Designation: D2187 – 17

# Standard Test Methods and Practices for Evaluating Physical and Chemical Properties of Particulate Ion-Exchange Resins[1]

This standard is issued under the fixed designation D2187; 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 These test methods cover the determination of the physical and chemical properties of ion-exchange resins when used for the treatment of water. They are intended for use in testing both new and used materials. The following thirteen test methods are included:



1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered 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, health and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 10.8.

1.4 *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]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1293 Test Methods for pH of Water

D2687 Practices for Sampling Particulate Ion-Exchange Materials

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in these standards, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *ion-exchange resin*—a synthetic organic ion-exchange material.

3.2.4 *mixed bed*—a physical mixture of anion-exchange material and cation-exchange material.

## 4. Reagents

4.1 *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,

[1] These test methods and practices are under the jurisdiction of ASTM Committee D19 on Water and are 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.

where such specifications are available.[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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water described in Specification D1193.

## 5. Sampling

5.1 Obtain a representative sample of the ion-exchange resin in accordance with Practices D2687.

5.2 A minimum sample size of 1 L is recommended for a complete testing program.

## TEST PRACTICE A—PRETREATMENT

## 6. Scope

6.1 This test practice covers the conversion of ion-exchange resins to a known ionic form and is intended for application to both new and used material.

## 7. Significance and Use

7.1 The ionic form of an ion-exchange material affects both its equivalent mass and its equilibrium water content. These in turn influence the numerical values obtained in exchange capacity determinations, in density measurements, and in the size of the particles. To provide a uniform basis for comparison, therefore, the sample should be converted to a known ionic form before analysis. This procedure provides for the conversion of cation-exchange materials to the sodium form and anion-exchange materials to the chloride form prior to analysis. These forms are chosen since they permit samples to be weighed and dried without concern for air contamination or decomposition. If other ionic forms are used this fact should be noted in reporting the results.

## 8. Apparatus

8.1 *Pretreatment Apparatus* (see Fig. 1):

8.1.1 *Column,* transparent, vertically-supported, 25 ± 2.5 mm (1.0 ± 0.1 in.) inside diameter and approximately 1500 mm (60 in.) long. The bottom of the column shall be closed and provided with an outlet of approximately 6-mm inside diameter. Connections shall be provided at top and bottom for admission and removal of solutions as described in Section 10. Adequate means for measuring and regulating flow shall be provided. Calibrate the column in such a manner that the volume readings required by the test practice can be made. Make all measurements at 25 ± 5°C.

8.1.2 *Support,* for the sample, so designed that the distance from the sample to the column outlet is at least 50 mm. Suggested supports are corrosion-resistant screen or porous plate.

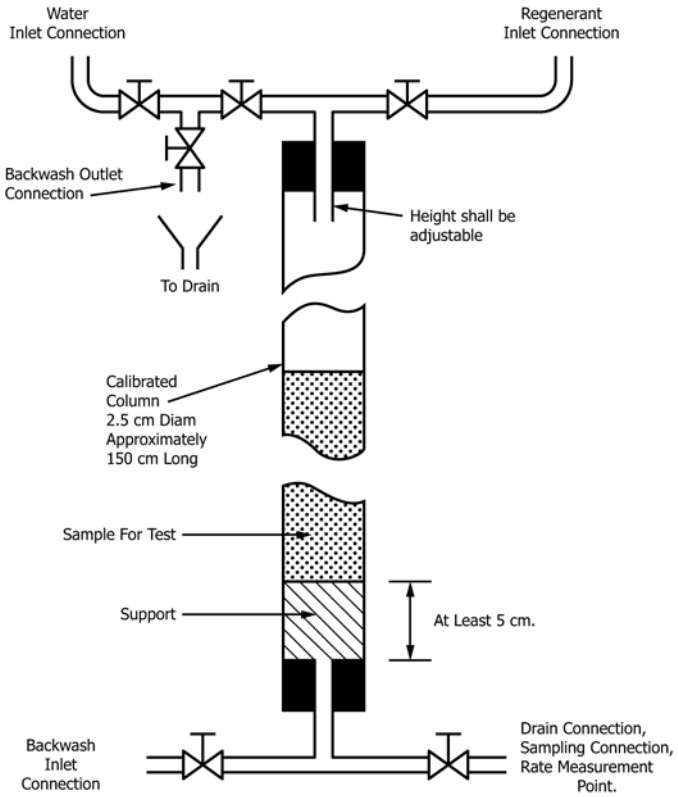


**FIG. 1 Typical Arrangement of Apparatus for Pretreatment of Ion-Exchange Materials**

8.2 *Draining Apparatus* (Fig. 2):

8.2.1 *Buchner-Type Funnel,* containing a 125-mm filter paper and supported in a 1-L suction flask.

8.2.2 *Open-Arm Mercury Manometer,* connected by a T-tube to a vacuum train.

8.2.3 *Gas-Humidifying Tower,* of at least 500 mL capacity, two thirds filled with glass beads or similar material.

8.2.4 *Vacuum Pump,* capable of creating a pressure differential 40 mm Hg below atmospheric pressure.

## 9. Reagents

9.1 *Hydrochloric Acid* (1 + 9)—Carefully pour 100 mL of hydrochloric acid (HCl, sp gr 1.19) into 900 mL of water, stirring constantly. Cool to 25 ± 5°C.

9.2 *Sodium Chloride Solution* (100 g/L)—Dissolve 100.0 g of sodium chloride (NaCl) in 800 mL of water and dilute to 1 L.

9.3 *Sodium Chloride Solution* (240 g/L)—Dissolve 240 g of sodium chloride (NaCl) in 800 mL of water and dilute to 1 L.

9.4 *Sodium Hydroxide Solution* (40 g/L)—Dissolve 40.0 g of sodium hydroxide (NaOH) in 800 mL of water. Cool and dilute to 1 L.

9.5 *Thymol Blue Indicator Solution*—Dissolve 0.1 g of thymol blue (thymol sulfonphthalein) in 10.75 mL of 0.02 N NaOH solution. Dilute to 250 mL with water.

9.6 *Tropaeolin O Indicator Solution*—Dissolve 0.10 g of tropaeolin O (p-benzene-sulfonic acid-azoresorcinol) in 50 mL of water and dilute to 100 mL in a volumetric flask.

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

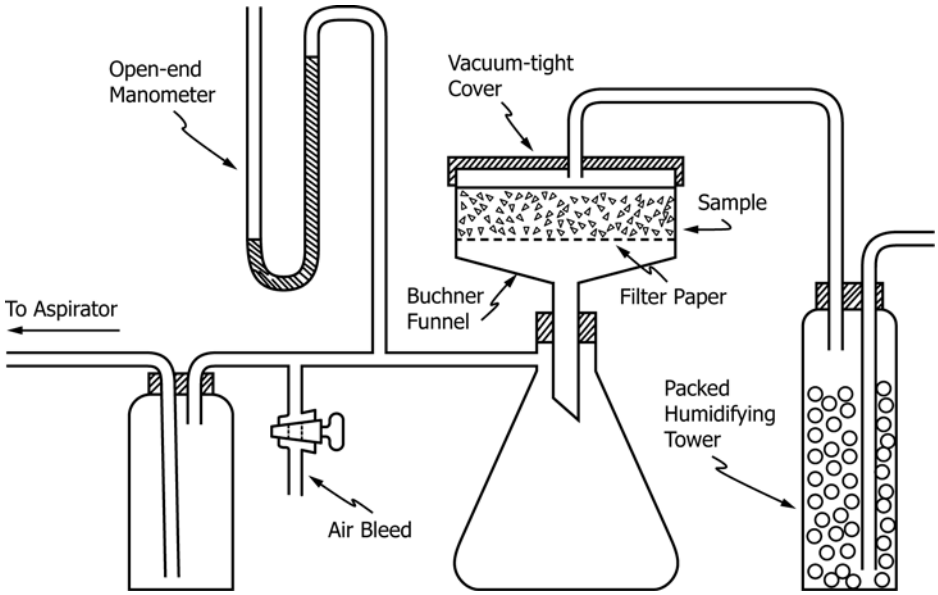


**FIG. 2 Typical Arrangement of Water-Draining Apparatus**

## 10. Procedure

10.1 Adjust the temperature of the water and all solutions to be used in the procedure to 25 ± 5°C and maintain this temperature throughout the test.

10.2 Transfer the entire sample as received to a 2-L beaker using water to rinse out the container. Adjust the water level to the sample level. Let stand a minimum of 1 h. Mix thoroughly and transfer a representative sample to fill a 400-mL beaker.

10.3 Fill the pretreatment column one half full of water. Transfer the entire contents of the 400-mL beaker to the column using additional water if necessary.

10.4 Backwash with water using a flow rate that will maintain a 50 % expansion of the bed. Adjust the backwash outlet tube to a height above the bed equal to 75 % of the bed height. Continue backwashing for a minimum of 10 min or until the effluent is clear. For mixed bed samples proceed in accordance with 10.5. For single component samples, proceed in accordance with 10.6.

10.5 If the sample is a mixed bed, displace the backwash water from the bed by slowly introducing NaCl solution (100 g/L) at the bottom of the column and allowing it to flow upward through the sample. When the water has been displaced, increase the flow rate until the anion-exchange resin is separated from and suspended above the cation-exchange resin. Lower the backwash outlet tube as required to siphon off the anion-exchange resin, collecting it in a separate pretreatment apparatus. Exercise care to prevent the removal of cation-exchange resin in this operation. When the transfer of the anion-exchange resin is complete, discontinue the flow of NaCl solution. If the separation of anion and cation-exchange resins has not been complete and a mixed band is left in the center, repeat the siphoning procedure to remove this band from the cation-portion of the sample. This mixed material that should not constitute more than 5 % of the original sample volume, is not included in subsequent tests. If more than 5 % of the sample remains unseparated, the separation should be repeated using NaCl solution (240 g/L). In either case proceed with the separated anion and cation components as separate samples as described in 10.6.

10.6 Allow the resin to settle until the liquid level is 20 to 30 mm above the top of the bed, and estimate its volume. Pass NaCl solution (100 g/L) downflow through the single component sample or the separated components of the mixed bed resin at the approximate rate of 0.133 mL/min/mL of sample for 1 h. Discontinue the flow of NaCl solution. Backwash with water for 10 min at a flow rate sufficient to maintain a 50 % expansion of the bed. Discontinue the flow of water.

10.7 Allow the bed to settle and then drain off the water at a rate of approximately 100 mL/min until the water level is 20 to 30 mm above the top of the bed. Estimate the volume of ion-exchange resin in millilitres.

10.8 Determine the amount of reagent and the flow rate required for the initial pretreatment from Table 1 using the sample volume determined in 10.7. (**Warning—**Swelling of the resin in the column may occur in subsequent steps.)

10.9 Pass the specified volume of reagent through the bed at the specified rate until only a 20 or 30 mm layer of liquid remains above the bed. Rinse the bed with two sample volumes of water at the same rate.

**TABLE 1 Requirements for Initial Pretreatment**

| | Anion-Exchange Resins | Cation-Exchange Resins |
|---|---|---|
| Reagent | NaOH | HCl |
| Concentration | 40 g/L | 1 + 9 |
| Volume required | 8 sample volumes | 8 sample volumes |
| Contact time | 1 h | 1 h |
| Flow rate, mL/min-mL sample | 0.133 | 0.133 |
| Regeneration level: | | |
| lb/ft $^3$ | 20.0 | 21.2 |
| g/L | 320 | 340 |

10.10 Determine the amount of reagent and the flow rate required for the second pretreatment from Table 2 using the sample volume determined in 10.7. Note that this second pretreatment is not used for some methods.

10.11 Pass the specified volume of reagent through a bed at the specified rate until only a 20 to 30-mm layer of liquid remains above the bed. Rinse the bed with one sample volume of water at the same rate. Increase the rinse rate to 100 mL/min. Rinse for 15 min. Thereafter test successive 100-mL portions of the effluent from anion-exchange resins by adding two drops of thymol blue indicator solution. Continue rinsing until a 100 mL portion of the effluent remains yellow (pH > 2.5) on the addition of the indicator. Test the effluent from the cation-exchange resins in the same manner with two drops of tropaeolin-O indicator solution. Continue rinsing until a 100-mL portion of the effluent remains yellow (pH < 11.0)[3] on the addition of the indicator.

10.12 Remove the ion-exchange resin from the pretreatment column, discarding any extraneous material that may have accumulated at the bottom of the bed. Transfer the resin to the Buchner funnel of the draining apparatus that has been fitted with a medium porosity filter paper. Drain the water to the top of the sample using suction if required. Cover the funnel with a suitable vacuum-tight cover, which is fitted with an inlet for air from the water-filled humidifying tower. Apply sufficient suction to maintain a pressure differential of 40 ± 5 mm Hg below atmospheric pressure. Continue passing humidified air through the sample for 10 min.

10.13 Transfer the entire drained sample to a clean, dry, 1-L (1-qt.), wide-mouthed bottle with a screw top or other vapor-tight closure.

## TEST METHOD B—WATER RETENTION CAPACITY

### 11. Scope

11.1 This test method covers the determination of the amount of water retained by ion-exchange resins and is intended for testing both new and used materials.

### 12. Summary of Test Method

12.1 This test method consists of the determination of the loss of mass on drying at 104 ± 2°C.

### 13. Significance and Use

13.1 The water retention capacity of an ion-exchange material is proportional to its pore volume. For new materials of the same functionality and polymer type, higher values indicate lower effective crosslinking. Increases in water retention capacity of used materials as compared with the values for new material serve as an indicator of polymer decrosslinking: decreases may indicate either loss of functionality or fouling of the ion-exchange material. Since the numerical value is directly dependent on the ionic form of the material, careful preconditioning of both original and used samples to known ionic forms as outlined in Section 7 is essential when such comparisons are made.

**TABLE 2 Requirements for Second Pretreatment**

| | Anion-Exchange Resins | Cation-Exchange Resins |
|---|---|---|
| Reagent | HCl | NaOH |
| Concentration | 1 + 9 | 40 g/L |
| Volume required | 8 sample volumes | 4 sample volumes |
| Contact time | 1 h | 0.5 h |
| Flow rate, mL/min-mL sample | 0.133 | 0.133 |
| Regeneration level: | | |
| lb/ft $^3$ | 21.2 | 10.0 |
| g/L | 340 | 160 |

### 14. Procedure

14.1 Weigh three approximately 5-g representative samples of material pretreated in accordance with Section 10 to the nearest 1 mg into previously tared weighing vessels.

14.2 Dry the samples for 18 ± 2 h at 104 ± 2°C.

14.3 Remove the samples from the oven. Cool 30 min in a desiccator, and reweigh.

### 15. Calculation

15.1 Calculate the water retention capacity, in percent, as follows:

$$\text{water retained, } \% = [(A - B)/A] \times 100 \quad (1)$$

where:

$A$ = amount of wet sample used, g, and
$B$ = amount of dry sample obtained, g.

### 16. Report

16.1 Report the percent water retained as the average of the three values obtained.

### 17. Precision and Bias[4]

17.1 *Precision*—The precision of this test method of determining water retention capacity of ion exchange resins may be expressed as follows:

$$S_T = 0.017x$$
$$S_o = 0.004x$$

where:

$S_T$ = overall precision,
$S_o$ = single-operator precision, and
$x$ = water retention capacity determined in percent.

17.1.1 Information given for the precision statement is derived from round robin testing in which eight laboratories, including ten operators, participated. Four samples were included in the testing. The range of water retention capacity in the samples tested was 40 to 60 %.

17.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D19-0139 and RR:D19-1007. Contact ASTM Customer Service at service@astm.org.

## 18. Quality Control

18.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

18.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 17.

# TEST METHOD C—BACKWASHED AND SETTLED DENSITY

## 19. Scope

19.1 This test method covers the determination of the backwashed and settled density of ion-exchange resin and is intended for testing both new and used material.

## 20. Summary of Test Method

20.1 The test method consists of the determination of the backwashed and settled volume of a known number of grams of chemically pretreated resin.

## 21. Significance and Use

21.1 This test method for the determination of backwashed and settled density of a hydraulically classified and settled bed was developed to correlate with the density of ion-exchange materials in operating units. Results obtained by this test method in a 25-mm (1-in.) column may be expected to agree with those obtained in larger diameter units within the over-all precision limits of the test, but the bias of these results, as compared with measurements in larger diameters, is toward lower values.

## 22. Procedure

22.1 Weigh a 200-g sample of resin, pretreated in accordance with Section 10, to the nearest 0.1 g. Transfer it quantitatively to a column that has been calibrated every 5 mL above the 200-mL volume.

22.2 Backwash with water for 10 min using a slow rate that will maintain a 50 % expansion of the bed.

22.3 Allow the bed to settle and then drain at a rate of approximately 100 mL/min until the water level is 20 to 30 mm above the top of the bed. Do not jar. Record the volume, in millilitres, of ion-exchange resin. Repeat the 10-min backwash until two successive readings of volume agree within 5 mL.

## 23. Calculation

23.1 Calculate the backwashed and settled density, in grams per millilitre as follows:

$$\text{density, g/mL} = A/B \quad (2)$$

where:

$A$ = amount of sample used, g, and
$B$ = volume of sample from 22.3, mL.

23.2 Calculate the backwashed and settled density in pounds (grams) per cubic foot, as follows:

$$\text{density, lb/ft}^3\ (\text{g/ft}^3) = C \times 62.4 \quad (3)$$

where:

$C$ = density, g/mL.

## 24. Report

24.1 Report the density of the tested material as the average of that calculated from two volumes that agree within 5 mL.

## 25. Precision and Bias[4]

25.1 *Precision*—The precision of this test method of determining backwashed and settled density of ion exchange resins may be expressed as follows:

$$S_T = 0.035x$$
$$S_o = 0.005x$$

where:

$S_T$ = overall precision,
$S_o$ = single-operator precision, and
$x$ = density determined in g/mL.

25.1.1 Information given for the precision statement is derived from round robin testing in which eight laboratories, including ten operators, participated. Four samples were included in the testing. Six of the operators ran each sample in duplicate. The remainder were single observations.

25.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 26. Quality Control

26.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

26.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 25.

# TEST METHOD D—PARTICLE SIZE DISTRIBUTION

## 27. Scope

27.1 This test method covers the wet sieve analysis of ion-exchange materials.

## 28. Summary of Test Method

28.1 This test method consists of hand-sieving the chemically pretreated resin in water through a series of standard sieves of progressively decreasing size of opening. The volume retained on each of the sieves is measured.

## 29. Significance and Use

29.1 The particle size distribution of ion-exchange materials is determined in the fully-hydrated state and in known ionic

form to provide a reproducible base for comparison of changes in size due to particle breakage in use.

## 30. Apparatus

30.1 *Sieves,* 203 mm (8 in.) in diameter, conforming to Specification E11. A suitable series of such sieves consists of U.S. Standard Sieves Numbers 8 (2.36-mm), 12 (1.70-mm), 16 (1.18-mm), 20 (850-µm), 30 (600-µm), 40 (425-µm), 50 (300-µm), 70 (212-µm), and 100 (150-µm).

30.2 *Water Bath,* minimum diameter 305 mm (12 in.); minimum depth, 152 mm (6 in.).

## 31. Procedure

31.1 Add sufficient water to the water bath to fill it to the level of the top rim of a sieve placed on the bottom of it.

31.2 Fill a 100-mL beaker with a representative portion of the sample pretreated in accordance with Section 10.

31.3 Transfer the entire sample onto the sieve with the largest mesh opening using water as required.

31.4 Gently raise and lower the sieve through the water interface in the bath so as to alternately lift the particles on the sieve and float them off again. Exercise care that none of the material on the sieve is floated over the edge. Repeat the operation until no further material passes through the screen.

31.5 Remove the sieve from the water bath. Transfer the particles in the bath quantitatively to a suitably-sized beaker.

31.6 Invert the sieve containing the ion-exchange material in the bath and wash the material from the openings with water. Remove the sieve and transfer the particles quantitatively to a suitable-sized graduated cylinder. Tap the material collected in the graduated cylinder until a constant volume is obtained. Record this volume in millilitres.

31.7 Place the sieve of next smaller mesh opening in the bath. Pour the particles that passed the first sieve onto it and adjust the bath level as described in 31.1. Repeat the operation described in 31.4 to 31.6 using this smaller mesh sieve.

31.8 Repeat the sieving operation with sieves of progressively smaller mesh size until all the sieves in the series have been used. After the final sieving, collect and record the volume of any material remaining in the bath.

## 32. Calculation

32.1 Calculate the percentage of ion-exchange material retained on each sieve as follows:

$$\text{volume retained, \%} = 100X/\sum \quad (4)$$

where:

$X$ = amount of material retained on a particular sieve, mL, and

$\sum$ = summation of all volumes retained by the sieves used, plus the volume passing the smallest sieve, mL.

32.2 Calculate the cumulative percent retained on each sieve by adding to the percentage retained on it the percentages retained on all of the sieves used having larger mesh openings. For example: in a series where U.S. Standard Sieves Nos. 8, 12, 16, 20, 30, 40, 50, 70, and 100 have been used, the cumulative percent retained on No. 16 equals:

$$\text{percent retained on No. 8} + \text{percent retained on No. 12} + \text{percent retained on No. 16}$$

32.3 Using normal probability paper, plot the cumulative percent retained on each sieve on the probability axis as a function of the sieve opening in millimetres on the linear axis. Draw the best straight line through the points giving greater weight to the points representing the largest resin fractions.

32.4 On the line drawn as described in 32.3, determine the sieve openings that will retain 40 and 90 % of the sample. The sieve opening in millimetres that will retain 90 % of the sample is the effective size of that sample.

32.5 Calculate the uniformity coefficient of the sample as follows:

$$\text{uniformity coefficient} = \frac{\text{mesh size (mm) retaining 40\% of the sample}}{\text{mesh size (mm) retaining 90\% of the sample}} \quad (5)$$

## 33. Report

33.1 Report the numbers of the sieves used, and the cumulative percent retained on each. Report also the effective size and the uniformity coefficient.

## 34. Precision and Bias[4]

34.1 *Precision*—The precision for this test method of determining particle size distribution and uniformity coefficient of ion exchange resins may be expressed as follows:

34.1.1 *Spheroidal Materials:*

$$S_T = 0.061 \text{ (for uniformity coefficient)}$$

and

34.1.2 *Granular Materials:*

$$S_T = 0.05 \text{ (for effective size)}$$

$$S_T = 0.157 \text{ (for uniformity coefficient)}$$

where:

$S_T$ = overall precision in millimetres for effective size, and a dimensionless unit for uniformity coefficient.

34.1.3 Information given for the precision statement is derived from round robin testing in which eight laboratories, including ten operators, participated. Four samples were included in the testing, and of these, three were spherically shaped and one was granular. All tests were single observations.

34.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 35. Quality Control

35.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the

actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

35.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 34.

## TEST METHOD E—SALT-SPLITTING CAPACITY OF CATION EXCHANGE RESINS

### 36. Scope

36.1 This test method covers the determination of the number of milliequivalents of exchangeable hydrogen in a cation-exchange resin sufficiently acidic to split neutral salts.

### 37. Summary of Test Method

37.1 This test method consists of conversion of the sample to the hydrogen form, elution with sodium chloride solution, followed by titration of the hydrogen ion exchanged in this process.

### 38. Significance and Use

38.1 This test method is generally assumed to measure only the sulfonic acid groups in ion-exchange materials. It should be pointed out, however, that some phosphonic acid and carboxylic acid groups will also exhibit salt-splitting when tested by this procedure.

### 39. Apparatus

39.1 *Test Apparatus,* as shown in Fig. 3 shall consist of a filter tube of at least 30-mL 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.

39.2 *Electrometric pH Measurement Apparatus,* conforming to the requirements given in Section 4 of Test Methods D1293.

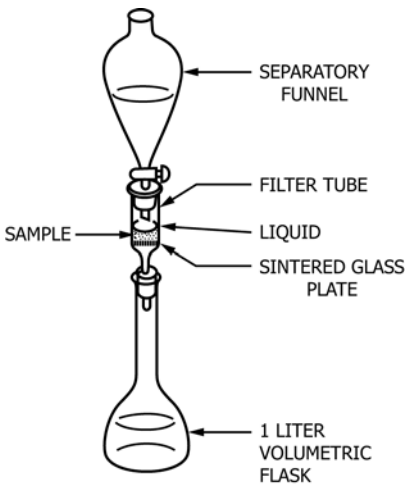


**FIG. 3 Typical Arrangement of Apparatus for Salt-Splitting Capacity**

### 40. Reagents

40.1 *Carbon Dioxide-Free Water*—Prepare carbon dioxide-free water by heating Type II reagent water (see Specification D1193) to boiling in a conical flask. Boil vigorously for 10 min. Stopper with a one-hole rubber stopper fitted with a soda-lime drying tube and cool to 25 ± 5°C.

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

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

40.4 *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—Specifically denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95 % ethyl alcohol.

40.5 *Sodium Chloride Solution* (50 g/L)—Dissolve 50 g of sodium chloride (NaCl) in 800 mL of water and dilute to 1 L.

40.6 *Sodium Hydroxide Solution*, 50 %—Prepare a saturated solution by dissolving 162 g of sodium hydroxide (NaOH) pellets in 150 mL of carbon dioxide-free water. Cool to 25 ± 5°C and decant the free liquid. Store in a plastic bottle.

40.7 *Sodium Hydroxide Solution Standard* (0.10 *N*)—Measure 5.45 mL or 8.0 g of 50 % sodium hydroxide (NaOH) solution into a 10 mL graduated cylinder. Rinse it into a 1 L volumetric flask with carbon dioxide-free water at 25 ± 5°C, dilute to 1 L with like water and mix well. Standardize monthly.

40.7.1 To standardize, dry approximately 10 g of primary standard grade potassium hydrogen phthalate ($KHC_5H_4O_4$) 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 carbon dioxide-free water and stir gently to dissolve the sample. Titrate with the 0.10 *N* NaOH solution electrometrically to a pH of 8.2 or add two drops of phenolphthalein indicator solution and titrate to the first pink that persists for 15 s with swirling.

40.7.2 Calculate the normality of the NaOH solution as follows:

$$N = B/(0.20423 \times C) \quad (6)$$

where:

$N$ = normality of the NaOH solution,
$B$ = actual amount of $KHC_5H_4O_4$ used, g, and
$C$ = amount of NaOH solution used, mL.

### 41. Procedure

41.1 Weigh accurately into separate 100-mL beakers, three 10-g representative samples of material pretreated in accordance with Section 10.

41.2 Rinse the weighed samples with water quantitatively into the filter tubes. Fill the separatory funnel with 1 L of HCl

(1 + 9). Fill the sample tube with acid and tap to remove air bubbles. Attach the stem of the funnel to the filter tube with a suitable-size rubber stopper. Pass the acid through the sample at a rate of 20 to 25 mL/min, keeping the sample covered with acid at all times. Drain the liquid to the resin level. Discard the effluent.

41.3 Rinse the separatory funnel thoroughly with water. Run water through the acid-treated samples at the rate of 20 to 25 mL/min until the effluent is yellow to methyl orange or has a pH above 3.9. Drain to the resin level and discard the effluent water.

41.4 Position a clean 1-L volumetric flask under the tip of the filter tube. Fill the separatory funnel with 1 L of NaCl solution (50 g/L). Pass the NaCl solution through the sample at a rate of 20 to 25 mL/min keeping the sample covered with solution at all times. Collect the effluent in the volumetric flask. Discontinue the flow of the liquid when 1.0 L has been collected.

41.5 Stopper and mix the NaCl effluent thoroughly. Pipet out three 100-mL portions of each sample of effluent. Add 2 drops of phenolphthalein indicator solution to each and titrate with 0.1 *N* NaOH solution to the first pink color that will persist on 15-s swirling, or titrate electrometrically to a pH of 8.2. Record the volume of NaOH solution used in each titration to the nearest 0.01 mL. Use the average of the three titrations for each sample as *E*.

## 42. Calculation

42.1 Calculate the salt-splitting capacity in milliequivalents per wet gram as follows:

$$\frac{\text{milliequivalents cationic salt} - \text{splitting capacity}}{\text{wet gram}} = (E \times N \times 10)/W \quad (7)$$

where:

$E$ = average millilitres of NaOH solution required for the titration in 41.5,
$W$ = wet grams of the sample, and
$N$ = normality of NaOH solution used.

42.2 Calculate the cationic salt-splitting capacity in milliequivalents per dry gram as follows:

$$\frac{\text{milliequivalents cationic salt} - \text{splitting capacity}}{\text{dry gram}} = H/(1 - (M/100)) \quad (8)$$

where:

$H$ = milliequivalents cationic salt-splitting capacity per wet gram, and
$M$ = percent water retained as determined in accordance with Sections 11 – 17.

42.3 Calculate the cationic salt-splitting capacity in milliequivalents per millilitre of back-washed and settled materials as follows:

$$\frac{\text{milliequivalents cationic salt} - \text{splitting capacity}}{\text{millilitre settled bed}} = H \times C \quad (9)$$

where:

$H$ = milliequivalents cationic salt-splitting capacity per wet gram, and
$C$ = wet, settled density, in grams per millilitre, as determined in accordance with Sections 19 – 25.

## 43. Report

43.1 Report the cationic salt-splitting capacity as the average of the results of the three samples.

## 44. Precision and Bias[4]

44.1 *Precision*—The precision for this test method of determining salt-splitting cation exchange capacity of ion exchange materials may be expressed as follows:

$$S_T = 0.075$$
$$S_o = 0.084$$

where:

$S_T$ = overall precision in meq/dry g, and
$S_o$ = single operator precision in meq/dry g.

44.1.1 Information for the precision statement is derived from round-robin testing in which five laboratories, including ten operators, participated. Six laboratories are required by the 1986 edition of Practice D2777; however, this interlaboratory test was performed at a time when five was acceptable. Four samples were included in the round-robin test, and of these, three were new resin and the other had been used in a commercial unit for some period of time. Two laboratories ran tests in duplicate, two in triplicate and the fifth ran four to six replicates.

44.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 45. Quality Control

45.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

45.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 44.

45.3 Analysis of the resin column effluent is subject to the quality control requirements of the referenced analytical methods.

# TEST METHOD F—TOTAL CAPACITY OF CATION-EXCHANGE RESINS

## 46. Scope

46.1 This test method covers the determination of the total number of milliequivalents of exchangeable hydrogen in a cation-exchange resin.

## 47. Summary of Test Method

47.1 This test method consists of conversion of the sample to the hydrogen form, equilibration within a known excess of standard sodium hydroxide solution in the presence of sodium chloride, followed by titration of the residual hydroxide ion with standard acid.

## 48. Significance and Use

48.1 This test method is generally used for ion-exchange materials that contain functional groups other than or in addition to sulfonic acid groups.

## 49. Apparatus

49.1 *Test Apparatus,* as described in 39.1 and shown in Fig. 3.

49.2 *Electrometric pH Measurement Apparatus,* conforming to the requirements in Section 4 of Test Methods D1293.

49.3 *Vacuum Pump,* capable of creating a pressure differential of 40 mm Hg below atmospheric pressure.

49.4 *Flasks or Bottles,* 500-mL, with glass stoppers.

## 50. Reagents

50.1 *Bromcresol Green Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromcresol green in 2.9 mL of 0.02 *N* sodium hydroxide (NaOH) solution. Dilute to 100 mL with water.

50.2 *Carbon Dioxide-Free Water*—See 40.1.

50.3 *Hydrochloric Acid* (1 + 9)—See 40.2.

50.4 *Hydrochloric Acid, Standard Solution,* (0.10 *N*)—Measure 8.5 mL of hydrochloric acid (HCl, sp gr 1.19) into a 10-mL graduated cylinder. Rinse it into a 1-L volumetric flask and dilute to 1 L with water at 25 ± 5°C. Mix well.

50.4.1 To standardize, dry primary standard sodium carbonate at 250°C for 4 h and cool in a desiccator. Weigh three 0.22-g samples of dried sodium carbonate into separate 250-mL conical flasks. Titrate electrometrically to a pH of 3.9 or colorimetrically using bromcresol green indicator.

50.4.2 Calculate the normality of the HCl as follows:

$$N_A = D/(0.05299 \times E) \quad (10)$$

where:

$N_A$ = normality of HCl,
$D$ = actual amount of $Na_2CO_3$ used, g, and
$E$ = amount of HCl used, mL.

50.5 *Isopropyl Alcohol,* neutral.

50.6 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

50.7 *Phenolphthalein Indicator Solution* (5.0 g/L)—See 40.4.

50.8 *Sodium Hydroxide Solution*, 50 %—See 40.6.

50.9 *Sodium Hydroxide Solution, Standard* (0.10 *N*) *in Sodium Chloride Solution* (50 g/L)—Dissolve 50.0 g of sodium chloride (NaCl) in 500 mL of carbon dioxide-free water in a 1-L volumetric flask. Add 8 g of 50 % sodium hydroxide (NaOH) solution to the NaCl solution and rinse the graduate with carbon dioxide-free water. Dilute to 1 L with carbon dioxide-free water at 25 ± 5°C and mix well. To standardize, see 40.7.1 and 40.7.2.

## 51. Procedure

51.1 Weigh into separate 100-mL beakers, three 2.00 g samples of material pretreated in accordance with Section 10.

51.2 Rinse the weighed samples with water quantitatively into the filter tubes of the test apparatus. Fill the separatory funnel with 1 L of HCl (1 + 9). Fill the sample tube with acid and tap to remove air bubbles. Attach the stem of the funnel to the filter tube with a suitable size rubber stopper. Pass the acid through the sample at a rate of 20 to 25 mL/min keeping the sample covered with acid at all times. Drain the liquid to the resin level and discard the effluent.

51.3 Rinse the separatory funnel thoroughly with water and then with isopropyl alcohol. Run isopropyl alcohol through the acid-treated samples at a rate of 20 to 25 mL/min until 10 mL of the effluent collected in 10 mL of water is yellow to methyl orange or has a pH above 3.9.

51.4 Transfer the filter tube to the top of a suction flask and drain the residual alcohol from the resin using a vacuum pump. Continue to aspirate until the sample is free-flowing.

51.5 Transfer the samples quantitatively to 500-mL flasks or bottles. Pipet in exactly 200 mL of standard NaOH solution (0.1 *N*) in NaCl. Stopper immediately and mix well.

51.6 Allow samples to equilibrate for 16 h.

51.7 Remix and allow the samples to settle. Pipet out three 50 mL portions of each sample taking the necessary precautions to avoid drawing resinous material up into the pipet. Titrate electrometrically with standard HCl (0.1 *N*) to a pH of 8.2 or colorimetrically using phenolphthalein indicator. Record the volume of HCl used in each titration to the nearest 0.01 mL. Use the average of the three titrations for each sample as *F*.

## 52. Calculation

52.1 Calculate the total cation-exchange capacity in milliequivalents per wet gram, $C_w$, as follows:

$$C_w = [(200 \times N_B) - (F \times N_A \times 4)]/W \quad (11)$$

where:

$F$ = average millilitres of HCl required for the titration in 51.7,
$W$ = wet grams of the sample,
$N_A$ = normality of HCl used, and
$N_B$ = normality of NaOH solution used.

52.2 Calculate the total cation exchange capacity in milliequivalents per dry gram, $C_d$, as follows:

$$C_d = C_w/(1 - (M/100)) \quad (12)$$

where:

$C_w$ = milliequivalents of total cation-exchange capacity per wet gram, and
$M$ = percentage water retained as determined in accordance with Sections 11 – 17.

52.3 Calculate the total cation exchange capacity in milliequivalents per millilitre of back-washed and settled material, $C_b$, as follows:

$$C_b = C_w \times C \quad (13)$$

where:

$C_w$ = milliequivalents of total cation exchange capacity per wet gram, and
$C$ = wet, settled density as determined in accordance with Sections 19 – 25, g/mL.

## 53. Report

53.1 Report the total cation exchange capacities as the average of results of the three samples.

## 54. Precision and Bias[4]

54.1 *Precision*—The precision of this test method may be expressed as follows:

$$S_T = 0.089$$
$$S_o = 0.029$$

where:

$S_T$ = overall precision in meq/wet g, and
$S_o$ = single operator precision in meq/wet g.

54.1.1 Information given for the precision statement is derived from round-robin testing in which seven laboratories, including seven operators, participated. Six samples were included in the testing, and of these, five were new resins and one had been used in a commercial unit for some period of time. All samples were tested in triplicate with the exception of one in one of the laboratories that was tested in duplicate. Data for one sample submitted by one laboratory was omitted. Data was not submitted by one laboratory (not necessarily the same) for three of the samples. Data was not submitted for two of the samples by one laboratory.

54.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 55. Quality Control

55.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

55.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 54.

55.3 Analysis of the resin column effluent is subject to the quality control requirements of the referenced analytical methods.

# TEST METHOD G—PERCENT REGENERATION OF HYDROGEN-FORM CATION-EXCHANGE RESINS

## 56. Scope

56.1 This test method covers the determination of the percentage of ion-exchanging groups in a cation-exchange resin that is in the hydrogen form.

## 57. Significance and Use

57.1 This test method is intended for the evaluation of new cation-exchange resin sold in the hydrogen form or for samples taken from operating units where acid is used as the regenerant. In the latter case, it is used as a measure of the efficiency of the regeneration procedure since the resin sample is not pretreated.

## 58. Apparatus

58.1 Test apparatus required is described in Section 39 and Fig. 3.

## 59. Reagents

59.1 *Carbon Dioxide-Free Water*—See 40.1.

59.2 *Hydrochloric Acid* (1 + 9)—See 40.2.

59.3 *Hydrochloric Acid, Standard Solution* (0.10 *N*)—See 50.4.

59.4 *Isopropyl Alcohol,* neutral.

59.5 *mMethyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

59.6 *Phenolphthalein Indicator Solution* (5.0 g/L)—See 40.4.

59.7 *Sodium Chloride Solution* (50 g/L)—See 40.5.

59.8 *Sodium Hydroxide Solution*—See 40.6.

59.9 *Sodium Hydroxide, Standard Solution* (0.10 *N*)—See 40.7.

59.10 *Sodium Hydroxide, Standard Solution* (0.10 *N*) *in Sodium Chloride Solution* (50 g/L)—See 50.9.

## 60. Procedure

60.1 For salt-splitting cation capacity only:

60.1.1 Weigh into separate 100-mL beakers, three 10.0 g representative samples of the material as received.

60.1.2 Rinse the weighed samples with water quantitatively into the filter tubes of the apparatus described in Section 39.

60.1.3 Proceed in accordance with 41.4 and 41.5. Record average titrations as $E_R$.

60.1.4 Using the same sample, begin the procedure described in 41.2 at the point "Fill the separatory funnel . . .", and continue through 41.3, 41.4, and 41.5, recording the second titration average as $E$.

60.2 For total cation capacity:

60.2.1 Weigh into separate 100-mL beakers, three 2.00 g portions of material as received.

60.2.2 Proceed in accordance with 51.2 through 51.7.

60.2.3 Weigh into separate 500-mL bottles of flasks, three 2.00-g portions of material as received. Continue with the procedure described in 51.5 at the point "Pipet in exactly 200

mL . . .” and continue through 51.7. Record the average of the second titration as $F_R$.

## 61. Calculation

61.1 *Percent Regeneration of Cationic Salt-Splitting Capacity*—Calculate the percent regeneration of cationic salt-splitting cation-exchange capacity as follows:

Percent regeneration of cationic salt-splitting

$$\text{capacity} = \left[\left(E_R \times N_R\right)/\left(E \times N_E\right)\right] \times 100 \quad (14)$$

where:

$E_R$ = average titration in 60.1.3, mL,
$N_R$ = normality of titrant in 60.1.3,
$E$ = average titration in 60.1.4, mL, and
$N_E$ = normality of titrant in 60.1.4.

61.2 *Percent Regeneration of Total Cation Capacity:*

61.2.1 Calculate the total cation exchange capacity in milliequivalents per wet gram, $C_w$ as shown in 52.1, using titration F from 60.2.2.

61.2.2 Calculate the cation exchange capacity as received in milliequivalents per wet gram. $C_{WR}$, as shown in 52.1, using titration $F_R$ from 60.2.3.

61.2.3 Calculate the percent regeneration of cation groups as follows:

$$\left(C_{WR}/C_W\right) \times 100 = \text{percent} \quad (15)$$

regeneration of total cationic groups to hydrogen form

## 62. Report

62.1 Report the percent regeneration of salt-splitting cation groups to the hydrogen form or the percent regeneration of total cationic groups to the hydrogen form as the average of the results of the three samples.

## 63. Precision and Bias[4]

63.1 *Precision:*

63.1.1 The precision of this test method for the determination of the percent regeneration of cationic salt-splitting capacity may be expressed as follows:

$$S_{ST} = \frac{6.00}{E \times N_E}\left[\frac{\left(E_R \times N_R\right)}{\left(E \times N_E\right)} + 1\right] \quad (16)$$

$$S_{SO} = \frac{4.38}{E \times N_E}\left[\frac{\left(E_R \times N_R\right)}{\left(E \times N_E\right)} + 1\right] \quad (17)$$

where:

$S_{ST}$ = overall precision, %,
$S_{SO}$ = single-operator precision, %,
$E_R$ = average titration in 60.1.3, mL,
$N_R$ = normality of titrant in 60.1.3,
$E$ = average titration in 60.1.4, mL, and
$N_E$ = normality of titrant in 60.1.4.

63.1.2 The precision of this test method for the determination of the percent regeneration of total cationic groups may be expressed as follows:

$$S_T = \frac{8.86}{C_w}\left[\frac{C_{WR}}{C_w} + 1\right] \quad S_o = \frac{2.90}{C_w}\left[\frac{C_{WR}}{C_w} + 1\right]$$

where:

$S_T$ = overall precision, %,
$S_o$ = single-operator precision, %,
$C_{WR}$ = received cation-exchange capacity in milliequivalents per wet gram calculated in 61.2.2, and
$C_w$ = total cation-exchange capacity in milliequivalents per wet gram calculated in 61.2.1.

63.1.3 Information given for the precision statements is derived from round-robin testing in which five laboratories, including five operators, participated. Six laboratories are required by the 1986 edition of Practice D2777; however, the interlaboratory test was performed at a time when five was acceptable. Four samples were included in the round-robin test. One laboratory tested all samples in duplicate; two tested all samples in triplicate, and one tested three samples in quadruplicate and one sample six times.

63.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 64. Quality Control

64.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

64.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 63.

# TEST METHOD H—TOTAL AND SALT-SPLITTING CAPACITY OF ANION-EXCHANGE RESINS

## 65. Scope

65.1 The test method covers the determination of the total number of milliequivalents of exchangeable chloride in a test method anion-exchange material and also the number of milliequivalents of exchangeable chloride capacity associated with functional groups sufficiently basic to split neutral salts.

## 66. Summary of Test Method

66.1 This test method consists of conversion of the sample to the chloride form, elution of chloride from nonsalt-splitting groups with ammonium hydroxide, the subsequent elution of chloride from salt-splitting groups with sodium nitrate, followed by the determination of chloride ion in the separate eluates.

## 67. Significance and Use

67.1 Anion-exchange materials are available in a broad spectrum of base strengths, the true nature of which can only be determined by titration curve measurements. In commercial application to the treatment of water, however, they are usually characterized by their ability to split neutral salts or “salt-splitting capacity” and their total capacity for strong acid

removal. As a general rule materials with salt-splitting capacity have quaternary ammonium groups in their structure. They are capable of reactions such as:

$$R - CH_2N + R_3OH^- + Na^+NO_3 \rightarrow RCH_2N^+R_3NO_3^- + Na^+ + OH^-$$

in neutral waters and are also capable of removing anions of weak acids such as silicic acid from water. Anion-exchange materials without split-splitting capacity, that may contain primary, secondary, or tertiary amine groups as functionality, either singly or in combination, are primarily used to remove anions from acidic waters, as, for example, those obtained by passage through the hydrogen form of a cation-exchange resin. The multiplicity of the amine groups available and the fact that base strength reflects the entire polymer structure and not just that of the functional groups, implies that any method that separates materials into only two categories must be somewhat arbitrary. The test methods outlined herein are based on the combined experience of representatives of 20 laboratories. They have been tested on a variety of commercially available anion-exchange materials of different chemical structure. They are of use not only in determining the capacity of new materials, but for following the changes in capacity of materials that have been in service. In latter case the interpretation of the results is greatly simplified by comparison with the analyses of the materials when new.

## 68. Apparatus

68.1 Test apparatus required is described in Section 39 and shown in Fig. 3.

## 69. Reagents

69.1 *Ammonium Hydroxide* (1 + 19)—Carefully pour 50 mL of ammonium hydroxide ($NH_4OH$, sp gr 0.90) into 500 mL of water, stirring constantly. Cool to 25 ± 5°C and dilute to 1 L with water. Mix well.

69.2 *Bromcresol Green Indicator Solution* (1 g/L)—See 50.1.

69.3 *Hydrochloric Acid* (1 + 9)—See 40.2.

69.4 *Hydrochloric Acid, Standard* (0.1 *N*)—See 50.4.

69.5 *Isopropyl Alcohol.*

69.6 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

69.7 *Nitric Acid* (1 + 9)—Pour one volume of nitric acid ($HNO_3$, sp gr 1.42) into nine volumes of water and mix thoroughly.

69.8 *Phenolphthalein Indicator Solution* (5 g/L)—See 40.4.

69.9 *Potassium Chromate Solution* (50 g/L)—Dissolve 5.0 g of potassium chromate ($K_2CrO_4$) in 50 mL of water. Dilute to 100 mL with water.

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

69.10.1 To standardize, dry approximately 5 g of sodium chloride (NaCl) 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 swirl to dissolve the NaCl. Pipet in 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 of the solution changes from yellow to red-orange and persists for 30 s.

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

$$N = D/(0.05845 \times E) \quad (18)$$

where:

$N$ = normality of the $AgNO_3$ standard solution,
$D$ = weight of NaCl used, g, and
$E$ = amount of $AgNO_3$ standard solution required for the titration, mL.

69.11 *Sodium Chloride Solution* (50 g/L)—See 40.5.

69.12 *Sodium Nitrate Solution* (20 g/L)—Dissolve 20 g of sodium nitrate ($NaNO_3$) in 500 mL of water. Mix and dilute to 1 L.

## 70. Procedure

70.1 Weigh into separate 100-mL beakers three 10.0-g representative portions of the material pretreated in accordance with Section 10.

70.2 Quantitatively rinse the weighed samples into filter tubes with water. Fill three separatory funnels with 1 L each of HCl (1 + 9). Fill the sample 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 the 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.

70.3 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 alcohol.

70.4 Rinse the volumetric flasks thoroughly with water and reposition them under the tip of the filter tubes. Add 500 mL of $NH_4OH$ (1 + 19) through the samples at the rate of 20 to 25 mL/min, keeping the sample covered at all times. When the separatory funnels are empty, rinse them thoroughly and refill with water. Rinse the samples with water at the rate of 20 to 25 mL/min. Collect the water rinse in the volumetric flasks with the $NH_4OH$ effluent, discontinuing the flow of liquid when 1 L of combined solution has been collected.

70.4.1 Mix the combined effluents thoroughly. Pipet three 100-mL portions of each into separate 250-mL conical flasks. Add three drops of methyl orange indicator solution to each flask. Add $HNO_3$ (1 + 9) dropwise until the solution is red. Add $NH_4OH$ (1 + 9) dropwise until the solution is again just yellow. Pipet in 1 mL of $K_2CrO_4$ solution (50 g/L) into the flask and

titrate with vigorous swirling with the 0.1 *N* $AgNO_3$ standard solution until the supernatant liquid changes from yellow to red-orange and the color change persists for 30 s. Record the number of millilitres of $AgNO_3$ standard solution used to ±0.02 mL as *F*.

70.5 Position another 1-L volumetric flask under the tip of each filter tube. Place 200 mL of NaCl solution (50 g/L) in each of the separatory funnels and pass it through the sample at the rate of 20 to 25 mL/min, keeping the sample covered with solution at all times. Rinse the separatory funnels thoroughly with water to remove all traces of chloride. Wash the samples with water at the rate of 20 to 25 mL/min, collecting the washings in the flask with the NaCl effluent. Continue washing until 1 L of combined solution is collected.

70.5.1 Mix each combined effluent thoroughly. Pipet three 100-mL portions of each into separate 250-mL conical flasks. Titrate with 0.1 *N* HCl electrometrically to a pH of 3.9 or colorimetrically using 1 drop of bromcresol green indicator solution. Record the millilitres of 0.1 *N* HCl used to ±0.02 mL as *G*.

70.6 Position another 1-L volumetric flask under the tip of each filter tube. Fill the separatory funnels with $NaNO_3$ solution (20 g/L). Pass this solution through the samples at the rate of 20 to 25 mL/min until 1 L of effluent has been collected, keeping the sample covered with liquid at all times.

70.6.1 Mix each $NaNO_3$ effluent thoroughly. Pipet three 100-mL portions of each into separate 250-mL conical flasks. Add one drop of phenolphthalein indicator solution and one drop of methyl orange indicator solution to each flask. Add $HNO_3$ (1 + 9) or $NH_4OH$ (1 + 19) dropwise as required to adjust the pH into the range where the phenolphthalein indicator solution is colorless and the methyl orange indicator solution is yellow. Add 1 mL of $K_2CrO_4$ solution (50 g/L). Titrate with vigorous swirling with standard 0.1 *N* $AgNO_3$ standard solution until the color of the supernatant liquid changes from yellow to red-orange and persists for 30 s.

## 71. Calculation

71.1 Calculate the anionic salt-splitting capacity in milliequivalents per wet gram as follows:

$$\frac{\text{milliequivalents anionic salt} - \text{splitting capacity}}{\text{wet gram}} = (H \times N \times 10)/W \quad (19)$$

where:

- *H* = average millilitres of $AgNO_3$ standard solution required for the titrations in 70.6.1,
- *W* = wet grams of the sample, and
- *N* = normality of $AgNO_3$ standard solution.

71.2 Calculate the total anion-exchange capacity per wet gram as follows:

$$\frac{\text{milliequivalents total anion} - \text{exchange capacity}}{\text{wet gram}} = \left(10\left[(F+H)\times N\right] - 10\left[G \times N_A\right]\right)/W \quad (20)$$

where:

- *F* = average millilitres of $AgNO_3$ standard solution required for the titrations in 70.4.1,
- *G* = average millilitres of 0.1 *N* HCl required for the titrations in 70.5.1,
- *H* = average millilitres of $AgNO_3$ standard solution required for the titrations 70.6.1,
- *W* = wet grams of the sample,
- *N* = normality of $AgNO_3$ standard solution, and
- $N_A$ = normality of 0.1 *N* HCl.

71.3 Calculate the anionic salt-splitting capacity in milliequivalents per dry gram as follows:

$$\frac{\text{milliequivalents anionic salt} - \text{splitting capacity}}{\text{dry gram}} = K/\left[1 - (M/100)\right] \quad (21)$$

where:

- *K* = milliequivalents anionic salt-splitting capacity per wet gram, and
- *M* = percent water retained as determined in accordance with Sections 11 – 17.

71.4 Calculate the total anion-exchange capacity in milliequivalents per dry gram as follows:

$$\frac{\text{milliequivalents total anion} - \text{exchange capacity}}{\text{dry gram}} = L/\left[1 - (M/100)\right] \quad (22)$$

where:

- *L* = milliequivalents total anion-exchange capacity per wet gram, and
- *M* = percent water retained as determined in accordance with Sections 11 – 17.

71.5 Calculate the anionic salt-splitting capacity in milliequivalents per millilitre of back-washed and settled material as follows:

$$\frac{\text{milliequivalents anionic salt} - \text{splitting capacity}}{\text{millilitre}} = K \times C \quad (23)$$

where:

- *K* = milliequivalents anionic salt-splitting capacity per wet gram, and
- *C* = wet, settled density, as determined in accordance with Sections 19 – 25, g/mL.

71.6 Calculate the total anion-exchange capacity in milliequivalents per millilitre of back-washed and settled material as follows:

$$\frac{\text{milliequivalents total anion} - \text{exchange capacity}}{\text{millilitres settled bed}} = L \times C \quad (24)$$

where:

- *L* = milliequivalents total anion-exchange capacity per wet gram, and
- *C* = wet, settled density, in grams per millilitre, as determined in accordance with Sections 19 – 25.

## 72. Precision and Bias[4]

72.1 *Precision*—The precision of these test methods in milliequivalents per dry gram may be expressed as follows:

72.1.1 Anionic salt-splitting capacity:

$$S_T = 0.069$$

$$S_o = 0.033$$

and

72.1.2 Total anion exchange capacity:

$$S_T = 0.215$$

$$S_o = 0.083$$

where:

$S_T$ = over-all precision, meq/dry g, and
$S_o$ = single-operator precision, meq/dry g.

72.1.3 Information given in the precision statement is derived from round-robin testing involving nine laboratories and seven samples, of which six were new and one was used in a commercial unit for some period of time. None of the laboratories tested all seven samples. Two laboratories tested five samples, three tested three samples, and four tested two samples. The results were reported July 3, 1970.

72.2 *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 place functional groups on the polymeric structure. Consequently, the true value for any property of the finished product is unknown and a bias statement cannot be given.

## 73. Quality Control

73.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

73.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 72.

# TEST PRACTICE I—PERCENT REGENERATION OF ANION EXCHANGE RESINS

## 74. Scope

74.1 This test practice covers the determination of the percentage of anion-exchanging groups regenerated to the hydroxide ion form, and the total percentage of anionic groups regenerated to a form capable of neutralizing free mineral acids.

## 75. Summary of Test Practice

75.1 This test practice consists of the elution of the sample with sodium chloride and the titration of the hydroxide ion so removed, the subsequent elution with a known amount of free mineral acid and the determination of the acid not neutralized, followed by an elution with sodium nitrate and the determination of the total chloride eluted.

## 76. Significance and Use

76.1 In cases where an anion resin is sold in the regenerated form or has been regenerated in a field unit, the efficiency of the regeneration process as measured by the relative percentage of functional groups in the hydroxide free base and salt forms is determined. This test practice provides for a distinction between the salt-splitting groups from which hydroxide may be eluted with a neutral sodium chloride and groups of lesser basicity that will not exchange hydroxide for chloride but that are capable of absorbing free mineral acids.

76.2 If the resin contains quaternary ammonium groups, extreme caution must be taken in handling the regenerated sample to prevent the absorption of carbon dioxide by the hydroxide-form resin. Materials sampled for such analysis should, if possible, be shipped covered with deionized water in tightly sealed containers and analyzed as soon as practicable after sampling.

## 77. Apparatus

77.1 *Test Apparatus*—See Section 39 and Fig. 3.

## 78. Reagents

78.1 *Bromcresol Green Indicator Solution*—See 50.1.

78.2 *Hydrochloric Acid, Standard Solution* (1.0 *N*)—Measure 85 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) in a 100-mL graduated cylinder. Rinse it into a 1-L volumetric flask and dilute to 1 L with water at 25 ± 5°C. Mix well.

78.2.1 To standardize, dry primary standard sodium carbonate at 250°C for 4 h and cool in a desiccator. Weigh accurately three 2.2-g samples of dried sodium carbonate into separate 250 mL conical flasks. Titrate electrometrically to a pH of 3.9 or colorimetrically using bromcresol green indicator to the yellow end point.

78.2.2 Calculate the normality of the HCl as follows:

$$N_D = D/(0.05299 \times E) \quad (25)$$

where:

$N_D$ = normality of the HCl,
$E$ = amount of HCl used, g, and
$D$ = actual weight of $Na_2CO_3$ used, g.

78.3 *Hydrochloric Acid, Standard Solution* (0.10 *N*)—See 50.4.

78.4 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

78.5 *Nitric Acid* (1 + 9)—See 69.7.

78.6 *Phenolphthalein Indicator Solution* (5.0 g/L)—See 40.4.

78.7 *Potassium Chromate Solution* (50 g/L)—See 69.9.

78.8 *Silver Nitrate, Stand Solution* (0.10 *N*)—See 69.10.

78.9 *Sodium Chloride Solution* (50 g/L)—See 40.5.

78.10 *Sodium Hydroxide, Solution Standard* (0.10 *N*)—See 40.7.

78.11 *Sodium Nitrate Solution* (20 g/L)—See 69.12.

## 79. Procedure

79.1 Weigh rapidly into separate 100-mL beakers containing 25 mL of water three 10-g representative as-received

samples. The beakers should be kept covered with a watch glass or plastic film at all times.

79.2 Rinse the weighed samples with water into the filter tubes. Position a 1-L volumetric flask under the filter tube. Add 1 L of NaCl solution (50 g/L) to the separatory funnel. Immediately fill the sample tube with NaCl solution. Tap to remove air bubbles and attach the stem of the funnel to the filter tube with a suitable sized rubber stopper. Take care that all solution passing through the sample is collected in the volumetric flask.

79.3 Pass the NaCl solution through the sample at the rate of 20 to 25 mL/min, keeping the sample covered with solution at all times. Collect exactly 1 L of effluent in the volumetric flask. Shut off the flow of the NaCl solution leaving the sample covered with solution.

79.3.1 Mix the sodium chloride effluent thoroughly. Pipet out three 100-mL portions into separate beakers. Titrate electrometrically to pH 9 or add one drop of phenolphthalein indicator solution and titrate with 0.1 *N* HCl until the pink color disappears. Record the number of millilitres of HCl used as *A*. Add two to three drops of bromcresol green indicator solution and continue the titration to the yellow end point or an electrometric pH of 3.9. Record the additional number of millilitres of HCl used as *Y*.

79.4 Position a second 1-L volumetric flask under the filter tube. Remove and rinse the separatory funnel with water. Pipet exactly 100 mL of 1.0 *N* HCl into the separatory funnel. Add 500 mL of water and swirl to mix. Reattach the separatory funnel to the filter tube and pass the solution through the sample at the rate of 20 to 25 mL/min, keeping the sample covered with solution at all times. When the separatory funnel is empty, rinse it with four 100-mL portions of isopropyl alcohol, washing down the sides of the funnel in each case. Allow each 100-mL portion to drain to the top of the sample at the rate of 20 to 25 mL/min before the next portion is added. Collect the isopropyl alcohol rinse in the same volumetric flask as the HCl effluent, discontinuing the flow of liquid when 1 L of combined solution has been collected.

79.4.1 Mix the combined effluent thoroughly. Pipet out three 50-mL portions into separate beakers. Titrate electrometrically to pH 9 or add one drop of phenolphthalein indicator solution and titrate with 0.1 *N* NaOH solution until a pink color persists of 30 s. Record the number of millilitres of NaOH solution as *B*.

79.5 Position a third 1-L volumetric flask under the tip of the filter tube. Fill the separatory funnel with 1 L of $NaNO_3$ solution (20 g/L). Pass this solution through the sample at the rate of 20 to 25 mL/min until 1 L of effluent has been collected, keeping the sample covered with liquid at all times.

79.5.1 Mix the $NaNO_3$ effluent thoroughly. Pipet three 100-mL portions of it into separate beakers or conical flasks. Add one drop of phenolphthalein indicator solution and one drop of methyl orange indicator solution to be certain that the sample is neutral (colorless) to phenolphthalein and also neutral (yellow) to methyl orange. If necessary adjust the pH to this range by dropwise addition of NaOH solution or $HNO_3$. Pipet in 1 mL of $K_2CrO_4$ solution (50 g/L). Titrate with 0.1 *N* $AgNO_3$ solution until the color of the supernatant liquid changes from yellow to red-orange and persists for 30 s with vigorous swirling. Record the number of millilitres of $AgNO_3$ solution used as *C*.

NOTE 2—Good laboratory practice would advise that a 100-mL portion of $NaNO_3$ solution be titrated as a blank to verify the purity of reagents.

## 80. Calculation

80.1 Calculate the percent of functional groups in the hydroxide form as follows:

$$\text{hydroxide form, } \% = [(A - Y) \times N_A \times 100]/(C \times N_c) \quad (26)$$

where:

$A$ and $Y$ = averages of the millilitres of HCl required for the titrations in 79.3.1,
$N_A$ = normality of the HCl used in 79.3.1,
$C$ = average millilitres of $AgNO_3$ solution required for the titration in 79.5.1, and
$N_c$ = normality of the $AgNO_3$ solution used in 79.5.1.

80.2 Calculate the total percent of functional groups regenerated as follows:

$$\text{anionic groups regenerated} = \frac{[(A - Y) \times N_A] + [(10 \times N_D) - 2(B \times N_B)]}{C \times N_c} \times 100 \quad (27)$$

where:

$A$ and $Y$ = averages of the millilitres of HCl required for the titrations in 79.3.1,
$N_A$ = normality of the HCl used in 79.3.1,
$C$ = average millilitres of $AgNO_3$ solution required for the titration in 79.5.1,
$N_c$ = normality of the $AgNO_3$ solution used in 79.5.1,
$N_D$ = normality of HCl used in 79.4,
$B$ = average milliliters of NaOH solution required for the titration in 79.4.1, and
$N_B$ = normality of NaOH solution used in 79.4.1.

## 81. Report

81.1 Report the percent hydroxide from strong base groups (Eq 26) and the total percent anionic groups regenerated (Eq 27) as the average of the results of the three samples.

## 82. Precision and Bias[4]

82.1 *Precision*—The precision of this test practice within its designated range for a single operator at a single test facility has been found to be equal to ±2.9 % of the value reported. A collaborative study will be done to determine the precision of this test practice in accordance with the 1986 edition of Practice D2777.[5]

82.2 *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 place functional groups on the polymeric structure. Consequently,

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D19-0138, RR:D19-0139, and RR:D19-1007. Contact ASTM Customer Service at service@astm.org.

the true value for any property of the finished product is unknown and a bias statement cannot be given.

## TEST PRACTICE J—IONIC CHLORIDE CONTENT OF ANION EXCHANGE RESINS

### 83. Scope

83.1 This test practice covers the determination of the percentage of anion-exchanging groups in the chloride form at levels of 1 % or greater.

### 84. Summary of Test Practice

84.1 This test practice consists of the elution of the sample with sodium nitrate and the titration of the chloride ion so removed, the conversion of the same sample to the chloride form with hydrochloric acid followed again by elution with sodium nitrate and the determination of the total chloride eluted.

### 85. Significance and Use

85.1 This test practice is designated primarily for the analysis of anion-exchange resin sold in the regenerated form that is intended for use in applications where the chloride content of the treated water is of prime importance. It is therefore written with the anticipation that the chloride ions will occupy no more than 5 % of the total resin sites. It may, however, be used to determine the fraction of chloride present in samples taken from the field. If in such cases the chloride content is greater than 5 % of total resin sites all titrations may be made using 0.1 *N* silver nitrate solution. In addition the potentiometric titration of chloride has been found to be adequate for this test practice.

### 86. Apparatus

86.1 *Microburet,* 5 or 10-mL, with 0.1-mL graduations.

86.2 *Test Apparatus*—See Section 39 and Fig. 3.

### 87. Reagents

87.1 *Hydrochloric Acid* (1 + 9)—See 40.2.

87.2 *Isopropyl Alcohol.*

87.3 *Mercuric Nitrate, Standard Solution* (0.025 *N*)—Dissolve 4.283 g of mercuric nitrate ($Hg(NO_3)_2 \cdot H_2O$) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid ($HNO_3$, sp gr 1.42). Dilute the acidified $Hg(NO_3)_2$ solution with water to 1 L. Filter if necessary and standardize against the standard sodium chloride (NaCl) solution, using the procedure described in 88.2.2.

87.4 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

87.5 *Mixed Indicator Solution*—Dissolve 0.5 g of crystalline diphenylcarbazone and 0.05 g of bromophenol blue powder in 75 mL of ethyl alcohol (95 %), and dilute to 100 mL with the alcohol (see Note 3 and Note 4). Store in a brown bottle and discard after six months.

NOTE 3—Denatured alcohol is not suitable. Methanol or isopropanol may be used if pure ethyl alcohol is not available.

NOTE 4—Liquid indicator generally deteriorates to the point that it yields no endpoint color after 12 to 18 months of storage. High temperature (above 37.8°C or (100°F)) and exposure to bright light may shorten storage life. A dry powder mixture of two indicator ingredients is stable for much longer periods. Both the powder mixture (capsule form) and the liquid indicator are available commercially.

87.6 *Nitric Acid* (1 + 9)—See 69.7.

87.7 *Phenolphthalein Indicator Solution* (5.0 g/L)—See 40.4.

87.8 *Potassium Chromate Solution* (50 g/L)—See 69.9.

87.9 *Silver Nitrate, Standard Solution* (0.10 *N*)—See 69.10.

87.10 *Sodium Chloride, Standard Solution* (0.025 *N*)—Dry several grams of sodium chloride (NaCl) for 1 h at 600°C. Dissolve 1.4613 ± 0.0002 g of the dry salt in water, and dilute to 1 L at 20°C in a volumetric flask.

87.11 *Sodium Hydroxide Solution Standard* (0.10 *N*)—See 40.7.

87.12 *Sodium Nitrate Solution* (20 g/L)—See 69.12.

### 88. Procedure

88.1 Weigh into separate 100-mL beakers three 20-g representative as-received samples.

88.2 Rinse the weighed samples with water into the filter tubes. Fill the separatory funnel with 1 L of $NaNO_3$ solution (20 g/L). Pass this solution through the sample at the rate of 20 to 25 mL/min until 1 L of effluent has been collected, keeping the sample covered with liquid at all times.

88.2.1 Mix the $NaNO_3$ solution effluent thoroughly. Pipet three 100-mL portions of it into separate beakers or conical flasks. Add one drop of phenolphthalein indicator solution. Add nitric acid (1 + 9) dropwise until the indicator color is discharged.

88.2.2 Add ten drops of mixed indicator solution (see 87.5) and continue the dropwise addition of nitric acid until a yellow color is produced. Add two drops of nitric acid in excess.

88.2.3 Titrate the solution with 0.025 *N* $Hg(NO_3)_2$ solution until a blue-violet color, as viewed by transmitted light, persists throughout the solution for at least 15 s. Record the millilitres of $Hg(NO_3)_2$ solution used as *P*.

88.2.4 Determine a titration blank using 100 mL of $NaNO_3$ and the same volume of indicators used in the sample titration. Record the millilitres of $Hg(NO_3)_2$ used as *Q*.

88.3 Fill the separatory funnel with 1 L of HCl (1 + 9). Pass this solution through the sample at the rate of 20 to 25 mL/min. Discard effluent.

88.4 Rinse the separatory funnel thoroughly with water and then with three 10-mL portions of isopropyl alcohol. Final rinsing should be neutral (orange) to methyl orange. Run isopropyl alcohol through the acid-treated samples of 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 alcohol.

88.5 Rinse the volumetric flasks thoroughly with water and reposition them under the tip of the filter tubes. Repeat 88.2 and 88.2.1 starting at "Fill the separatory funnel . . .".

88.5.1 Add one drop of methyl orange indicator solution to the partially neutralized aliquots and adjust the pH by further addition of $HNO_3$ and NaOH solution (0.1 *N*), or both, until they are neutral (colorless) to phenolphthalein and also neutral (yellow) to methyl orange. Pipet in 1 mL of $K_2CrO_4$ solution (50 g/L). Titrate with 0.1 *N* $AgNO_3$ standard solution until the color of the supernatant liquid changes from yellow to red-orange and persists for 30 s with vigorous swirling. Record the number of millilitres of $AgNO_3$ solution used as *C*.

88.5.2 Determine the blank for the titration using 100 mL of $NaNO_3$ solution neutralized as the sample and containing the same volume of $K_2CrO_4$ solution. Record this volume as *D*.

## 89. Calculation

89.1 *Percent Chloride Sites*—Calculate the percent chloride sites as follows:

$$\%\ \text{chloride sites} = \frac{(P - Q) \times N_{Hg(NO_3)_2}}{(C - D) \times N_{AgNO_3}} \times 100 \qquad (28)$$

where:

*P* = average millilitres of $Hg(NO_3)_2$ solution used in 88.2.3,

*Q* = average millilitres of $Hg(NO_3)_2$ solution blank (88.2.4),

*C* = average millilitres of $AgNO_3$ solution used in 88.5.1, and

*D* = average millilitres of $AgNO_3$ solution blank in 88.5.2.

## 90. Precision[6] and Bias

90.1 *Precision*—Data from previous studies is no longer available. A collaborative study will be done to determine the precision of this test practice in accordance with the 1986 edition of Practice D2777.

90.2 *Bias*—Since it is impossible to prepare anion exchange resin samples with a known amount of chloride, bias cannot be determined.

# TEST METHOD K—CARBONATE CONTENT OF ANION EXCHANGE RESINS

## 91. Scope

91.1 This test method covers the determination of the percentage anion-exchanging groups in the carbonate-form.

## 92. Summary of Test Method

92.1 This test method consists of the elution of the sample with sodium nitrate and the titration of the carbonate ion so removed, the conversion of the same sample to the chloride form with hydrochloric acid followed again by elution with sodium nitrate and the determination of the total chloride eluted.

## 93. Significance and Use

93.1 This test method is designed for the analysis of anion exchange resin sold in the regenerated form, and for the analysis of samples taken from field units after regeneration with sodium hydroxide. It may also be used, however, to determine the fraction of the groups in the carbonate form at the end of a service cycle.

93.2 Bicarbonate solutions are sometimes used as intermediate steps in the conversion of anion exchange resins to the hydroxide form. In such cases the residual carbonate ion concentration is used as part of the analytical process for monitoring the degree of conversion to the hydroxide form.

93.3 The presence of carbonate in a regenerated anion-exchange resin may indicate that it has been exposed to atmospheric carbon dioxide or that the sodium hydroxide regenerant or the rinse water contained carbonate. Its presence shortens the operating runs and frequently is the cause of a drop in resistance during the service run to a lower plateau where a slightly acidic effluent is produced.

93.4 The test method is designed to permit chloride (see Test Practice J) carbonate and sulfate (see Test Method L) ions all to be determined in the same solution. It may also be combined with the determination of the percent regeneration of anion exchange resins (see Test Practice I).

## 94. Apparatus

94.1 *Test Apparatus*—See Section 39 and Fig. 3.

## 95. Reagents

95.1 *Hydrochloric Acid Solution* (1 + 9)—See 40.2.

95.2 *Hydrochloride Acid, Standard Solution* (0.10 *N*)—See 50.4.

95.3 *Isopropyl Alcohol.*

95.4 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

95.5 *Nitric Acid* (1 + 9)—See 69.7.

95.6 *Phenolphthalein Indicator Solution* (5.0 g/L)—See 69.9.

95.7 *Potassium Chromate Solution* (50 g/L)—See 69.9.

95.8 *Silver Nitrate, Standard Solution* (0.10 *N*)—See 69.10.

95.9 *Sodium Nitrate Solution* (20 g/L)—See 69.12.

## 96. Procedure

96.1 Weigh samples and elute with $NaNO_3$ (20 g/L) as in Test Practice J (88.1 and 88.2).

96.2 Pipet three additional 100-mL portions of the $NaNO_3$ effluent produced in 88.2 into separate beakers or conical flasks. Add one drop of phenolphthalein indicator.

96.3 Titrate with standard 0.1 *N*HCl until the solution turns from pink to colorless. Record the mL of titrant used to the nearest 0.02 mL as *R*.

96.4 Add two to three drops of methyl orange indicator solution. Continued the titration with hydrochloric acid until the solution turns from yellow to orange. Record the total volume used to the nearest 0.02 mL as *S*.

96.5 Continue the procedure in Test Practice J (88.3 through 88.5.2).

[6] Applicable reports are not available from ASTM.

## 97. Calculation

97.1 Calculate the percent carbonate sites as follows:

$$\% \text{ carbonate sites} = \frac{[2(S - R) \times N_{HCl}] \times 100}{(C - D) \times N_{AgNO_3}} \quad (29)$$

where:

$S$ = average mL of HCl used in 96.4,
$R$ = average mL of HCl used in 96.3,
$C$ = average mL of $AgNO_3$ used in 88.5.1, and
$D$ = average mL of $AgNO_3$ used in 88.5.2.

97.2 Report the results as the average of the three samples in percent.

## 98. Precision[6] and Bias

98.1 *Precision*—Precision was determined from the results of the analyses by eight operators, each analyzing three samples on each of three different days, as follows:

| Mean Found, % Carbonate Sites | Precision, % Carbonate Sites | |
|---|---|---|
| | Overall, $S_T$ | Single Operator, $S_o$ |
| 3.62 | 0.84 | 0.51 |
| 4.02 | 1.22 | 0.83 |
| 26.19 | 2.08 | 0.96 |

98.2 *Bias*—Since it is impossible to prepare anion exchange resin samples with a known amount of carbonate, bias cannot be determined.

## 99. Quality Control

99.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

99.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 98.

# TEST METHOD L—SULFATE CONTENT OF ANION EXCHANGE RESINS

## 100. Scope

100.1 This test method covers the determination of the percentage of anion-exchanging groups in the sulfate-form at levels of 1 % or greater.

## 101. Summary of Test Method

101.1 This test method consists of the elution of the sample with sodium nitrate and the determination of the sulfate ions so removed, the conversion of the same sample to the chloride form with hydrochloride acid followed again by elution with sodium nitrate and the determination of the total chloride eluted.

## 102. Significance and Use

102.1 This test method is designed for the analysis of anion exchange resin sold in the regenerated form, and for the analysis of samples taken from field units after regeneration with sodium hydroxide. It may also be used, however, to determine the fraction of the groups in the sulfate form at the end of a service cycle.

102.2 Sulfate solutions are sometimes used as intermediate steps in the conversion of anion exchange resins to the hydroxide form. In such cases the residual sulfate ion concentration is used as part of the analytical process for monitoring the degree of conversion to the hydroxide form.

102.3 The test method as written calculates milliequivalents sulfate assuming that $SO_4$ is the ion being exchanged. Generally this is appropriate when the pH of this first elution is above 7.0 as it is in regenerated resins. In analyzing field samples, cases are found where the first elution is acidic. In such cases the ion retained may be $HSO_4^-$, and the number of milliequivalents involved will be doubled. A complete analysis of the anion population may be required in such cases to obtain true ion balance.

102.4 This test method is written to permit chloride (see Test Practice J), carbonate (see Test Method K) and sulfate ions all to be determined in the same solution. It may also be combined with the determination of the percent regeneration of anion exchange resins (See Test Practice I).

## 103. Apparatus

103.1 *Test Apparatus*—See Section 39 and Fig. 3.

## 104. Reagents

104.1 *Barium Chloride Solution* (50 g/L)—Dissolve 50.0 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L.

104.2 *Hydrochloric Acid* (1 + 9)—See 40.2.

104.3 *Isopropyl Alcohol.*

104.4 *Methyl Orange Indicator Solution* (0.5 g/L)—See 40.3.

104.5 *Nitric Acid* (1 + 9)—See 69.7.

104.6 *Potassium Chromate Solution* (50 g/L)—See 69.9.

104.7 *Silver Nitrate, Stand Solution* (0.10 *N*)—See 69.10.

104.8 *Sodium Nitrate Solution* (20 g/L)—See 69.12.

## 105. Procedure

105.1 Weigh samples and elute with $NaNO_3$ (20 g/L) as in Test Practice J, Sections 88.1 and 88.2.

105.2 Pipet one additional 200-mL portion from the sodium nitrate effluent from each sample. If field samples taken at the end of the service run are being analyzed, a 100-mL aliquot is usually sufficient.

105.3 Also pipet two portions of the sodium nitrate solution used in 88.2 of the same volume as the samples to be used as blanks.

105.4 Adjust the acidity of each solution to the methyl orange endpoint with $HNO_3$ (1 + 9) and add 10 mL excess.

105.5 Heat to boiling and very slowly add 5 mL of $BaCl_2$ solution. Stir the sample vigorously while adding the $BaCl_2$ solution to avoid occlusion of $BaCl_2$ in the precipitate. Keep the temperature just below boiling until the liquid has become

clear and the precipitate has settled out completely. In no case shall this settling period be less than 2 h.

105.6 Filter the $BaSO_4$ on a fine, ashless filter paper, and wash the precipitate with hot water until the washings are substantially free of chloride, as indicated by testing a small portion with silver nitrate. Avoid excessive washing.

105.7 Place filter paper and precipitate in a previously ignited, cooled and weighed 30 mL porcelain crucible. Dry, and char to consume the paper without flaming. Ignite on a Meker burner or at approximately 800°C in a muffle furnace. Cool in a desiccator and weigh to the nearest 0.1 mg. Repeat until a constant weight is obtained.

105.8 While the barium sulfate is being precipitated proceed with 88.3 through 88.5.2.

## 106. Calculation

106.1 Subtract the weight of the empty crucible from the weight of the crucible plus barium sulfate for each of the samples and blanks.

106.2 Average the weight of the blanks and subtract this weight from that of the barium sulfate in each of the samples. Record the differences as *W*.

106.3 Calculate the percent sulfate sites (as $SO_4$) as follows:

$$\% \text{ sulfate sites} = \frac{(W/0.1167) \times (10000 / A)}{(C - D) \times N_{AgNO_3}} \quad (30)$$

where:

$A$ = volume taken for analysis, mL (104.2),
$C$ = average mL of $AgNO_3$ used in 88.5.1,
$D$ = average mL of $AgNO_3$ blank (88.5.2), and
$W$ = weight of $BaSO_4$ (see 106.2) corrected for blank.

106.4 Report the result as the average of the three values.

## 107. Precision[6] and Bias

107.1 *Precision*—Precision was determined from the results of the analyses by eight operators, each analyzing three samples on each of three different days, as follows:

| Mean Found, % Sulfate Sites | Precision, % Sulfate Sites | |
|---|---|---|
| | Overall, $S_T$ | Single Operator, $S_o$ |
| 0.06 | 0.06 | 0.053 |
| 2.50 | 0.96 | 0.46 |
| 7.48 | 0.49 | 0.18 |

107.2 *Bias*—Since it is impossible to prepare anion exchange resin samples with a known amount of sulfate, bias cannot be determined.

## 108. Quality Control

108.1 In the analysis of ion exchange resins, it is not possible to prepare a known standard resin for comparison with the actual sample. Therefore, it is impossible to test the accuracy of the results, and this test method does not include a bias statement.

108.2 Analysts are expected to use replicate samples to determine if the results are within the expected precision stated in Section 107.

# TEST PRACTICE M—TOTAL ANION CAPACITY OF ANION-EXCHANGE RESINS

## 109. Scope

109.1 This test practice covers the determination of the total number of milliequivalents of exchangeable chloride in an anion-exchange material.

## 110. Summary of Test Practice

110.1 The test practice consists of the conversion of the sample to the chloride form, elution of chloride with sodium nitrate, followed by determination of chloride ion in the eluate.[7]

## 111. Significance and Use

111.1 This simplified version of Test Method H is applicable to determination of the total exchange capacity of all types of anion exchanging materials, whether they have quaternary, primary, secondary, or tertiary functionality.

111.2 This test practice is intended primarily for use in the characterization of new materials to provide numerical values to be used in specifications.

111.3 Used materials known to contain no quaternary functionality are also properly analyzed by this test practice. Where only total capacity is of interest, it is appropriate for used quaternary resins as well.

111.4 New resins are analyzed in the ionic form in which they are sold. When the test practice is applied to used resins, samples containing quaternary groups are pretreated to the chloride form by Test Practice A. Samples that do not contain quaternary functionality are analyzed in the free base form by omitting the treatment in Table 2, Test Practice A.

## 112. Apparatus

112.1 Test apparatus required is described in Section 39 and shown in Fig. 3.

## 113. Reagents

113.1 *Hydrochloric acid* (1 + 9)—See 40.2.

113.2 *Isopropyl Alcohol.*

113.3 *Methyl Orange Indicator Solution,* (0.5 g/L)—See 40.3).

113.4 *Nitric Acid*—See 69.7.

113.5 *Phenolphthalein Indicator Solution* (5 g/L)—See 40.4.

113.6 *Potassium Chromate Solution* (50 g/L)—See 69.9.

113.7 *Silver Nitrate Standard Solution* (0.10 N)—See 69.10.

113.8 *Sodium Nitrate Solution* (20 g/L)—See 69.12.

## 114. Sampling Pretreatment

114.1 If the samples are new, they are usually analyzed as shipped. In that case sample containers should be inverted,

[7] Fisher, S. F., and Kunin, R., "Routine Exchange Capacity Determinations of Ion Exchange Resins," *Analytical Chemistry*, Vol. 27, 1955, p. 1191.

preferably overnight, to redistribute the shipping water before samples are drawn from the containers. Samples are best drawn with a ½-in. plastic tube so that a core through the population in the containers is obtained. Enough sample for capacity, solid, density, and particle size should be removed from the container at the same time. Results of such samples are reported on an as-received basis.

114.2 Used samples containing no quaternary groups are pretreated in accordance with Test Practice A, omitting the second pretreatment in 10.10 and 10.11 and thus leaving the sample in the free base form. This fact should be noted when the results are reported.

114.3 Used samples containing quaternary groups are pretreated to the chloride form in accordance with Test Practice A. This fact should be noted when the results are reported.

## 115. Procedure

115.1 Weigh samples pretreated in accordance with Section 114 for solids and dry in accordance with Section 14, Test Method B.

115.2 Weigh into separate filter tubes (see Fig. 3) three 10.0-g representative portions of samples pretreated in accordance with Section 114. Insert the tubes in the capacity apparatus.

115.3 Fill three separatory funnels with 1 L each of HCl (1 + 9). Fill the sample 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 the rate of 20 to 25 mL/min, keeping the samples covered with acid at all times. Drain the liquid to the samples level. Discard the effluent.

115.4 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 alcohol.

115.5 Position another 1-L volumetric flask under each filter tube. Fill the separatory funnels with $NaNO_3$ solution (20 g/L). Pass this solution through the samples at the rate of 20 to 25 mL/min until 1 L of effluent has been collected, keeping the sample covered with liquid at all times.

115.5.1 Mix each $NaNO_3$ effluent thoroughly. Pipet three 100-mL portions of each into separate 250-mL conical flasks. Add 1 drop of methyl orange indicator solution and 1 drop of phenolphthalein indicator solution to each flask. Add $HNO_3$ (1 + 9) or $NH_4OH$ (1 + 19) dropwise as required to adjust the pH into the range where the phenolphthalein indicator solution is colorless and the methyl orange indicator solution is yellow. Add 1 mL of $K_2CrO_4$ solution (50 g/L). Titrate with vigorous swirling with standard 0.1 N $AgNO_3$ standard solution until the color of the supernatant liquid changes from yellow to red-orange and persists for 30 s. Record the number of millilitres of $AgNO_3$ standard solutions used to ± 0.02 mL as $M$.

NOTE 5—Good laboratory practice would advise that a 100-mL portion of $NaNO_3$ solution be titrated as a blank to verify the purity of reagents.

## 116. Calculation

116.1 Calculate the total anion capacity in milliequivalents per wet gram as follows:

$$\frac{\text{meq total anion capacity}}{\text{wet gram}} = \frac{M \times N \times 10}{W} \quad (31)$$

where:

$M$ = average millilitres of $AgNO_3$ standard solution required for the titration in 115.5.1,
$N$ = normality of $AgNO_3$ standard solution, and
$W$ = wet grams of sample.

116.2 Calculate the solids from the weights obtained in Section 14 as follows:

$$\text{Solids content in g/g wet resin} = \frac{B}{A} \quad (32)$$

where:

$B$ = grams dry resin
$A$ = grams wet resin

Use this value to calculate total anion capacity in milliequivalents per gram dry as follows:

$$\text{milliequivalents total anion capacity per g dry resin} = \frac{\text{milliequivalents total anion per wet gram}}{\text{solids in g/g wet resin}} \quad (33)$$

116.3 If a back-washed and settled density is determined, total-anion capacity in milliequivalents per millilitre may be calculated in accordance with 71.6.

## 117. Precision and Bias

117.1 *Precision Statement*—The precision of this test practice is expected to be equivalent to that of Test Method H (Section 72). A collaborative study will be done to determine the precision of this test practice in accordance with Practice D2777 – 86.

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

## 118. Keywords

118.1 anion resins; cation resins; exchange capacity; ion exchange