# Cracking the Code on Nitrogen Methods

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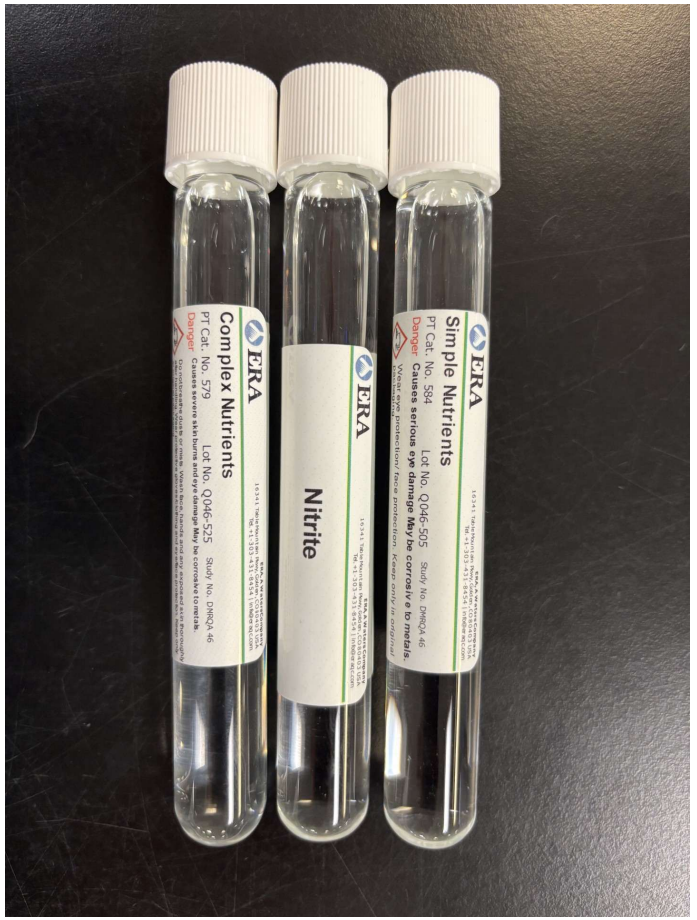
# Why Nitrogen Testing in Wastewater Is Challenging (and Critical)

- Nitrogen isn't "one test" – it's a family of measurements
  - Ammonia Nitrogen ($NH_3$ as N)
  - Nitrate + Nitrite Nitrogen ($NO_3$/$NO_2$ as N)
  - TKN (Total Kjeldahl Nitrogen)
  - Total Nitrogen (TN)
- Environmental impacts
  - Eutrophication and Hypoxia/Anoxia
- Human health risks
  - Nitrates interfere with the body's ability to transport oxygen
  - Excessive nitrogen fertilizer contributes to soil nutrient depletion

# Products Highlighted (Core Nitrogen Focus)

*Primary Nitrogen Parameters*

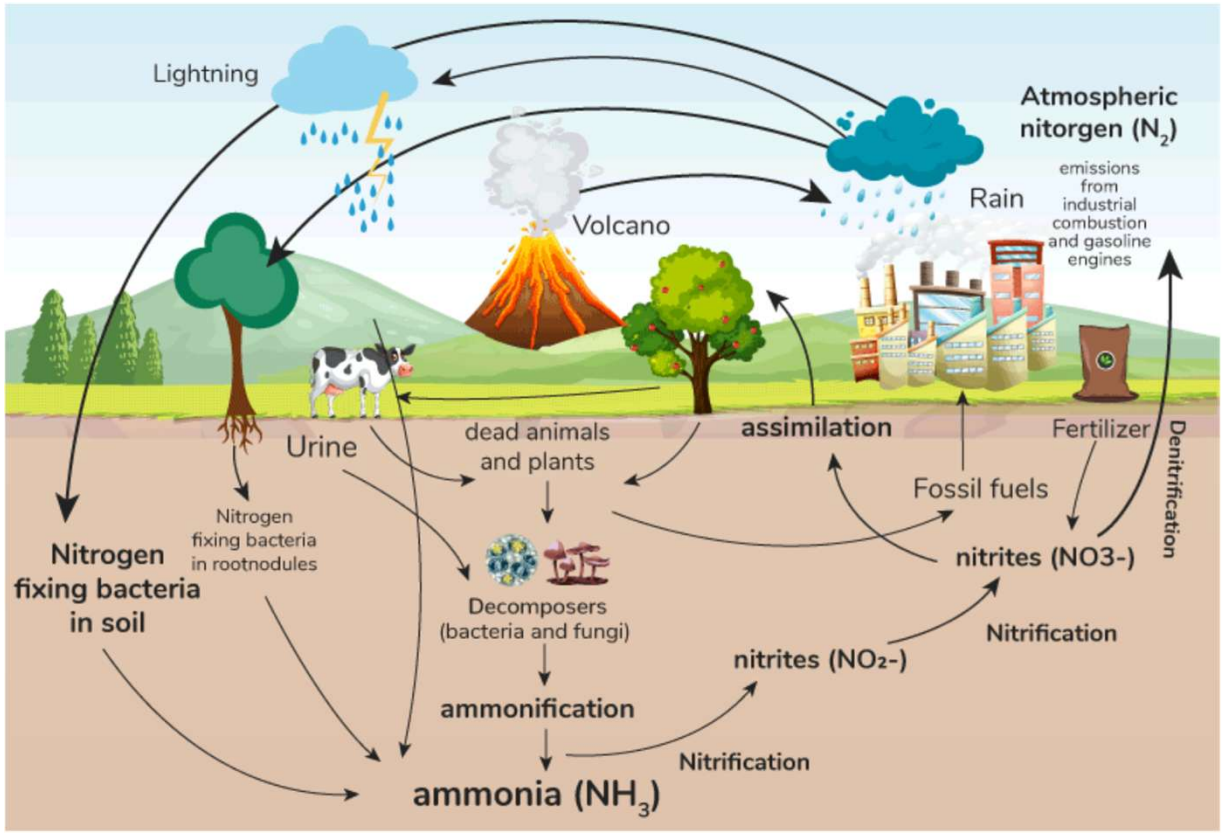
- Simple Nutrients (PT # 584 / QC # 505)
  - $NH_3$ as N (1 – 20 mg/L)
  - $NO_3$ as N (2 – 25 mg/L)
  - $NO_3$ + $NO_2$ as N (2.5 – 25 mg/L)
  - ortho $PO_4$ as P (0.5 – 5 mg/L)
  - Total Nitrogen (3 – 45 mg/L)
- Complex Nutrients (PT # 579 / QC # 525)
  - TKN (3 – 35 mg/L)
  - Total Phosphorus as P (0.5 – 10 mg/L)
- Nitrite (PT # 888 / QC # 770)
  - $NO_2$ as N (0.4 – 4 mg/L)
- Available as QR if needed



# Understanding Nitrogen Forms in Wastewater

*Nitrogen Cycle*

- Ammonia ($NH_3/NH_4^+$)
- Nitrate ($NO_3^-$)
- Nitrite ($NO_2^-$)
- Biological nitrification and denitrification



# Overview of Common Nitrogen Test Methods

*Ammonia / Ammonium*

- SM 4500-NH3 (Ion Sensitive Electrode)
  - Ion Strength Adjustment (ISA) pH to > 11 by converting $NH_4^+$ to $NH_3$
  - No distillation needed
  - pH electrode inside sensor
  - Gas permeable membrane
  - Filling solution reacts with NH3 to produce pH shift
- Low concentrations and drift of mV readings most common challenges

# Ammonia Methods Comparison

## Nessler Reagent

- Colorimetric; reaction of ammonia with Nessler's reagent ($K_2[HgI_4]$) in an alkaline solution to form a yellow-to brown complex.
- 0.05–1.0 mg/L $NH_3$-N
- High sensitivity, standardized (EPA Method 350.2),relatively straightforward post distillation.
- Contains toxic mercury, potential for interferences from amines and other compounds, distillation can be time-consuming.

## Berthelot (Indophenol)

- Colorimetric; reaction of ammonia with phenol and hypochlorite in an alkaline solution to form a blue-colored indophenol.
- 0.025–5.0 mg/L $NH_3$-N
- High sensitivity and accuracy, less toxic reagents than Nessler's method.
- Longer reaction time (1-2 hours), sensitive to pH and interferants.

## Ion-Sensitive Electrode

- Potentiometric; measurement of the potential difference across an ammonia specific membrane.
- Wide range, typically 0.01 to 17,000 mg/L $NH_3$-N.
- Wide dynamic range, real-time measurements, portable
- Potential for interference from volatile amines, requires careful frequent calibration and temperature control to maintain precision.

# Ammonia Methods Comparison

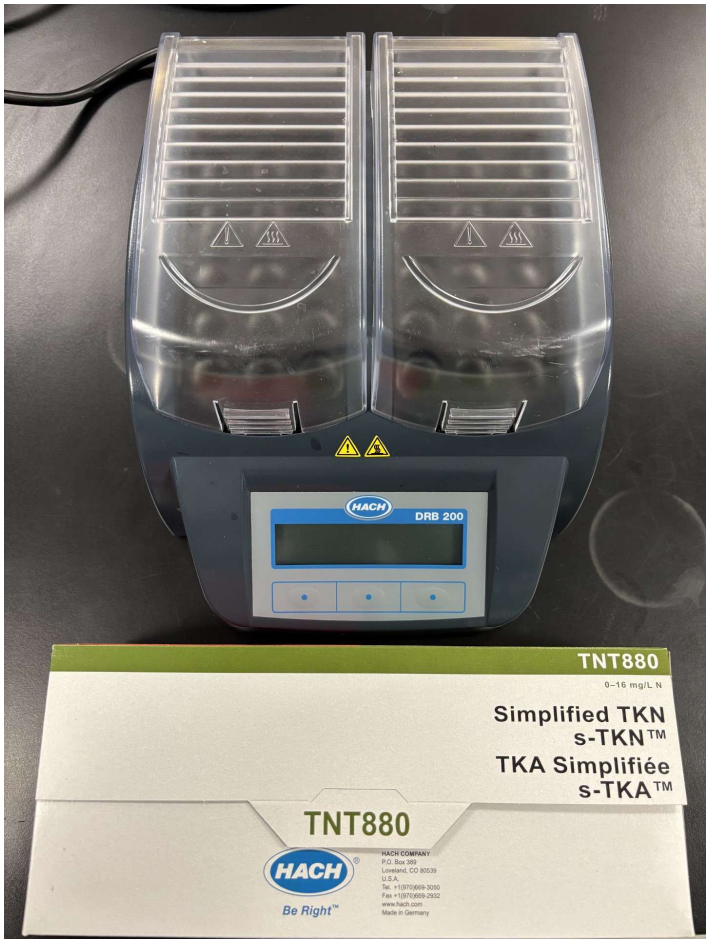
- Nessler USEPA Method 8038 (Hach kits)
  - UV Vis spectrophotometry
- Berthelot (Indophenol)
- ISE
- Ion Chromatography
  - Cations column
  - Automated
  - No hazardous waste

# Nitrate and Nitrite

- Nitrate is a regulated contaminant with a Maximum Contaminant Level (MCL) of 10 mg/L in drinking water
- EPA 300.0
- EPA 9056A
- EPA 353.2 (Colorimetry)
- SM 4500 NO2-B
- SM 4500 NO3-D (ISE)
- SM 4500 NO3-E (Manual Cd reduction)
- SM 4500 NO3-F (Automated Cd reduction)
- Hach 10206 and 10207

# Total Kjeldahl Nitrogen (TKN)

- Represents the sum of organic and ammonia nitrogen in a sample, excluding nitrate and nitrite
- EPA 351.2 / SM 4500-N
  - Sulfuric Acid / copper and potassium sulfate
  - Heat to 380°C to convert to ammonium sulfate
  - Run on ISE
- Hach Method 10242
  - Digest samples at 120°C
  - Colorimetric
  - Also allows for total nitrogen



# Data Reporting

*Required reporting "as N"*

- Report in mg/L units
- Use "as N" calibration standards
- H – 1.0079 g/mol
- N – 14.0067 g/mol
- O – 15.9994 g/mol
- $NH_3$ – 17.0304 g/mol (N = $NH_3$ / 1.2159)
- $NH_4$ – 18.0383 g/mol (N = $NH_4$ / 1.2878)
- $NO_2$ – 46.0055 g/mol (N = $NO_2$ / 3.2845)
- $NO_3$ – 62.0049 g/mol (N = $NO_3$ / 4.4268)
- Use CRMs to confirm your process is reading correctly

# Emerging Trends and Best Practices

- When submitting PT's, use the name and analyte code stated on your accreditation certificate or permit
- Know what the concentration ranges are for your PTs and if the method can achieve them.
- Clear understanding of nitrogen species in wastewater
- Confidence in selecting appropriate test methods
- Improved data quality and regulatory confidence
- Practical guidance for day-to-day lab and plant decisions
- Monitor your calibration and QC data – great indicators of potential quality issues
- Run CRMs alongside PTs

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# Thank you!