed with 10 mL of water, is yellow to methyl orange or has a pH above 3.9. Drain to the sample level and discard the effluent.

8.4 Rinse the volumetric flasks thoroughly with water and reposition them under the tip of the filter tubes. Fill the separatory funnels with 1 L each of $NaNO_3$ (20 g/L). Pass the $NaNO_3$ solution through the sample at a rate of 20 to 25 mL/min, keeping the sample covered at all times, until 1 L of effluent is collected.

8.5 Mix the effluent thoroughly. Pipet three 100 mL portions of each into separate 250 mL conical flasks. Add two drops of phenolphthalein indicator solution to each and titrate with 0.1 *N* NaOH solution to the first pink that will persist for 15 s with swirling or titrate electrometrically to a pH of 8.6. Record the volume of NaOH solution used in each titrating to the nearest 0.01 mL. Use the average of the three titrations for each sample as *E* (see Section 9).

8.6 To the neutralized solutions obtained in 8.5, add four drops of methyl orange indicator solution and HNO_3 (1 + 9) dropwise until the solution is red. Add NH_4OH (1 + 9) dropwise until the solution is again just yellow. Add 1 mL of K_2CrO_4 solution (50 g/L) and titrate with the 0.1 *N* $AgNO_3$ standard solution with vigorous swirling until the color change of the solution from yellow to red-orange persists for 30 s. Record the volume of $AgNO_3$ solution used in each titration to the nearest 0.01 mL. Use the average of the three titrations for each sample as *F* (see Section 9).

NOTE 2—Alternatively, pipet three 100 mL portions of the effluent into separate 250 mL conical flasks. Add four drops of methyl orange indicator solution and add NH_4OH (1 + 9) dropwise until the solution is just yellow. Then continue as described in 8.6.

9. Calculation

9.1 Calculate the anion-cation balance as follows:

$$R = \frac{F \times N_s}{E \times N_B}$$

where:

R = ratio between the anion capacity and the salt-splitting cation capacity,
F = $AgNO_3$ used in 8.6, mL,
N_s = normality of the $AgNO_3$ from 7.10.2,
E = NaOH used in 8.5, mL, and
N_B = normality of the NaOH from 7.12.2.

10. Report

10.1 Report the anion-cation balance in the mixed bed as the average of the results of the three samples.

11. Precision and Bias

11.1 *Precision*—Precision was determined from the results of the analyses of eight operators, each analyzing three different samples on each of three different days. The overall precision is expressed as follows:

$$S_t = 0.03\,x + 0.005$$

where:

S_t = overall precision and
x = value measured as anion-cation balance.

The single operator precision is as follows:

$$S_o = 0.02\,x - 0.01$$

where:

S_o = single operator precision and
x = value measured as anion-cation balance.

11.2 *Bias*—Ion-exchange resins are the product of a complex multiple step synthesis involving a polymerization reaction followed by one or more additional reactions to put functional groups on the polymeric structure. Consequently, the true value of any property of the finished product is unknown, and a bias statement cannot be given.

12. Keywords

12.1 anion-cation balance; ion exchange; mixed bed

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