Standard Operating Procedure

(SOP)

Anion Exchange Membrane

Ion Exchange Capacity

Test ID LTE-P-7

Rev 3

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation
02/28/2020	All	Initial Release
02/16/2021	6 - 7	Added instructions for IEC if automatic titrator is not available
02/12/2024	3 - 10	Protocol revision; updated Table of Contents; added alternative equipment choice; added detailed step by step procedure after operation; added detail from Front. Energy Res. protocol (2022); replaced the alternative titration method; updated the list of chemicals

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3. Procedures

a. Scope and Applicability – The purpose of this SOP is to describe the method for measuring the ion exchange capacity (IEC) of an anion exchange membrane (AEM). The membrane sample must be in dry solid-state form with a mass greater than 50 mg.

b. Summary of Method – An AEM sample (50–100 mg) in hydroxide, bicarbonate, chloride or bromide form is exchanged to the bromide form by soaking in a 4 M KBr solution with 0.02 M KOH (15–40 mL). After each exchange, the sample is rinsed in DI water (50–100 mL), and the procedure is repeated three times (up to 10 times for iodide). The small amount of KOH is added to ensure that any residual primary, secondary, and tertiary amines in the sample are not protonated and do not contribute to the measured IEC. Based on the relative affinity of bromide and hydroxide ions, the error caused by the exchange of hydroxide for bromide in the membrane is <0.1%. The membrane is then rinsed with DI water until the conductivity of the rinsate is within 10% of that of DI water. The dry weight of the membrane sample in the bromide form is obtained. The AEM sample is exchanged with 20 mL of 1 M KNO_3 solution twice for 24 h each with agitation. The exchange solutions are combined and several drops of 2% HNO_3 (~1 mL) are added to adjust the pH to *ca.* 3-4. The Hanna HI901 automatic titrator is used for titration with a 0.02 N $AgNO_3$ solution. A silver/sulfide combination ion selective electrode (HI4115) is used to monitor the progress of titration. For membranes with stability concerns when fully dry, the dry mass in nitrate form can be measured after the ion exchanges.

c. Definitions – Ion exchange capacity (IEC); anion exchange membrane (AEM), potassium bromide (KBr); deionized (DI); silver nitrate ($AgNO_3$), potassium nitrate (KNO_3), potassium hydroxide (KOH); nitric acid (HNO_3).

d. Health & Safety Warning – All solutions should be handled with care, using appropriate PPE. The operator should review the safety data sheets for the chemicals involved, specially the one of nitric acid. The membrane should never be handled without gloves, as the chloride ions in the sweat can interfere with the measurement. Additionally, the silver nitrate standard solution should be kept away from light, as it will hydrolyze and affect the measurement. Discard if you see brown deposits of silver oxide.

e. Cautions – Clean equipment after each use. Solutions used are not generally corrosive to the system, but they should still be removed immediately after experiment for best practices. Keep silver nitrate in an amber bottle, as it is light sensitive. The titration needs to be conducted in slightly acid conditions to avoid the formation of silver oxides. Never touch the membrane with bare hands, as it will lead to interfering ions.

f. Interferences

- Incomplete ion exchange—May lead to lower IEC value when non-halide anions are left in the AEM sample.
- Insufficient DI water rinse—Leads to higher IEC value when extra Br^- is left in AEM sample.

- Inaccurate membrane weight—Leads to lower IEC value due to falsely high membrane weight with extra water.
- Degraded $AgNO_3$ standard solution—Leads to higher IEC value due to extra volume needed with lower Ag^- concentration. $AgNO_3$ decomposes when exposed to light.
- Faulty sensor—Unable to determine the titration endpoint due to malfunctional sensor.
- Unprimed burette—Leads to lower IEC value due to air trapped inside the burette or pumping line.
- Violent stirring—Leads to lower IEC value due to analyte loss from splash.
- Poor lab hygiene—Leads to lower IEC value from $AgNO_3$ residue or higher IEC value from Br^- residue due to lack of clean up after experiments. Contact of the membrane with bare hands introduces chloride ions from the sweat.

g. Personnel Qualifications / Responsibilities – Operators should have basic laboratory knowledge on titration processes and should be trained on the operations of the Hanna HI901 potentiometric titrator and accompanying software before performing this experiment.

h. Equipment and Supplies – KBr, DI water, $AgNO_3$, KNO_3, HNO_3, KOH, a titrator paired with a silver/sulfide ion selective electrode, *e.g.,* Hanna HI901 with HI4115, Thermo Scientific™ Orion Star T910 pH Titrator and Kits with Orion™ Silver/Sulfide Electrode 9416BN, Mettler Toledo T90 Autotitrator with Silver Ring Electrode DM141-SC, or other equivalent instrument.

i. Step by Step Procedure (Hanna HI901 Automatic Titrator):

1. Ion-exchange to Br^- Form
    1. Exchange the counteranion of the AEM sample (50 ± 10 mg is recommended) by soaking in ~15 mL 4 M KBr + 0.02 M KOH solution in a 20 mL glass vial then rinse with ~50 mL of DI water for 30 min for each soaking. This can be done on a shaker table or gentle stirring at room temperature repeated three times with fresh solutions. Soak the membrane in ~15 mL 4 M KBr + 0.02 M KOH solution overnight after the last rinsing. For anion-exchange resins or thicker AEM (≥100 µm), longer soaking time (3 h), vigorous shaking, elevated temperature (50 °C), and extra exchange times (10 times) are recommended to prevent incomplete ion-exchange.
    2. Rinse the membrane with DI water and completely immersed in DI water at room temperature for 30 minutes in a vial while placing it again on a shaker table or gentle stirring. Repeat three times with fresh DI water until the conductivity of the rinsate is comparable to DI water.

2. Dry weight measurement
    1. Dry the membrane sample completely for 24 h. For anion-exchange resins or thicker AEM (≥ 100 µm), drying at an elevated temperature (80

°C) is recommended. Obtain the dry mass of the membrane sample using an analytical balance with a resolution of 0.1 mg. The weight measurement should be made promptly after removing the sample from the oven, as the membrane will absorb water from the atmosphere. The membrane does not need to be kept dry after weight measurement.
2. Alternatively, the bromide form membrane can be also dried in a sealed vial with an inlet/outlet of dry nitrogen flow overnight at room temperature. After removing the nitrogen flow and resealing, the vial with the sample inside it was transferred to the analytical balance. The sample dry weight measurement should be completed promptly within 5 min.

3. Sample pre-treatment
    1. Exchange the AEM sample with 20 mL 1 M KNO_3 for 24 h on a shaker table or gentle stirring at room temperature. Decant and save the solution. Rinse the vial and membrane once with a small amount of DI water (~2 mL) and add to the saved solution. Next, add 20 mL of 1 M KNO_3 and exchange a second time for another 24 h at room temperature. Decant the solution and add to the sample cup (250 mL beaker). Rinse twice with ~2 mL DI water and add to the sample cup. Add the saved solution from the first exchange to the sample cup and rinse the container.
    2. Prepare Hanna HI901 charged with a 0.02 N $AgNO_3$ solution to titrate the rinse solution (**Fig. 1**). The $AgNO_3$ solution must be kept in a dark or amber bottle. Verify the expiration date of this analytical standard. The sensor HI4115 must be charged with enough 1 M KNO_3 so that electrode solution is above ceramic junction. In the case of low electrode solution, 1 M KNO_3 standard solution should be purchased and filled.

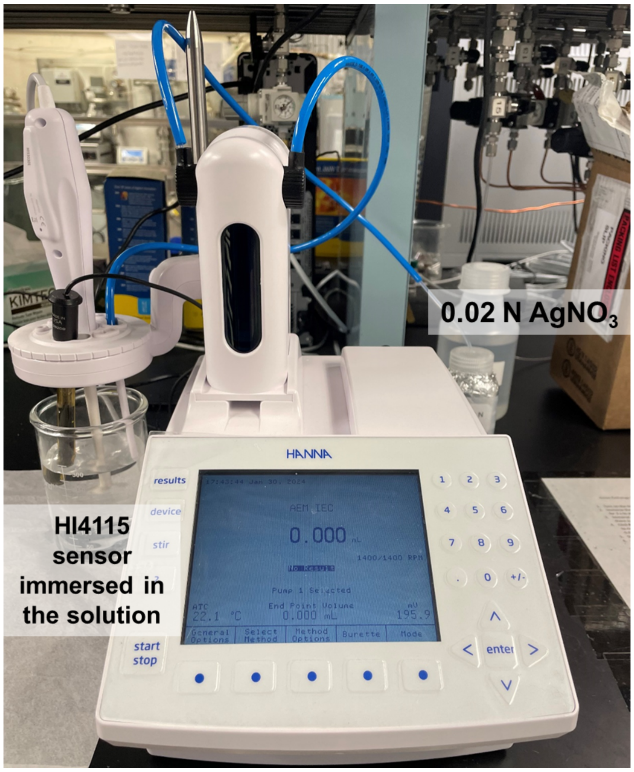

Figure 1. Hanna HI901 setup for IEC titration.

3. The Burette tip of Hanna HI901 must be primed three times through dispensing increasingly smaller amounts of titrant into waste solution until it can reliably dispense the smallest solution increment.
4. Add about 1 mL of 2% HNO_3 to tune the pH to *ca.* 3–4 required to ensure silver ions are completely immersed in the solution (**Fig. 2**). Adjust the beaker position and solution level with DI water so that all the electrodes are fully immersed.

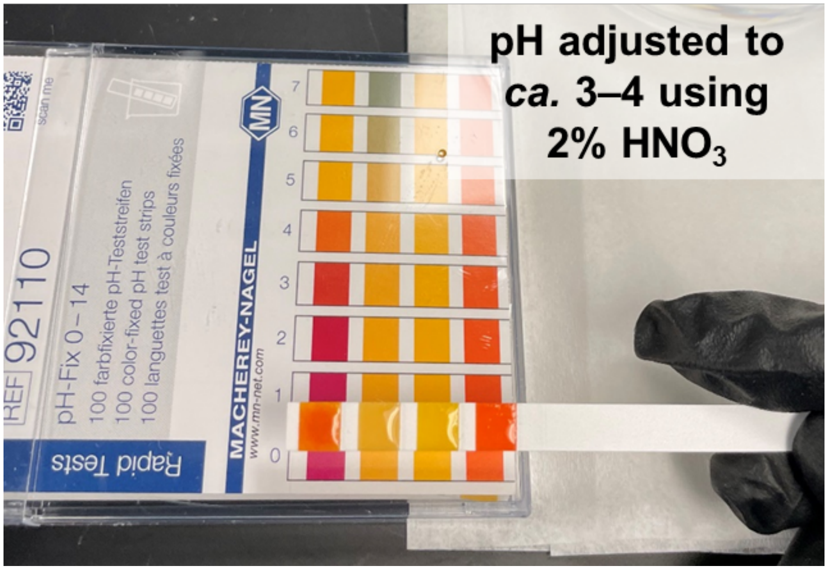

Figure 2. pH adjustment using 2% HNO_3.

4. Potentiometric titration
    1. Select the IEC titration program on the auto-titrator. Enter the mass of the AEM sample into the software to start the titration with 0.05 mL of 0.02 N $AgNO_3$ per increment.
    2. Stir the solution continuously and titrate automatically with sensor HI4115 recording the potential of the silver ion selective electrode, which is determined by the solubility product of silver bromide and the remaining free bromide concentration (**Fig. 3**).
    3. Upon the completion of the titration, collect the displayed IEC, potential, and volume dispensed results.
    4. Remove the sample cup and rinse the stir bar with DI water. Clean the sensor HI4115 by dabbing with KimWipes that has been wetted with DI water.
    5. The measured volume will be displayed on the auto titrator screen at the end of the titration. Calculations of IEC are performed by finding the maximum of the first derivative of the measured Ag ISE potential over volume (**Fig. 4**). This gives the equivalence point of the titration. The IEC value can be calculated with Equation [1]. The IEC in bromide form is determined as follows (meq/g):

$$IEC_{Br^-} = \frac{V_{AgNO_3} \times \ C_{AgNO_3}}{m_{dry}} = \frac{5.72\ (mL) \times 0.02\ (meq/mL)}{0.0602 (g)}$$

$$= 1.90\ (meq/g) \qquad [1]$$

where V_{AgNO3} is the titrated volume of $AgNO_3$ titrant (mL);
C_{AgNO3} is the normality of $AgNO_3$ (mmol/mL or meq/mL);
and m_{dry} is the weight of dry AEM sample (g).

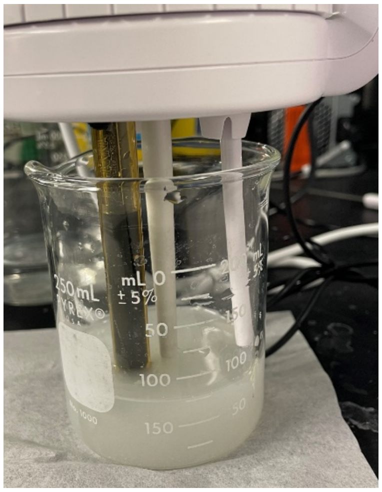

Figure 3. The solution with AgBr precipitate after completion of the titration.

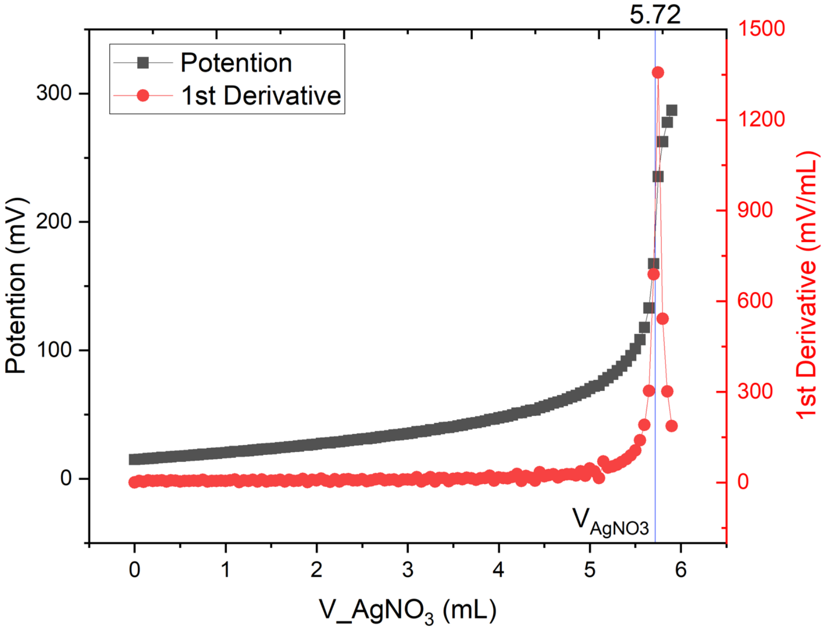

Figure 4. Titration curve and first derivative of potential over volume.

- Instrument or Method Calibration and Standardization – Hanna HI901 calibration check should be performed before experiments. This calibration is performed by dispensing a bromide standard solution into a sample cup at a known volume (*e.g.,* 2 mL, 10 mL), and running the IEC test. IEC test results should show the consumption matches the volume dispensed and the IEC is measured within 2% of the bromide standard concentration. Additionally, the IEC of each AEM should be measured in triplicate for verification, as well as having a sample weight of ~50 mg to minimize error.

- Sample Collection –

Bromide exchange	20 mL glass vial containing 15 mL of a 4 M KBr + 0.02 M KOH solution (repeated 3 times with fresh solution)
DI water washing	20 mL glass vial containing 10 mL of DI water
Sample	50 mg sample recommended
Ion exchange	20 mL glass vial, 1 M KNO_3 solution (repeated twice)
Sample Cup	250 mL beaker
Sensor	HI4115 (included with the Hanna HI901 analyzer)
Sensor solution	1 M KNO_3 solution
Titrant	0.02 N $AgNO_3$ solution, ~ 5 mL:

- Sample Handling and Preservation – Before and after experiment, AEM samples should be stored in clean sample bags.

- Sample Preparation and Analysis – A sample greater than 50 mg should be anion exchanged with KBr, washed with DI water, and dried overnight.

- Troubleshooting – instrument calibration is necessary to ensure accuracy of results. Excess bromide ions from insufficient washing with DI water (step 2) can result in reporting higher IEC values.

- Data Acquisition, Calculations & Data Reduction Requirements – calculations of IEC are performed by finding the maximum of the first derivative of the measured Ag ISE potential over volume. This gives the equivalence point of the titration.

- Computer Hardware & Software – Origin or an equivalent program can be used to find the maximum of the first derivative of the measured Ag ISE potential over volume. Data files can be moved to this computer from the Hanna HI901 using a thumb drive.

j. Alternative Step by Step Procedure (Mohr Titration Method)

- If an automated titrator is unavailable, the following method can be used:

1. The IECs of AEMs in chloride form will be determined by the Mohr titration method. Prepare AEM in chloride form with a weight of ~50 mg. (If the AEM is not in chloride form, immerse the AEM in 1 M NaCl solution and place on the shaker table or gentle stirring for 2 days. Wash AEM with DI water several times.)
2. The AEM sample is exchanged with 20 mL 0.5 M $NaNO_3$ for 2 days with agitation at 100 rpm and at room temperature. Decant and save the solution to the sample cup (250 mL beaker). Rinse the vial and membrane once with 10 mL DI water and add to the saved solution. Repeat the exchange with 0.5 M $NaNO_3$ with fresh solution two more times.
3. The solution is continuously stirred on a stir plate. Using the glass pipet and bulb, place a few drops of K_2CrO_4 indicator into solution until the solution is yellow. Draw up to 0.8 mL of 0.1 M $AgNO_3$ solution into the 1 mL pipet and start titrating the solution. Make sure the plunger of the pipet is not in the $AgNO_3$ solution and to always stop titrating at the zero line. Redraw 0.8 mL of 0.1 M $AgNO_3$ until the titrated solution turns to a peach-orange color. Record the amount of $AgNO_3$ used to titrate.
4. The volume used to titrate the sample solution is used for calculating the IEC (see equation [2]):

$$IEC_{Cl^-} = \frac{V_{AgNO_3} \times C_{AgNO_3}}{m_{dry}} = \frac{2.4\ (mL) \times 0.1\ (meq/mL)}{0.1024\ (g)}$$

$$= 2.34\ (meq/g) \qquad [2]$$

where IEC_{Cl^-} is the chloride ion-exchange capacity (mmol g^{-1}); V_{AgNO3} is the volume of 0.1 M $AgNO_3$ used to titrate the control sample (mL); C_{AgNO3} is the normality of $AgNO_3$ used (meq mL^{-1} or mmol mL^{-1}); and m_{dry} is the dry weight of the AEM (g).

k. Data and Records Management – Calculation of IEC should be recorded elsewhere both electronically and in a lab notebook by the user.

4. Quality Control and Quality Assurance

Hanna HI901 calibration check should be performed before experiments. This calibration is performed by dispensing bromide standard solution into a sample cup at a known volume (*e.g.,* 2 mL, 10 mL), and running the IEC test. IEC test results should show the consumption matches the volume dispensed and the IEC should match the bromide standard concentration within 2%. Additionally, IEC of each AEM should be measured in duplicate for verification, as well as having a sample weight of ~50 mg to minimize error.

Grade II or ASTM Type II DI water (conductivity ≤1 µS/cm) is required in all the processes.

5. Reference

Standard Operating Protocol for Ion-Exchange Capacity of Anion Exchange Membranes. Front. Energy Res. 10:887893. doi: 10.3389/fenrg.2022.887893

6. Required Chemicals

a. Hanna HI901 Automatic Titrator

- Potassium Bromide (KBr)
  ReagentPlus®, ≥99.0% Sigma Aldrich (P9881)
  ACS reagent, ≥99.0% Sigma Aldrich (243418) Deionized (DI)
  Type 1 Ultrapure Water (Thermo Scientific Smart2Pure 12 UV)
- Silver Nitrate ($AgNO_3$)
  ReagentPlus®, ≥99.0% Sigma Aldrich (S6506)
  ACS reagent, ≥99.0% Sigma Aldrich (209139)
- Potassium Nitrate (KNO_3)
  for analysis ≥99.0%, Acros Organics (AC205915000)
  ACS reagent ≥99.0% Sigma Aldrich (221295)
- Potassium Hydroxide (KOH)
  Pellets, 85%, thermoscientific (A18854.0E)
  Semiconductor grade, pellets, 99.99% trace metals basis (Purity excludes sodium content.) Sigma Aldrich (306568)
- Nitric Acid (HNO_3)

ACS reagent, 70% Sigma Aldrich (438073)

b. Mohr Titration Method
    - Sodium Chloride (NaCl)
      ≥99.0% ACS, VWR Chemicals BDH® (BDH9286)
      https://us.vwr.com/store/product/9902221/sodium-chloride-99-0-
      ReagentPlus®, ≥99.0% Sigma Aldrich (P9881)
    - Sodium Nitrate (NaNO3)
      98+%, Alfa Aesar (A12327)
    - Potassium Chromate (K_2CrO_4)
      5% (w/v) in aqueous solution indicator, VWR Chemicals BDH® (BDH7350)