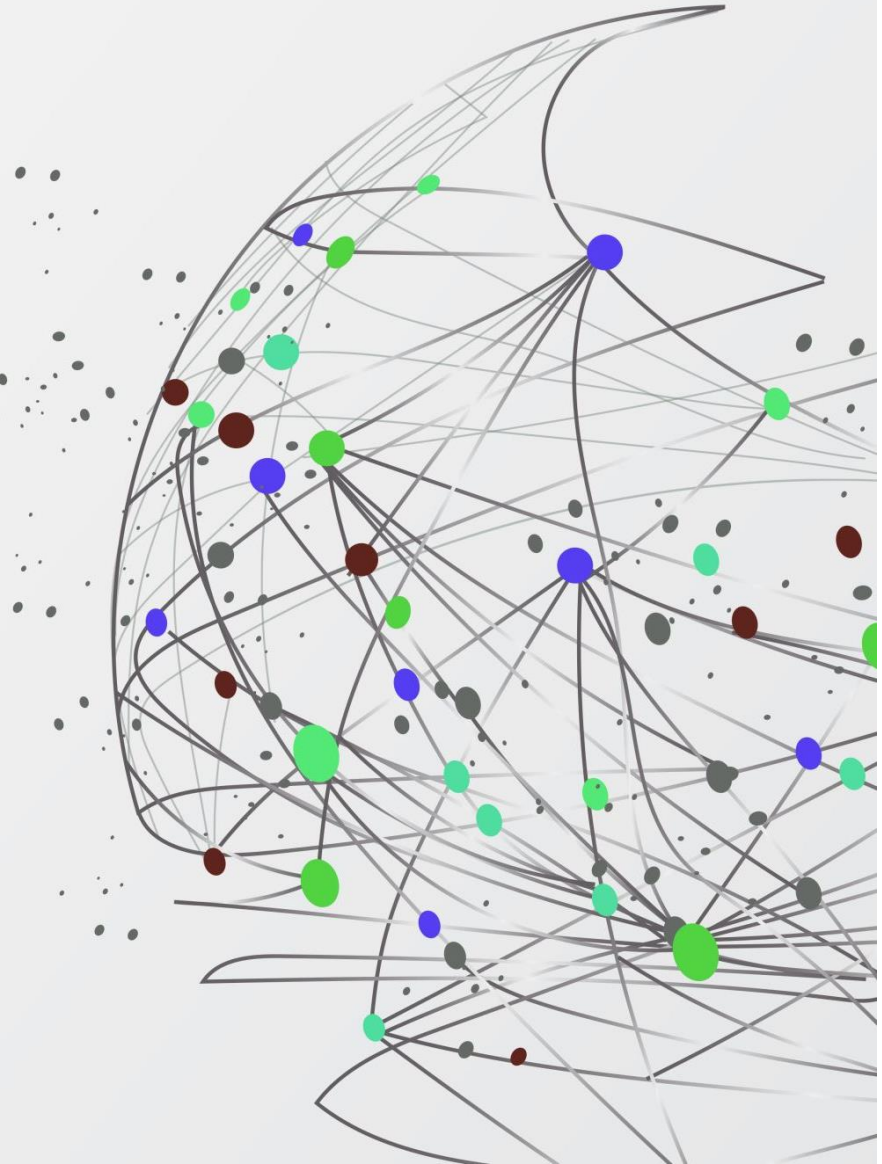


Ammonia Ion Selective Electrode Troubleshooting

Addressing Drift Issues in Ammonia Measurement

Tiffany Ishaya

Silicon Valley Clean Water

August 13th, 2024

Equipment

- **Meter**: Thermo Orion #2 VersaStar Ammonia Meter
- **Electrode**: High Performance Ammonia Ion Selective Electrode (ISE)
  Cat #: 9512HPBNWP
- **Membrane**: Pre-Assembled Membrane for Ammonia ISE
  Cat#: 951215

Quality Control

- Four-point calibration prepared using an ammonium chloride 1,000 mg/L standard from Ricca. (Note: The calibration should be five-point.)
  - 1 mg/L, 10 mg/L, 50 mg/L and 100 mg/L
- Calibration Curve Relative Standard Error Verification
- Method Blank
- Laboratory Fortified Blank prepared using an ammonium chloride 1,000 mg/L second source standard from La Mar Ka.
  - 25 mg/L
- Reporting Limit Verification = Method Detection Limit
  - 1 mg/L
- Continuous Calibration Verification (CCV)
  - 50 mg/L
- Matrix Spike/Matrix Spike Duplicate

Method: SM 4500 NH3 D-2011

Sample Matrices

- Plant Process and Regulatory Sites: Influent, Final Effluent, and everything in between.
  - Typical Concentration: 0 mg/L - 50 mg/L
  - Dilution: 4x
- Centrifuged Digester Sludge
  - Typical Concentration: 1,000 mg/L – 2,000 mg/L
  - Dilution: 100x
- Industrial Users
  - Typical Concentration: 0 mg/L – 600 mg/L
  - Dilution: Varies depending on sites and historical data

Routine Analysis Schedule

Analysis Frequency: 1 to 2 times a week

Analysis Batch Size: 8 to 10 Samples

Special Projects: Frequency could rise to 1 to 2 times per week, these projects often span over several months.

Timeline: Issues Encountered

December 2021 – June 2022

- CCV recovery failure occurred at least once per month

Note: CCV recovery failure is defined as a % recovery outside of the control limit of 90-110%.

July 2022 - Present

- Increased Calibration Curve Relative Standard Error Failures

Note: Calibration Curve Relative Standard Error Failure is defined as a % recovery outside of the control limit of 10%.

- Increased Calibration Slope outside of the acceptance range: -54mV to -60mV
- Increased CCV recovery failures
- Digester sludge analysis increased chance of failed CCV recovery

---

Identified problems likely caused by an upward drift.

Potential Causes

Membrane Damage

- Scratches or punctures can impair its function.

Membrane Contamination

- Exposure to interfering chemicals or fouling can change how the membrane responds.

Temperature Variations

- Changes in sample temperature can cause the electrode to drift.

Inadequate Electrode Conditioning

- Electrodes not properly conditioned before use can result in inconsistent readings.

Matrix Effects

- High ionic strength can affect the electrode's ability to accurately measure ammonia.

Presence of Interfering Ions

- Ions such as potassium, chlorine, or calcium.

Improper Electrode Storage

- Storing the electrode dry or under inappropriate conditions can damage the membrane and impair performance.

Troubleshooting Tips: Analysis

Use Ionic Strength Adjuster (ISA)

- Maintain consistent pH across all samples for accurate measurements.

Control Temperature

- Keep the temperature uniform for all samples and reagents to prevent reading inconsistencies.

Recondition electrode

- Use a 1 mg/L standard solution with ISA to refresh the electrode between samples.

Consistency

- Apply the same analysis procedure for all samples.

Adjust Stirring

- Set the magnetic stirrer to avoid creating a vortex, ensuring even mixing.

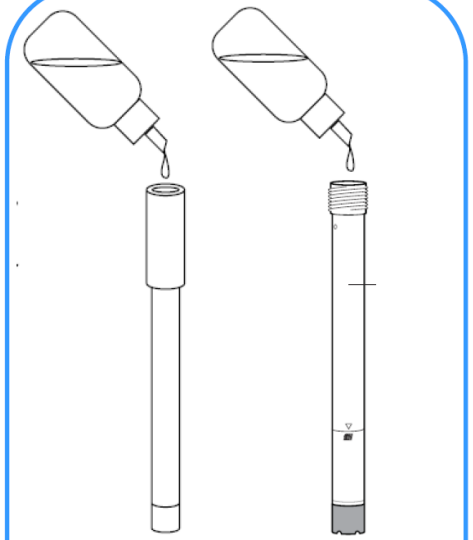
Minimize Carryover

- Rinse the electrode in a beaker of deionized (DI) water until the reading drops below 0.75 mg/L before analyzing new samples.

Troubleshooting Tips: Membrane

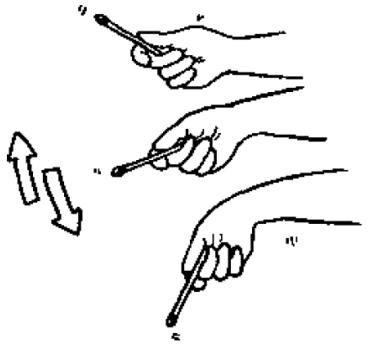
- Replace the membrane cap at least once a month.
- Avoid touching the membrane directly to prevent contamination and damage.
- Inspect the membrane regularly and use an angled electrode holder to help avoid air bubbles.

Filling the ISE

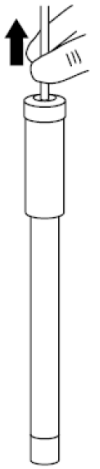


9512
2-2.5 mL
(~50 drops)

9512 HP
Fill to line



Carefully shake down, like a thermometer



Gently pull up on the cable. Soak.

Troubleshooting Tips: Calibration

- Prepare standards by serial dilution. Use only fresh standards and do not reuse.
  - Note: Ammonia content dissipates 2 minutes after adding ISA.
- Condition the electrode for 15 minutes using a 1 mg/L standard solution before calibration.
- Always use clean, Class A volumetric glassware for standard preparation.

Electrode Drift Study:

Test the electrode with a 50 mg/L standard two hours after calibration to ensure the drift is not caused by the probe.

Calibration performed two hours prior to reading:

- Measured CCV1 (prepared by serial dilution): Result = 50.97 mg/L
- Measured CCV2 (prepared by direct dilution): Result = 52.50 mg/L
- Measured CCV3 (prepared by serial dilution): Result = 53.03 mg/L
- Measured CCV4 (prepared by direct dilution): Result = 53.44 mg/L

Comments, Questions, or Suggestions?

Discussion Questions

1. What has been your experience with drift issues when using ion-selective electrodes?

2. How do you identify and mitigate matrix interferences in your samples?