

Standard Operating Procedure (SOP)

Anion Exchange Membrane Ion Exchange Capacity

Test ID LTE-P-7

Rev 2

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02/28/2020

Date

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Date: 02/16/2021

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

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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, in the chloride anion form, and have a mass greater than 50 mg.

b. Summary of Method – An AEM sample in bicarbonate or chloride form is exchanged to the bromide form by soaking in a 4 M KBr solution with 0.02 M KOH. The small amount of KOH is added to ensure that any 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 is obtained. The AEM sample is exchanged with 20 mL of 1 M KNO₃ solution twice for 1 day each with agitation. The exchange solutions are combined and several drops of 2% HNO₃ are added to adjust the pH to ca. 3-4. The Hanna HI901 automatic titrator is used for titration with a 0.02N AgNO₃ solution. A silver/sulfide combination ion selective electrode (HI 4115) is used to monitor the 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 (AgNO₃), potassium nitrate (KNO₃), potassium hydroxide (KOH); nitric acid (HNO₃).

d. Health & Safety Warning – procedure is generally safe, but all solutions should be handled with care, using appropriate PPE. The person running the measurement should review the safety data sheets for the chemicals involved, specially the one of nitric acid.

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 – instrument calibration is necessary to ensure accuracy of results. Excess bromide ions from insufficient washing with DI water (step 2) can result in falsely high IEC. Any contaminant anions that form insoluble silver salts will cause interference. If exchanging from iodide form, additional exchanges will be necessary due to the high affinity of AEMs for iodide.

g. Personnel Qualifications / Responsibilities – users should have basic laboratory knowledge and skills and should be led through operations of the Hanna HI901 and accompanying software before performing this experiment.

h. Equipment and Supplies – KBR, DI water, Hanna HI901, AgNO_3 , KNO_3 , HNO_3 , KOH, sensor HI 4115.

i. Step by Step Procedure:

1. The AEM sample, originally in bicarbonate or chloride form, is exchanged to the bromide form by soaking in ~10 mL 4 M KBr + 0.02 M KOH solution in a 20 mL glass vial for 24 hours. This is completed on a shaker table at room temperature and repeated a total of two times with fresh solutions.
2. The membrane is then rinsed with DI water and completely immersed in DI water at room temperature for 30 minutes in sealed 20 mL scintillation vial. This is repeated at least 3 times with fresh DI water until the conductivity of the rinsate is comparable to DI water (within 10%).
3. The membrane sample is dried overnight at 60°C on a glass vial using a convection oven. The dry mass of the membrane sample is obtained using an analytical balance with a resolution of 0.1 mg. 50 mg sample weight is recommended. The weight measurement should be made promptly after removing the sample from the oven, as the membrane will absorb water from the atmosphere.
4. The AEM sample is exchanged with 20 mL 1 M KNO_3 for 1 day with agitation at 100 rpm and at room temperature.
5. Decant and save the solution. Rinse the vial and membrane once with 1-2 mL DI water and add to the saved solution. Then 20 mL of 1 M KNO_3 and exchange a second time for 1 day with agitation at room temperature.
6. Decant the solution and add to the sample cup (50-100 mL beaker or vial). 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.
7. A Hanna HI901 charged with a 0.02N AgNO_3 solution is used to titrate the rinse solution contained within the centrifuge tube. The AgNO_3 solution must be kept in a dark or amber bottle. Verify the expiration date of this analytical standard.
8. The sample cup must be stirred while titrating. The HI901 has a built-in impeller, but for small-volume sample cups, a magnetic stir bar can be used.
9. The sensor HI 4115 must be charged with enough 1M KNO_3 so that electrode solution is above ceramic junction.

10. The Burette tip of Hanna HI901 must be primed through dispensing increasingly smaller amounts of titrant into waste solution until it can reliably dispense the smallest solution increment.
 11. The mass of the AEM sample is entered into the software and the titration begins.
 12. Solution is continuously stirred and automatically titrated with sensor HI 4115 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.
 13. IEC, potential, and volume dispensed results are displayed.
 14. Sample cup is removed and stir bar is rinsed with DI water. Sensor HI 4115 should also be cleaned by dabbing with a Kimwipe that has been wetted with DI water.
- 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.

- Sample Collection –

Bromide exchange	20 mL glass vial containing 10 mL of a 4 m KBr 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, 1M KNO ₃ solution
Sample Cup	50 mL polypropylene centrifuge tube
Sensor	HI 4115(included with the Hanna HI901 analyzer)
Sensor solution	1M KNO ₃ solution
Titrant	0.02N 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 of >50 mg should be anion exchanged with KBr, washed with DI water, and dried overnight. If an automated titrator is unavailable, the following method can be used:

Ion exchange capacity

The IECs of membranes in chloride form will be determined by the Volhard titration method. (Arges, Parrondo et al. 2012) A vacuum dried AEM in the chloride form (dried at < 0.1 in Hg at 60 °C for 12 hours) is weighed (about 0.1 g) and immersed in 20 mL of 1 M sodium nitrate for 48 h at room temperature. Subsequent, 5.0 mL of 0.1 M silver nitrate are added to precipitate the chloride ions. An excess of silver is added to assure the complete precipitation of the chloride.

Then, 2-3 drops of 11 wt.% iron (III) nitrate dissolved in DI water are added as indicator to detect the titration endpoint. The solution is titrated with 0.1 molar potassium thiocyanate (0.1 M KSCN, standard solution) until the color changes from a light orange to a medium-dark orange color (equivalence point). An automatic titrator with potentiometric end-point detection can also be used to automate the titration.

A control sample prepared by mixing 20 mL of 1 M NaNO₃ with 5.0 mL of 0.1 M AgNO₃ and 2-3 drops of 11wt% of Fe(NO₃)₃ is also titrated with 0.1 M KSCN. The difference in volume used to titrate the control solution and the sample solution is used for calculating the IEC (see equation [1]):

$$\left[\begin{aligned} IEC_{Cl^-} [\text{mmol g}^{-1}] &= \frac{(\text{Vol}_{\text{cont.}} - \text{Vol}_{\text{test}}) \cdot 100 \text{ mM KSCN}}{W_{\text{dry}}} \\ IEC_{Cl^-} [\text{mmol g}^{-1}] &= \frac{(V_{\text{ctrl}} - V_{\text{test}}) \times 0.1 \text{ M KSCN}}{W_{\text{dry}}} \end{aligned} \right] \quad [1]$$

Where, IEC_{Cl^-} is the chloride ion-exchange capacity (mmol g⁻¹); V_{ctrl} is the volume of 0.1 M KSCN used to titrate the control sample (mL); V_{test} is the volume of 0.1 M KSCN used to titrate the sample (mL); and W_{dry} is the dry weight of the AEM (g).

- 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. 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 Section

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.

5. Reference Section

Not applicable for this SOP.