Optimizing the Performance of Your Ammonia Ion Selective Electrode

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Overview

• Choosing the right electrode and meter

• Preparing your standards

• Performing the measurement

• Optimizing performance

• How to troubleshoot your procedure

• Question and answer
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Ammonia ISE: 9512 vs. 9512HP

• Standard (or Classic) 9512BNWP
  • Reliable and stable performance
  • Best performance at concentrations > 0.1 mg/L

• High Performance 9512HPBNWP
  • Better slopes & sensitivity at lowest concentrations
  • Faster response
  • The better performer when analyzing < 0.1 mg/L NH3
Choosing the right electrode

- Good news! There is not a right or wrong choice.
- If you are satisfied with your current choice, stick with it.
- If you have the standard electrode, but want faster response or better sensitivity at < 0.1 mg/L NH3, try the 9512HPBNWP.
ISE Meters

- ISE meters report concentrations
  - No manual calibration curves are required
  - The potentials of known standards are stored in memory to produce a calibration curve
  - The potential of the sample is then compared to the calibration curve to determine the concentration

- ISE meters generate sophisticated curves which are held in the meter’s memory

Direct Testing =
  1. Run standards
  2. Run unknowns
  3. Read results
Useful Features in ISE Meters

• Rugged and durable
• Large, bright screen - information at a glance
• Easy to learn and use – intuitive, user-friendly interface
• Flexible calibration options
• Ability to create and save methods
• Memory to store test data and multiple calibrations
• Ability to transfer data electronically
• Ability to update meter software
• Stirring options – mechanical stirrer
• Good warranty
Thermo Scientific Orion ISE Meters

• Versa Star pH/ISE Benchtop Meters
  • Single and dual channel systems for one or two pH, ORP or ion selective electrodes; up to four channels by adding modules
  • Large color display with adjustable text sizes and simultaneously or individual channel measurement
  • Numeric keypad for quick and simple data entry
  • Direct concentration measurement or incremental technique options

*Premium option, great for flexibility and performance*
Thermo Scientific Orion ISE Meters

- Orion Dual Star pH/ISE Benchtop Meter
  - Dual channel for two pH, ORP or ion selective electrodes
  - Flexible graphic display with backlight and simultaneously or individual channel measurement
  - Numeric keypad for quick and simple data entry
  - Direct concentration measurement or incremental technique options

Redesigned Orion Dual Star meters are shown and will be available beginning on July 28, 2015

**Advanced option, easy-to-use and dependable meter**
Thermo Scientific Orion ISE Meters

- Orion Star A214 pH/ISE Benchtop Meter
  - Single channel for one pH, ORP or ion selective electrode
  - Informative graphic display with backlight
  - Comprehensive keypad with dual purpose scroll/shortcut keys
  - Direct concentration measurement

*Basic option, economical and simplified meter*
Feedback

- What are your measurement or calibration challenges when testing for ammonia?
Overview

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Preparing Your Standards

When it comes to making standards, which image best describes you?
Serial Dilutions - Concept

Serial Dilutions: Easy and Accurate
NH3 Standards, serial dilution: step 1

1. Prepare a **100 ppm ammonia standard** by measuring 100 mL of the 1000 ppm ammonia as nitrogen (N) standard (Orion 951007) using a graduated cylinder. Add the 100 mL measured to a 1000 mL volumetric flask. Add 900 mL of distilled/deionized (DI) water, diluting to the mark indicated on the flask. Mix the solution well.

1. **Orion 1000 mg/L ammonia stock standard**

2. Dilute 1:10 to obtain a 100 mg/L standard
   a) Dilute 100 mL of 1000 mg/L to vol in 1L volumetric.
   b) Or mix 100 mL of 1000 mg/L with 900 mL DI water

3. Makes 1L (1000 mL) of 100 mg/L ammonia standard.
NH3 Standards, serial dilution: step 2

2. Prepare a 10 ppm ammonia standard by measuring 100 mL of the 100 ppm ammonia standard from Step 1 using a graduated cylinder. Add the 100 mL measured into a 1000 mL volumetric flask. Add 900 mL DI water, diluting to the mark indicated on the flask. Mix the solution well.

1. Orion 100 mg/L ammonia standard – from step 1
2. Dilute 1:10 to obtain a 10 mg/L standard
   a) Dilute 100 mL of 100 mg/L to vol in 1L volumetric
   b) Or mix 100 mL of 100 mg/L with 900 mL DI water
3. Makes 1L (1000 mL) of 10 mg/L ammonia standard.
This App Note is available on the Thermo Scientific website (search on “ammonia standards”, choose “Resources”.

It is also available in the Online Library at thermoscientific.com/waterlibrary.
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Ammonia ISE Measurement

- Measure from 0.01 ppm to 17,000 ppm ammonia
- Also use for ammonium and organic nitrogen

- Must adjust sample pH

- The sensor is a pH electrode – it measures change in pH across the membrane

- EPA approved method for waste water – Direct method (SM 4500-NH3 D) or Known Addition method (E)

- Do pay attention to manufacturer’s instructions
Ammonia ISE – Big Picture

1. Dissolved NH3 diffuses through the membrane.
2. The pH of the fill solution (FS) changes.
3. The pH change indicates the amount of ammonia-N in the sample.
Gas Sensing Electrode: Ammonia

- Works by measuring the pH change caused by diffusion of ammonia gas through a hydrophobic but porous membrane
Ammonia and Ammonium Nitrogen

- Ammonia-N = $\text{NH}_4^+$ (aq) + $\text{NH}_3$(g)

  ammonium ion  dissolved ammonia gas
Ammonia and Ammonium Nitrogen

- Ammonia-N = $\text{NH}_4^+ \text{(aq)} + \text{NH}_3(\text{g})$

  ammonium ion  ammonia gas

$\% \text{ Ammonia vs. Ammonium} @ \sim \text{pH} > 11$

$\text{NH}_3(\text{g})$

100%
Using Ion Strength Adjustor (ISA)

1mL to 50 mL

Standards

Samples
What the ISA Does – Three Versions

• Blue ISA
  • Adjusts the pH to > pH11, converts NH₄⁺ to NH₃
  • Blue color indicates that the pH is sufficiently high
  • Raises the ionic strength to a consistent level.
  • Complexes metals – such as mercury and silver – that could interfere
  • Methanol content may help to keep the membrane clean

• Low Level Blue ISA
  • Same as above but without the metals complexing agent.
  • Formulated for very low level ammonia analysis where metals are not present
What the ISA Does – Three Versions

• Alkaline ISA
  • Adjusts the pH to > pH11, converts NH4+ to NH3
  • Raises the ionic strength to a consistent level.
  • Used at a ratio of 1:100
    • Use 0.5 mL of alkaline reagent for 50 mL of sample, or
    • Use 1 mL of alkaline reagent for 100 mL of sample
Testing Sequence – Direct Method

**Make Standards**
- Serial Dilutions

**Prepare Standards and Samples**
- Into beakers, at RT, add ISA just before test

EPA-approved method; a good method for large batches, wide range of ammonia, fast

**Analyze Samples & QC: Direct Reading**

**Calibrate and Verify**
- If good, proceed.
Direct Method Calibration

Slope -54 to -60 mV at 20-25 deg C

Consider enabling autoblank for low level testing
Testing Sequence – Known Addition

Make QC Check Standard
  • Serial Dilution

Prepare Standards and Samples
  • Into beakers, at RT, add ISA just before test

EPA-approved method; a good method for small batches, varied or challenging samples

Analyze Samples & QC: Known addition(s)
Single Known Addition (SKA)

**Step 1**
- Test sample (mV)

**Step 2**
- Add known amount of standard

**Step 3**
- Test sample + standard (mV)

**Step 4**
- Read result from meter or calculate
Single Known Addition (SKA)

How does it work?

- The meter calculates the result based on the sample reading, the sample + standard reading, and the information that we input.
- We input slope, standard concentration, volume, and sample volume.
- The meter calculates ammonia result based on the graph shown here.
Double Known Addition (DKA)

• Like SKA, but two additions of standard are made and three mV readings are taken.
  • Sample,
  • sample + standard,
  • sample + more standard
• The meter calculates the slope and the ammonia result.
• “Calibration in a beaker”
• We only input standard concentration, volumes, and sample volume.
Known Addition - SKA vs. DKA

• Single known addition (SKA)
  • Slope is determined once each day and input to the meter
  • Concentration is determined by a single increment
  • Single incremental techniques are quick and easy

• Double known addition (DKA)
  • Slope is determined automatically during each sample analysis
  • Concentration is determined by two increments
  • Greater accuracy is achieved for samples with complex matrices
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Optimizing Performance

• Electrode Maintenance and Storage
  • Be an ammonia “mechanic” – keep the ISE in tune
  • Change fill solution and membrane
  • Store in ammonia storage solution (overnight/weekends)
  • Store in standard + ISA, e.g. mid-level (between samples)
  • Rinse thoroughly with deionized or distilled (DI) water before and after each reading and before storage
  • Don’t touch the membrane
Membrane Application Video

www.youtube.com/watch?v=Sv43b8-LNcw
Inspecting the membrane

Inspect the membrane for damage, wrinkles, drum-tight surface.

In these photos, one is damaged and not smoothed tight. Another has a bit of a wrinkle. The others look good.
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.
Optimizing Performance

- Ammonia Standards
  - Do it right the first time and save yourself a lot of time
  - Stock standard - not expired.
  - Store properly – tightly closed, out of direct sunlight, at room temperature (or refrigerated)
  - Never put anything into your stock standard bottle – not even a pipet. Never pour any solution back in.
  - Use ammonia-free DI water to prepare standards and rinse glassware.
  - Make sure all glassware and containers (any contact surface) is clean before use.
Optimizing Performance

• Keep it Clean
  • Contamination can be a significant source of error.
  • Clean all labware thoroughly. 1% laboratory detergent solution is useful.
  • Rinse thoroughly with DI water.
  • Store labware away from ammonia sources.
  • Clean up spills and puddles. Spilled ammonia-containing liquids can put ammonia in the air.
  • Use a clean graduated cylinder to measure out each sample
  • Test clean samples first, proceeding to more concentrated samples after.
Optimizing Performance

• Prepare Samples Carefully (including standards)
  • Bring samples & standards to the same temperature
    • Room temperature is good. Keep all +/- 1 or 2 degrees.
    • Use an ATC or thermometer to verify and record.
  • Make sure all glassware and containers are clean before use. Don’t reuse glassware without wash/rinse.
  • Cover samples, esp. if they will be on the bench awhile
  • Be accurate:
    • Measure sample volume with graduated cylinder
    • Measure ISA with a pipet
      – Add ISA just before sample testing
    • Measure known addition volumes with a pipet.
Optimizing Performance

• Analyze Samples Consistently (including standards)
  • Add ISA just before making the measurement
  • Rinse electrodes and stirrer (and ATC) thoroughly with DI water before and after each test.
    • Best practice – avoid touching the membrane
    • If/when blotting, be careful around the membrane
  • Stir with mechanical or magnetic stirrer to mix thoroughly and speed the response.
    • Watch for temperature changes if using a magnetic stirrer
    • Stir just fast enough to avoid a vortex
  • Use an electrode holder with an angled position
  • Check for air bubbles on the membrane surface
Optimizing Performance

• Run the Standard Curve
  • Use standards in decade increments – for example, use 0.10, 1.0 and 10 mg/L standards.
  • Consider conditioning the electrode before running the standard curve.
  • Use freshly prepared standards – don’t reuse a standard that has already been tested.
  • Expect a slope of -54 to -60 mV
    • If not, check electrode operation (slope) per User Guide.
    • If Autoblank option is on, slope may be > 60 mV
  • Verify the calibration every two hours or per your SOP.
Tips for low level testing <0.10 mg/L

- Consider using the Orion HP model (9512HPBNWP).
- Try using low-level Blue ISA (951210) or Alkaline reagent (951011).
- Keep all labware and benches clean.
- Use freshly prepared DI water. Gaseous ammonia tends to contaminate water stored in the laboratory.
- Segregate low-level ammonia samples. Test first.
- Consider using the Autoblank function for improved low level results.
- Wait for complete electrode response. Don’t rush.
  - If unsure, wait +1 minute after “ready” to confirm.
- Try immersing in DI+ISA solution or pH 4 between samples.
Autoblank feature at low levels

- Useful for low levels, where ISE response becomes non-linear.
- Autoblank is like drawing a smooth curve.
- More accurate than measuring a zero standard (blank).
- If calibrate and test NH3 at < 0.1 mg/L, consider enabling the “autoblank” function in Setup.
- Meter only applies autoblank if the calibration mV indicate low-level non-linearity.
- When applied, calculated slope may be higher than typical range.
Tips to improve stability; reduce drift

• Keep your ammonia ISE in “tune” – do the maintenance.
• Pay attention to ISE storage – during testing & overnight
• Pay attention to temperature - measure it, record it
  • Electrode slope, NH3 partial pressure, sample chemistry
• Keep your technique consistent – rinsing, handling, stirring...
• Ensure the electrode is conditioned before calibration
  • e.g., place in a portion of the mid-level std for 15 min
  • e.g., overnight storage in yesterday’s mid-level std
• Use freshly prepared standards. Don’t reuse anything.
• Check for bubbles - on the membrane, inside the ISE
• Check membrane – installed properly, not damaged
• If drifting, try the cord/cable pull. Recalibrate as necessary.
Tips to improve slope

• Keep your ammonia ISE in “tune” – do the maintenance.
  • Do maintenance at the end of the shift. Let it soak overnight.
• Ensure the electrode is conditioned before calibration.
  • e.g., place in a portion of the mid-level std for 15 min
  • e.g., calibrate backwards, high to low standads
  • e.g., overnight storage in yesterday’s mid-level std
• Use freshly prepared standards. Don’t reuse anything.
• Check the electrode slope per the procedure in manual.
  • If not good, clean the pH bulb of the inner body. Try Orion 900024 or
    1M HCl soak, e.g. 30 minutes. Soak the pH glass only (not the reference
    wire).
Tips when switching to the HP model

- The membranes, the fill solution, and storage solution are different. Replace the old parts and solutions. Don’t use them on the HP.
- Do not stretch the membrane when applying. Smooth it for a drum-tight surface.
- Make sure the inner fill solution does not dry up. Ensure the fill solution always covers the entire reference wire.
- Don’t rush through the calibration. Wait for true stability. Consider analyzing the standards backwards, from high to low level.
- See Tips for low level testing for more ideas.
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Troubleshooting Ammonia - Fishbone Diagram

- **Solutions**
- **Electrode**
- **Method**
- **Conditions**
- **Samples**
- **Meter**

Ammonia test not working

Fishbone Diagram – potential sources of error in ammonia testing
Troubleshooting

• Solutions – standards, ISA, fill solution
  • Proper storage of all – purchased, prepared
  • Properly prepared standards – volumetric glassware
  • Not expired, not reused, not contaminated
  • Stored at room temperature or refrigerated
  • Water for standards is ammonia-free

• Electrode
  • In-tune:
    • properly stored, maintained, cleaned when required
  • Bubbles: check for bubbles, inside and out
  • Slope check per electrode manual - diagnostic
Electrode Slope Check

1) Put meter in mV mode. Stir.
2) Add 1 ml of 1000 mg/L (or 0.1M) ammonia standard. Read mV, e.g. 48.7 mV
3) Add 10 ml of the same standard. Read mV, e.g. -9.5 mV

Slope = 1st mV reading – 2nd mV reading.
In this case,
Slope = 48.7 – (-9.5) = 57.7 mV

100 mL DI + 2 mL Blue ISA
Troubleshooting

- **Method**
  - Follow SOP closely – training, documentation
  - Calibrate carefully and consistently
  - Monitor performance – cal verification, duplicates, spikes, control samples
  - Pay attention to rinsing, stirring, bubble elimination, electrode angle, & any other factors during testing

- **Conditions**
  - All samples and standards at room temperature
  - Consistent temperature during testing
  - Manage cross-contamination conditions
Troubleshooting

• **Samples**
  • Acidified samples – ensure pH is > 11 after adding ISA
  • Read temperature – ensure sample has reached RT
  • Analyze “dirty” and high-level samples after analysis of the “clean” and low-level samples
  • Choose the right ISA
  • Difficult samples – consider matrix-matched standards (e.g. standards in seawater) or known addition method.

• **Meter**
  • Ensure meter setup parameters have not been changed
  • Set up a pass-word protected method
  • Check calibration log – any significant changes?
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Contact Us for More Information

• Thermo Scientific Orion:
  • Technical Service (North America): 1-800-225-1480
  • Technical Service: wai.techservbev@thermofisher.com
  • Web resources: www.thermoscientific.com/water
Questions?