



MASTER TEST METHODS

MTM 0220: TOTAL ANION EXCHANGE CAPACITY, MOISTURE HOLDING CAPACITY, AND PERCENT REGENERATION: OH form resins

Objective

To determine moisture holding capacity and the exchange capacity by weight and volume of OH form anionic exchange resins. This procedure also determines the percent regeneration, as well as the equivalent percent CO_3 , Cl, and SO_4 .

Area of Application

This procedure is applicable to strong base anion resins in the OH ionic form.

Principle

A known weight and volume of resin in the OH form is prepared as for a normal moisture holding capacity. The resin is converted to the NO_3 form, then dried. The NO_3 effluent is analyzed for OH, CO_3 , and SO_4 ions. A separate portion of resin is evaluated for Cl ions. The moisture holding capacity, the exchange capacity, and equivalent percentages are then calculated.

Equipment

Dewatering apparatus.
Source of vacuum, 40 ± 2 torr below atmospheric pressure.
Analytical balance, ± 0.001 g precision or better.
Ventilated oven, 105 ± 2 °C.
Desiccator.
Tared weighing dishes.
Fritted glass filter tube.
25 ml graduated cylinder, Kimble 20022-25 or equivalent.
100 ml volumetric flask.
1 L volumetric flask.
0.5 ml pipet
1 ml pipet.
2 ml pipet.
5 ml pipet.
10 ml pipet.
100 ml pipet.
Stopwatch.
Magnetic stirrer.
Spectrophotometer.
1 to 10 cm cell for spectrophotometer



Equipment for AgNO₃ titration.
Equipment for acid/base titration.

Reagents

Deionized water.
0.0100 N AgNO₃, standardized.
6.0 N HCl.
0.1000 N HCl, standardized.
0.06 N HCl.
8.0 N HNO₃.
0.0100 N NaCl.
0.5 N NaNO₃, neutral.
1:1 Glycerin solution.
100 mg/L Sulfate standard.
Methyl orange indicator solution.
Phenolphthalein indicator solution.
BaCl₂·2H₂O.

Master Test Method

1. Take ≈ 50 ml of OH form resin and place in 50 ml of deionized water for 30 min. Cover to prevent CO₂ adsorption.
2. Transfer resin to Buchner funnel and dewater under vacuum for 5 min by the usual procedure for MHC. See note about CO₂ adsorption.
3. Weigh out 15.0 ± 0.5 g of the dewatered sample. Record the resin weight as **W_{moist,OH}** (to nearest 0.01 g).
4. Quantitatively transfer the sample to a 25 ml graduated cylinder.
5. Cover the resin with deionized water to the 25 ml mark.
6. Shake the sample gently for 30 sec.
7. Allow the resin to settle, then tap the base of the graduated cylinder until no further settling is observed. Record the resin volume as **V_{moist,OH}** (to nearest 0.25 ml).
8. Quantitatively transfer the sample to a fritted glass filter tube.
9. Pass 1 L of neutral 0.5 N NaNO₃ through the sample at a rate of 25 ml/min. Collect exactly 1 L of effluent in a clean 1 L volumetric flask.
10. Stopper the flask and mix the contents thoroughly by inverting at least 5 times. Save the effluent for steps 15 and 31.
11. Rinse the sample with 1 L of deionized water at a rate of 25 ml/min.
12. Quantitatively transfer the resin into a tared crucible and place into a 105 ± 2°C oven for at least 12 hrs.
13. Remove the dry sample to a desiccator and let cool.
14. Reweigh to obtain dry weight of resin. Record resin weight as **W_{dry,NO3}** (to nearest 0.01 g).

OH and CO₃ Determination

15. Pipet 100 ml of the NaNO₃ effluent into a 250 ml titration beaker. Cover beaker to prevent CO₂ adsorption.



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16. Remove cover from titration beaker. Titrate with standardized 0.1000 N HCl to a double endpoint. The first endpoint is a phenolphthalein endpoint (pH≈9), the second is a methyl orange endpoint (pH≈4). Record the titration volumes as $V_{1, \text{HCl}}$, $V_{2, \text{HCl}}$ (to nearest 0.01 ml) and the HCl normality as N_{HCl} (to the nearest 0.0001 eq/L)
17. Calculate

$$\text{Eq}_{\text{OH}} \text{ (eq/kg)} = \frac{10 \times (2 \times V_{1, \text{HCl}} \text{ (ml)} - V_{2, \text{HCl}} \text{ (ml)}) \times N_{\text{HCl}} \text{ (eq/L)}}{W_{\text{moist, OH}} \text{ (g)}}$$

$$\text{Eq}_{\text{CO}_3} \text{ (eq/kg)} = \frac{10 \times 2 \times (V_{2, \text{HCl}} \text{ (ml)} - V_{1, \text{HCl}} \text{ (ml)}) \times N_{\text{HCl}} \text{ (eq/L)}}{W_{\text{moist, OH}} \text{ (g)}}$$

Cl determination, low level

18. Weigh out 10.0 ± 0.1 g of the dewatered sample. Record the resin weight as $W_{\text{moist,2 OH}}$ (to nearest 0.01 g).
19. Quantitatively transfer the sample into a titration beaker.
20. Add 75ml of deionized water.
21. Add 8 ml of 8 N HNO_3 .
22. Stir gently on magnetic stirrer for 10 min.
23. Add 1.00 ml of 0.01 N NaCl solution.
24. Titrate the sample for chloride using 0.0100 N AgNO_3 . Record the titration volume as V_{AgNO_3} (to nearest 0.01 ml) and the AgNO_3 normality as N_{AgNO_3} (to nearest 0.0001 eq/L).
25. Add 75ml of deionized water to a separate titration beaker.
26. Add 8 ml of 8 N HNO_3 .
27. Stir gently on magnetic stirrer for 10 min.
28. Add 1.00 ml of 0.01 N NaCl solution.
29. Titrate the blank for chloride using 0.0100 N AgNO_3 . Record the titration volume as $V_{\text{Blank, AgNO}_3}$ (to nearest 0.01 ml).
30. Calculate

$$\text{Eq}_{\text{Cl}} \text{ (eq/kg)} = \frac{(V_{\text{AgNO}_3} \text{ (ml)} - V_{\text{Blank, AgNO}_3} \text{ (ml)}) \times N_{\text{AgNO}_3} \text{ (eq/L)}}{W_{\text{moist,2 OH}} \text{ (g)}}$$

SO₄ Determination, low level

31. Pipet 100 ml of the NaNO_3 effluent into a beaker.
32. Pipet 5 ml of 100 mg/L SO_4^{2-} standard into the beaker.
33. Add 1 drop of phenolphthalein indicator solution. Neutralize to a clear endpoint using 6 N HCl.
34. Pipet 5 ml of 0.06 N HCl solution into the beaker.
35. Pipet 10 ml of a 1:1 glycerin solution into the beaker.



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36. Add 0.3 g BaCl₂·2H₂O to the beaker. Start timer. Stir the mixture with a glass stirring rod for 1 min. Wait 4 min, then stir for an additional 15 s. THIS STEP MUST BE DONE IN A HOOD.
37. Allow turbidity to develop for 30 min total.
38. Measure the absorbance of the sample solution in a 1 to 10 cm cell at 420 nm using a spectrophotometer. The spectrophotometer should read zero absorbance for deionized water. Record the absorbance as **A_{Sample}** (to nearest 0.001).
39. Use the appropriate calibration curve to determine the sulfate concentration. Record concentration as **C_{Sample, SO4}** (to nearest 0.1 mg/L).
40. Pipet 100 ml of the NaNO₃ influent into a beaker as a blank.
41. Pipet 5 ml of 100 ppm SO₄²⁻ standard into the beaker.
42. Add 1 drop of phenolphthalein indicator solution. Neutralize to a clear endpoint using 6 N HCl.
43. Pipet 5 ml of 0.06 N HCl solution into the beaker.
44. Pipet 10 ml of a 1:1 glycerin solution into the beaker.
45. Add 0.3 g BaCl₂·2H₂O to the beaker. Start timer. Stir the mixture with a glass stirring rod for 1 min. Wait 4 min, then stir for an additional 15 s. THIS STEP MUST BE DONE IN A HOOD.
46. Allow turbidity to develop for 30 min total.
47. Measure the absorbance of the blank solution using the spectrophotometer, with the same size cell and conditions as in step 38. The spectrophotometer should read zero absorbance for deionized water. Record the absorbance as **A_{Blank}** (to nearest 0.001).
48. Use the appropriate calibration curve to determine the sulfate concentration. Record concentration as **C_{Blank, SO4}** (to nearest 0.1 mg/L).
49. Calculate

$$Eq_{SO4} \text{ (eq/kg)} = \frac{C_{\text{Sample, SO4}} \text{ (mg/L)} - C_{\text{Blank, SO4}} \text{ (mg/L)}}{48.0 \text{ (g/eq)} \times W_{\text{moist, OH}} \text{ (g)}}$$

Final Calculations

50. Calculate

$$Cap_{\text{-moist, OH}} \text{ (eq/kg)} = Eq_{OH} \text{ (eq/kg)} + Eq_{CO3} \text{ (eq/kg)} + Eq_{Cl} \text{ (eq/kg)} + Eq_{SO4} \text{ (eq/kg)}$$

$$W_{\text{dry, OH}} \text{ (g)} = W_{\text{dry, NO3}} \text{ (g)} - \{ 0.045 \text{ (kg/eq)} \times Eq_{OH} \text{ (eq/kg)} \\ + 0.032 \text{ (kg/eq)} \times Eq_{CO3} \text{ (eq/kg)} \\ + 0.027 \text{ (kg/eq)} \times Eq_{Cl} \text{ (eq/kg)} \\ + 0.014 \text{ (kg/eq)} \times Eq_{SO4} \text{ (eq/kg)} \} \times W_{\text{moist, OH}} \text{ (g)}$$

$$MHC_{OH} \text{ (%) } = 100 \times (1 - W_{\text{dry, OH}} \text{ (g)} / W_{\text{moist, OH}} \text{ (g)})$$

$$Wt.Cap_{\text{-OH}} \text{ (eq/kg)} = Cap_{\text{-moist, OH}} \text{ (eq/kg)} / (1 - MHC_{OH} \text{ (%) } / 100)$$

$$Vol.Cap_{\text{-OH}} \text{ (eq/L)} = Cap_{\text{-moist, OH}} \text{ (eq/kg)} \times W_{\text{moist, OH}} \text{ (g)} / V_{\text{moist, OH}} \text{ (ml)}$$



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$$\text{Percent OH (\%)} = 100 \times \text{Eq}_{\text{OH}} (\text{eq/kg}) / \text{Cap}_{\text{moist, OH}} (\text{eq/kg})$$

$$\text{Percent CO}_3 (\%) = 100 \times \text{Eq}_{\text{CO}_3} (\text{eq/kg}) / \text{Cap}_{\text{moist, OH}} (\text{eq/kg})$$

$$\text{Percent Cl (\%)} = 100 \times \text{Eq}_{\text{Cl}} (\text{eq/kg}) / \text{Cap}_{\text{moist, OH}} (\text{eq/kg})$$

$$\text{Percent SO}_4 (\%) = 100 \times \text{Eq}_{\text{SO}_4} (\text{eq/kg}) / \text{Cap}_{\text{moist, OH}} (\text{eq/kg})$$

$$\text{Exchangeable Cl (mg/kg wet)} = 35500 (\text{mg/eq}) \times \text{Eq}_{\text{Cl}} (\text{eq/kg})$$

$$\text{Exchangeable SO}_4 (\text{mg/kg wet}) = 48000 (\text{mg/eq}) \times \text{Eq}_{\text{SO}_4} (\text{eq/kg})$$

51. Report MHC results to 1 decimal place, i.e., 60.0%.
52. Report capacity results to 2 decimal places, i.e., 4.00 eq/kg or 1.20 eq/L.
53. Report percentage for OH to 1 decimal place, i.e., 95.0%.
54. Report percentage for other ions to 1 decimal place, i.e., 0.5%
55. Report Exchangeable Cl or SO_4^{2-} to 0 decimal places, i.e., 100 mg/kg.

Notes

1. This test is run on new ion exchange resins "as received." New resins receive no pretreatment.
2. The preferred procedure assumes that the only anions on the resin are OH, HCO_3^- , CO_3^{2-} , Cl, and SO_4^{2-} . Samples returned from the field should be evaluated for other anions.
3. Precautions must be taken to prevent CO_2 adsorption by the resin sample. The sample must be kept in a closed container.
4. Precautions must be taken to prevent CO_2 adsorption when dewatering the sample. Options include N_2 instead of air, CO_2 removal tubes containing soda-lime, or a caustic solution instead of water in the humidifying tower.
5. Precautions must be taken to prevent CO_2 adsorption by the NaNO_3 effluent solution. The volumetric flask must be kept stoppered. Once the solution is pipetted into the titration beaker, the titration must be performed immediately.
6. The procedures for low level chloride and sulfate removal are extremely sensitive to contamination. Undue contamination can be minimized by the use of reagent grade chemicals. It is recommended that glassware be dedicated to each procedure. Glassware should be rinsed with dilute nitric acid and deionized water prior to use.
7. The Cl titration should be done potentiometrically. Because of the very low chloride levels, 1 ml of 0.01 N NaCl is added to enhance the ability to detect the Cl endpoint. A pH electrode should not be installed for this titration (the KCl filling solution may cause irregular results).
8. The sulfate procedure must be calibrated. Reference standards are prepared by diluting to volume in 100 ml volumetric flasks the following volumes of 100 mg/L sulfate standard, using 0.5 N NaNO_3 : 0, 0.5, 1, 2, 3, 4, 5, and 10 ml. These reference standards will have concentrations of 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 mg/L. Transfer the entire contents into a beaker. Follow the procedures in steps 32 through 38 for each standard to make the calibration curve.



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9. The turbidimetric determination of SO_4^{2-} is nonlinear at extremely low levels. The method adds a small amount of SO_4^{2-} to get out of this nonlinear regime. The determination is sensitive enough to detect the trace amounts of SO_4^{2-} in reagent grade NaNO_3 . Consequently, a reagent blank must be run with the samples.

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