Selecting the Right Ammonia Method for Your Lab

Choosing between Colorimetric and Gas Sensing Ion Selective Electrode Methodologies

Introduction

Gas Sensing Ion Selective Electrodes (ISE) have been the standard for ammonia measurement in many water and wastewater laboratories. The ISE ammonia method is USEPA Approved and has a wide dyanmic range making it attractive to many labs. However, ISE technology has some significant disadvantages including: Maintenance, calibration, poor low-level performance, and replacement of the sensor system. Hach® Company gained USEPA Equivalence on a simple colorimetric ammonia method for use in wastewater based on the TNTplus™ platform.

Overview of Two Technologies

Electrochemical – EPA Approved Ammonia Gas Sensing Ion Selective Electrode (ISE)

The ammonia electrode measures ammonia gas or ammonium ions in aqueous solutions. The electrode consists of a glass pH electrode, reference electrode, and gas-permeable membrane. The gas-permeable membrane separates the sample from a thin layer of electrolyte that is pressed between the pH bulb and the membrane. At high pH, ammonium ion is converted to ammonia gas. The gas diffuses through the membrane and causes a pH change in the thin layer of electrolyte. The change in pH is proportional to the ammonia concentration in the sample.

Colorimetric – EPA Equivalent TNTplus Ammonia – Salicylate Method

Ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol. The amount of color formed is directly proportional to the ammonia in the sample. Results are read at 690 nm. The TNTplus barcode communicates with the TNTplus-compatible spectrophotometer and displays the concentration of ammonia in the sample.

Now, many laboratory managers find themselves asking some basic questions:

- Has the TNTplus technology been proven in my type of facility?
- Which method is best for my facility?
- How do I switch methods and will my regulator allow it?
- Does it make financial sense to switch?

Laboratory managers all over the country have settled on a suitable ammonia method by following a simple three-step process:

1. Understand the advantages and disadvantages of each method including the costs and analyst training requirements
2. Talk with local regulator to understand the steps needed to change methods; most regulators have outlined a simple side-by-side analysis required to switch (Note: Some states have already accepted the TNTplus method outright and do not require the side-by-side analysis)
3. Acquire the technology and develop Standard Operating Procedures

Contact your local Hach Sales Manager for assistance through this process by visiting www.hach.com.

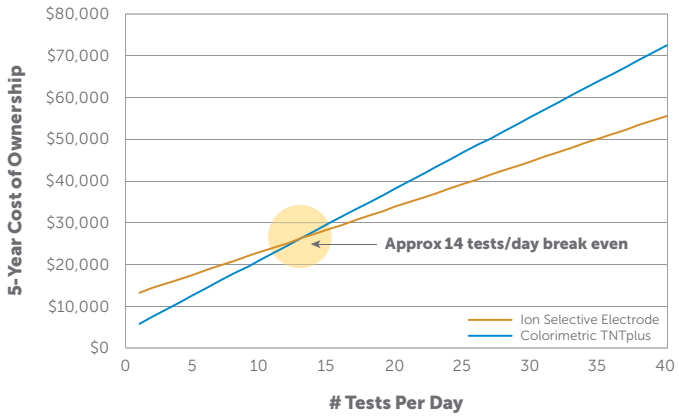
Comparison of ISE and Colorimetric TNTplus Methods

Technology	Advantages	Disadvantages
ISE	• Wide dynamic range • Cost effective for greater than approximately 15 tests/day • Few interferences • Common measurement system for ammonia in laboratories	• Time and labor intensive calibration procedure and standard preparation • Slow response at low level ammonia concentrations (<0.5-1 mg/L NH3-N) • Maintenance of electrode and membrane • Sensor drift during measurement
Colorimetric TNTplus	• Simple 15-minute test procedure (no calibration curve generation required) • Bar-coded TNTplus assure right method and range are selected • Cost effective for less than approximately 15 tests/day • Good low-level performance and linear throughout the measurement range • Mercury-free reagent (compared to EPA-approved Nesslers method)	• Range-specific reagent sets • Possible interferences (but not typical in most wastewater matrices)

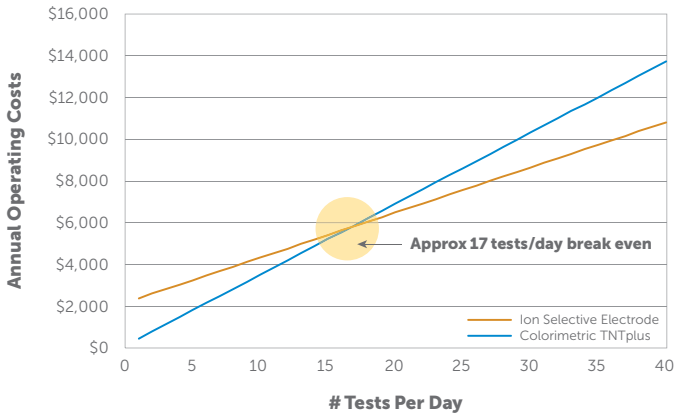
Relative Costs of Each Technology

Many laboratory managers are required to perform financial justification for changes. The financial return for each ammonia measurement technology is directly related to the number of tests run per day. Due to the laborious calibration and standard preparation process for the ammonia ISE, most facilities will find that TNTplus is the right choice for fewer than 15 ammonia measurements per day. ISE technology, once calibrated, can perform numerous measurements relatively quickly..

5-Year Cost of Ownership: Colorimetric vs. ISE



Annual Operating Costs: Colorimetric vs. ISE



Example Assumptions: Fully-burdened labor: $20/hour; Setup/calibration/standard preparation for ISE: 30 minutes; New ISE probe each year: $1000; New ISE Meter: $1700; New Spectrophotometer: $4500; Direct labor for each test: 5 minutes; Example Uses 100 Testing Days/Year (Relative Costs Increase/Decrease Linearly)

Low-Level Analytical Performance

Regulations on nutrients are getting tighter all over the country. This can cause significant challenges for ammonia ISE technology. Most high-quality ammonia ISEs have a linear and fast response from approximately 0.5 mg/L NH3-N to greater than 10,000 mg/L NH3-N. However, below 0.5 mg/L NH3-N, the response can be slow and many ISE systems display non-linearity forcing analysts to generate a multi-point calibration curve focused on this range. For extreme low-level samples, the TNTplus ammonia method has excellent low-level performance down to 0.015 mg/L NH3-N.

Technical Summary: Demonstration of Performance in Municipal and Industrial Wastewater Samples

Equipment for Colorimetric Tests

- Hach DR3900 Spectrophotometer
- Ultra-Low Range Ammonia TNTplus 0.015-2.000 mg/L NH3-N (TNT830)
- Low Range Ammonia TNTplus 1-12 mg/L NH3-N (TNT831)
- High Range Ammonia TNTplus 2-47 mg/L NH3-N (TNT832)
- Ultra-High Range Ammonia TNTplus 47-130 mg/L NH3-N (TNT833)

Equipment for Ion Selective Electrode Tests

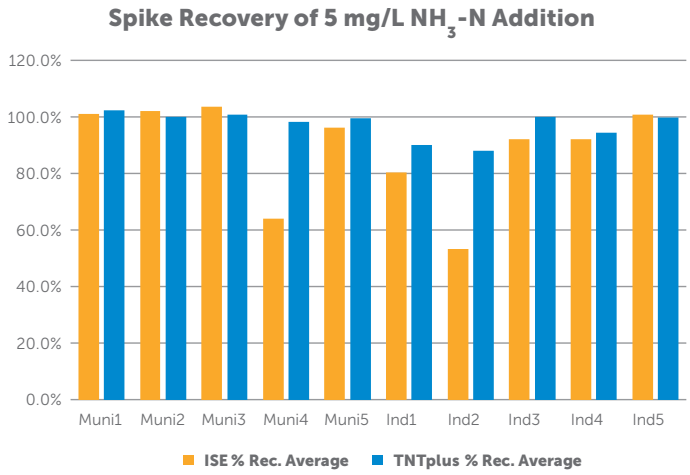
- HQ440D Laboratory Dual Input, Multi-Parameter Meter
- HQD IntelliCal Ammonia ISE
- Calibration standards were made fresh and the ISE was calibrated 3 times per day at 0.1, 1.0, and 10 mg/L NH3-N to assure accuracy (Slope 1: 58.8mV; Slope 2: 56.8mV; Slope 3: 57.2mV – All slopes were within the 58 +/-3mV performance criteria)

Application Note: Selecting the Right Ammonia Method

Five different Municipal Wastewater and five different Industrial Wastewater samples were analyzed side-by-side using each technology. A 5 mg/L NH3-N spike was added to each matrix to calculate percent recovery. Additional details of this experiment are available upon request (contact your local Hach Sales Manager).

	ISE Test 1	ISE Test 2	ISE Spike 1	ISE Spike 2	ISE % Rec. Average	TNTplus Test 1	TNTplus Test 2	TNTplus Spike 1	TNTplus Spike 2	TNTplus % Rec. Average
Muni1	0.237	0.243	5.36	5.22	101.0%	0.187	0.189	5.31	5.31	102.4%
Muni2	0.166	0.173	5.3	5.25	102.1%	0.09	0.092	5.16	5.03	100.1%
Muni3	0.362	0.343	5.58	5.48	103.6%	0.255	0.257	5.32	5.27	100.8%
Muni4	5.94	6.01	9.04	9.32	64.1% †	3.74	3.61	8.68	8.51	98.4%
Muni5	0.0733*	0.0753*	4.84	4.92	96.1%	0.023	0.023	5.03	4.97	99.5%
Ind1	4.82	4.88	8.8	8.93	80.3% †	3.95	3.9	8.45	8.4	90.0%
Ind2	7.63	7.63	10.3	10.3	53.4% †	5.9	5.9	10.3	10.3	88.0%
Ind3	0.546	0.546	5.15	5.15	92.1%	0.401	0.401	5.4	5.4	100.0%
Ind4	1.175	1.09	5.77	5.72	92.3%	0.945	0.921	5.61	5.7	94.4%
Ind5	0.253	0.236	5.3	5.28	100.9%	0.168	0.166	5.2	5.12	99.9%

** Outside of calibration range; † Outside of acceptance criteria. All results in mg/L NH_3-N*



DOC042.53.20300.Mar19

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
Tel: 800-227-4224 | E-mail: techhelp@hach.com
To locate the Hach office or distributor serving you, visit **hach.com**

HACH®
Be Right™