Total Phosphorus & Nitrate + Nitrite Analysis using a DR3900

City of Petaluma

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Method: Hach Method 10209 (SM4500-P E-2011) & Hach Method 10206

Topics


Background
Method Development
Pros and Cons
Challenges
Procedure
Questions

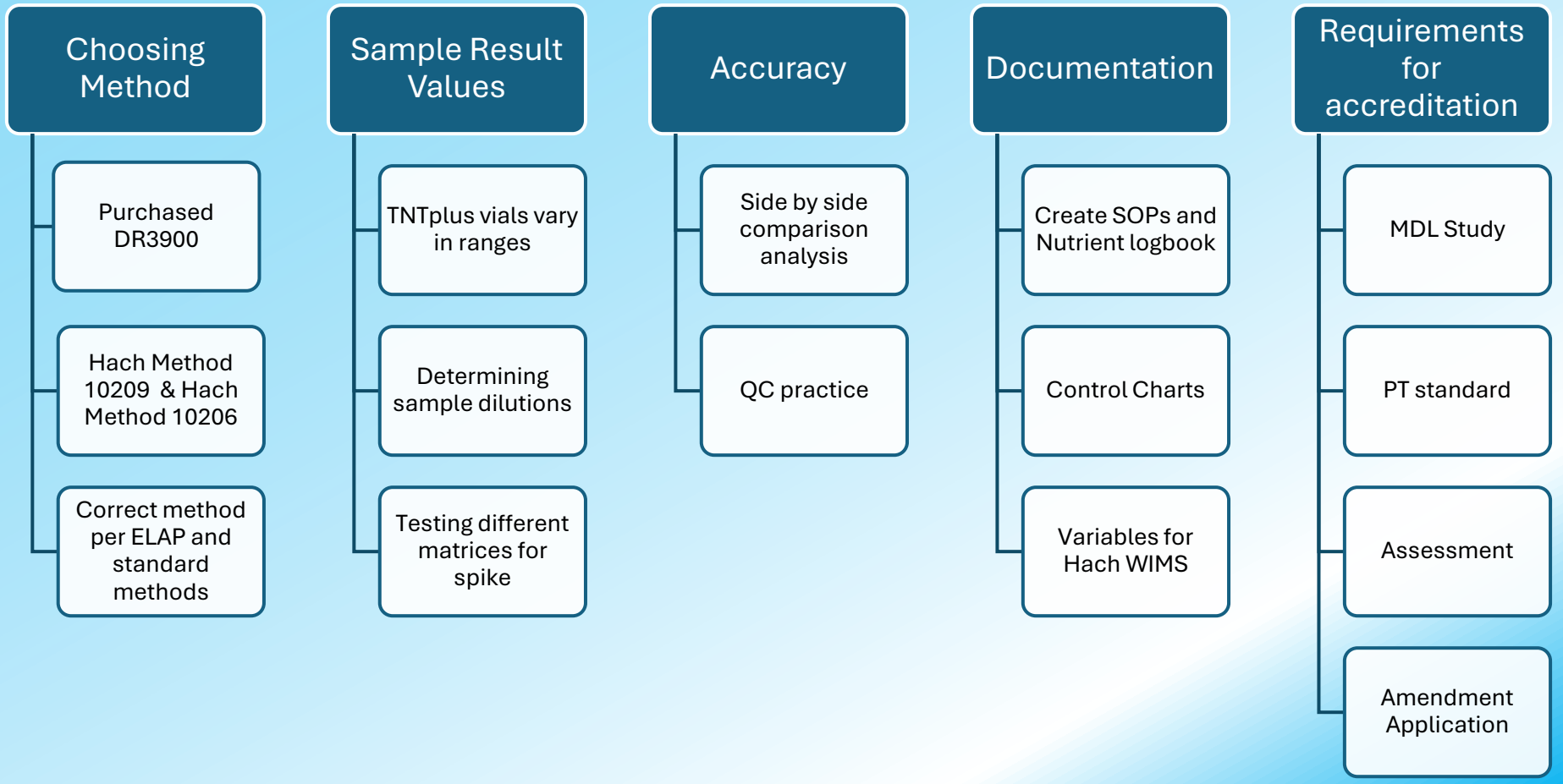
Total Phosphorus Background

- Helps indicate the overall amount of phosphorus, including dissolved and particulate forms.
- Total phosphorus is a nutrient that can cause water quality problems, such as, eutrophication when present in excess.
  - Algae blooms
  - oxygen
- Regulatory importance

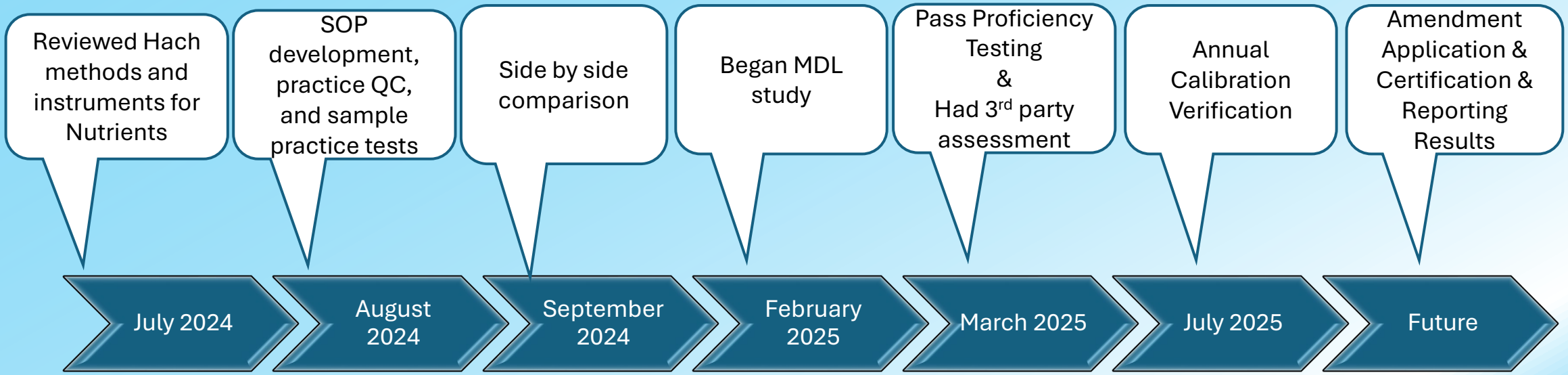
Nitrate +Nitrite Background

- Nitrate + nitrite has important roles in many industrial and municipal water-quality
- Excessive nitrite and nitrate concentration negatively effect water treatment process
- Nitrate-rich effluents discharged into receiving water can degrade water quality
  - Excess growth of algae

Method Development



Timeline


Reviewed Hach methods and instruments for Nutrients
July 2024
SOP development, practice QC, and sample practice tests
August 2024
Side by side comparison
September 2024
Began MDL study
February 2025
Pass Proficiency Testing & Had 3rd party assessment
March 2025
Annual Calibration Verification
July 2025
Amendment Application & Certification & Reporting Results
Future

Pros and Cons

Pros

- Automatic method detection
  - Bar-coded vials
- Documented shelf life
  - 2D barcode details batch number and expiration date of reagents
- Efficient
  - Easy, fast handling
- Reagents are contained
  - Safe

Cons

- Cost
- Ranges in each TNTplus vial
- Waste
- EPA approval

Challenges

- Method development on Nitrate + Nitrite
- Matrix spike interference
  - Percent recovery was low on certain matrices
  - Tested out various samples for matrix spike to determine interferences
- TNTplus vials concentration ranges
  - Analyzed which range suited our samples
- Method 10206 nitrate + nitrite turbid samples need sample blanks
- Interferences on method 10206 nitrate + nitrite
  - High load of oxidizable organic substance (COD) give high basis results
- Digestion Block: DRB200
- Timeline

Side by side comparison

Sample Name	Date	CALTEST Result Nitrate + Nitrite By EPA 353.2-93/SM-NO3 F-16 mg/L	City of Petaluma Nitrate + Nitrite By Hach 10206 mg/L	% Difference
Ox Ditch #1 CHA	7/2/25	ND	1.52	
Ox Ditch #1 CHB	7/2/25	2.7	3.85	35.1
Ox Ditch #1 CHC	7/2/25	6.7	9.73	36.9
Ox Split filtered w/0.45 µm	7/2/25	0.14	0.213	41.4
Ox Ditch #1 CHA w/0.45 µm	7/2/25	ND	0.31	
Ox Ditch #1 CHB w/0.45 µm	7/2/25	2.7	4.148	42.3
Ox Ditch #1 CHC w/0.45 µm	7/2/25	6.7	10.222	41.6
Tertiary Effluent	7/30/25	10	10.2	1.98
Secondary Effluent	7/30/25	9.0	9.12	1.32

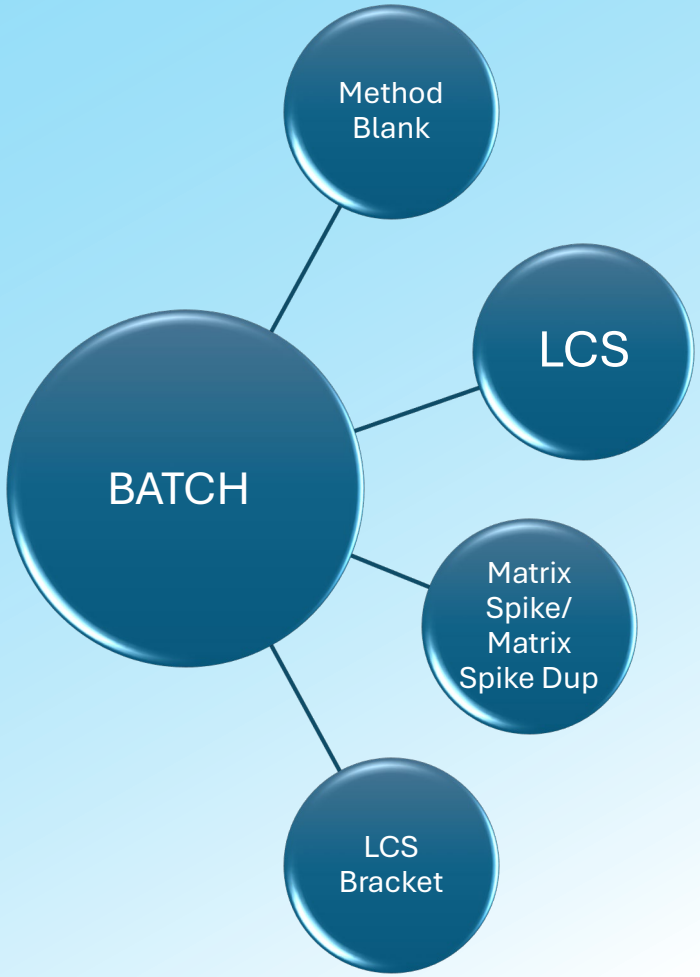
Side by side comparison

Sample Name	Date	CALTEST Result Total Phosphorus as P mg/L by SM4500 P B/F	City of Petaluma Result Total Phosphorus as P mg/L by 4500 P E	%Difference
EFF001	1/7/25	1.5	1.54	2.63
Tert EFF	1/7/25	1.9	1.8	5.41
Ox Ditch #1 CHA	7/2/25	76	68.75	10.02
Ox Ditch #1 CHB	7/2/25	76	75.75	0.33
Ox Ditch #1 CHC	7/2/25	80	77.25	3.50
Ox Split	7/2/25	12	11.4	5.13

Total Phosphorus Procedure
SM4500- P E. Ascorbic Acid & Hach 10209

- Samples collected unpreserved, recommended sample pH 6-8
- Analyze the samples as soon as possible for best results
- Preservation of samples for later analysis
  - Adjust sample pH to <2
  - Store samples below 6°C maximum 28 days
  - Before analysis, adjust pH to 7

Quality Control



Total Phosphorus Procedure

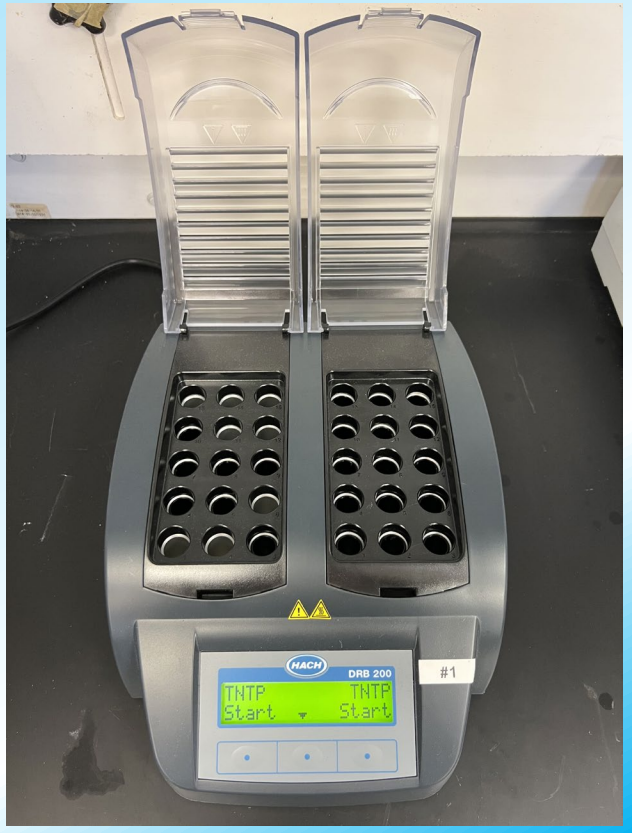
QC and sample preparation

- Prepare matrix spike
- Make dilutions for samples
- Remove lid from DosiCap Zip cap
- Add sample to test vial
- Turn DosiCap Zip over
- Shake vial 2-3 times to dissolve reagent in the cap

Total Phosphorus Procedure

Sample Digestion

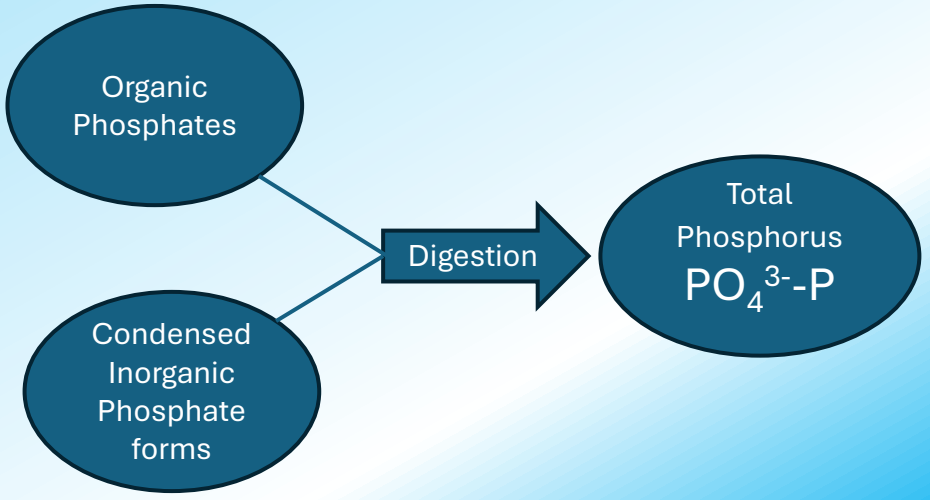
- DRB200
  - 13-mm wells for digestion, if reactor has 16-mm wells, put adapter sleeves into wells
  - 15 vials x 16mm + 15 vials x 16mm



Total Phosphorus Procedure

Digestion

- Keep vials in the reactor for 30 minutes at 120° C
- When timer expires remove vial from the reactor and let the vial decrease to room temperature
- Persulfate digestion
  - All phosphorus present in the sample, regardless of form
  - Acid and heat provide conditions for hydrolysis of the condensed inorganic forms
  - Organic phosphates are converted to orthophosphates by heating with acid and persulfate



Total Phosphorus Procedure

Aliquot reagents

- Add solution B to test vials
- Put a grey DosiCap C on the vial
- Invert vial
- Start 10 minute reaction time
- When time expires, invert the vial 2-3 times

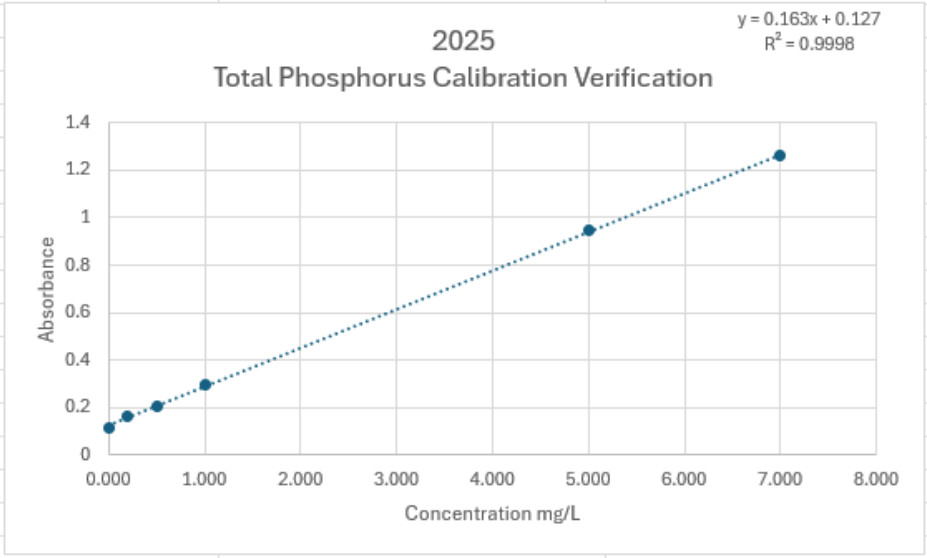
Total Phosphorus Procedure

Analyze Samples

- Insert the vial into the cell holder
- Measurement wavelength is 880 nm
- Results show in PO_4^{3-}-P

Calibration Verification

Total Phosphorus True Value mg/L	Total Phosphorus Absorbance Value	Total Phosphorus Measured Value mg/L
0.000	0.117	0.000
0.2	0.162	0.275
0.5	0.208	0.552
1.0	0.298	1.1
5.0	0.946	5.01
7.0	1.264	6.85



Nitrate + Nitrite Hach Method 10206

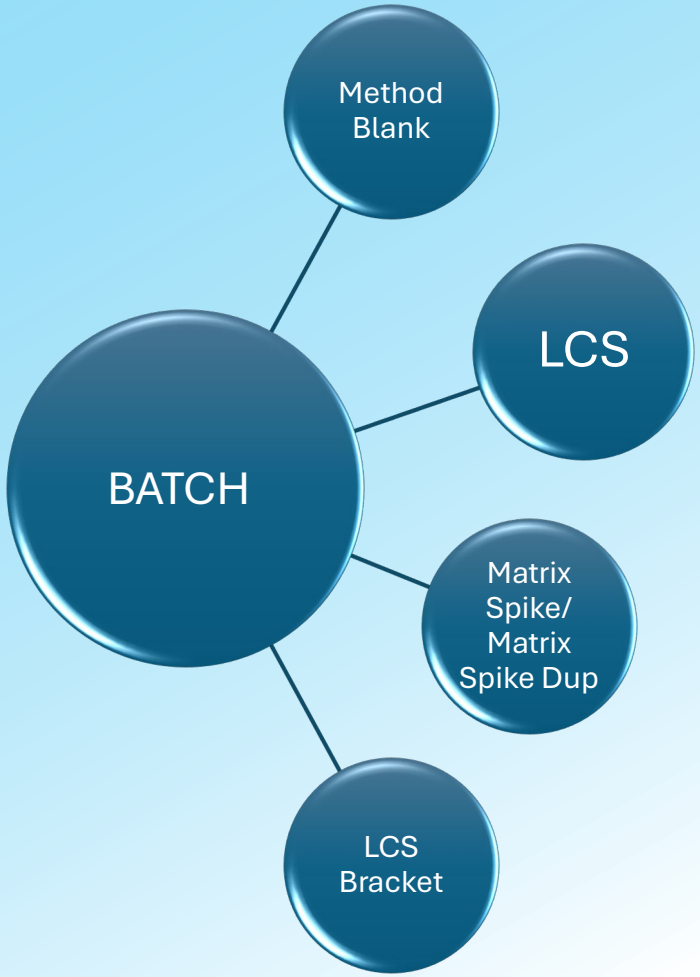
- Samples collected unpreserved, recommended pH 3-10
- Adjust the sample pH to <2 with concentrated sulfuric acid
  - Sample test then includes nitrate + nitrite
  - Samples can be store for 14 days and below 6°C
  - Before analysis, adjust the pH to 7 with 5N sodium hydroxide solution

Nitrate + Nitrite Procedure

QC and sample preparation

- Prepare matrix spike
- Make dilutions for samples if necessary
- Add sample to test vial

Quality Control



Nitrate + Nitrite Procedure

Aliquot reagents

- Add Solution A to test vial
- Tighten cap and invert until completely mixed
- Start the reaction time of 15 minutes

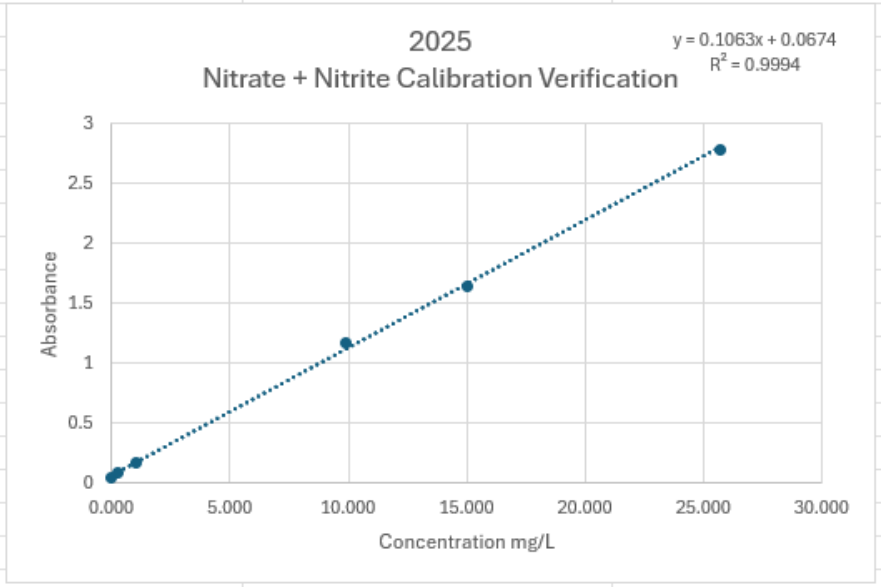
Nitrate + Nitrite Procedure

Analyze Samples

- Insert the vial into the cell holder
- Measurement wavelength is 345 nm
- Results show in NO3-N

Calibration Verification

Nitrate+ Nitrite True Value mg/L	Nitrate+ Nitrite Absorbance Value	Nitrate + Nitrite Measured Value mg/L
0.000	0.053	0.000
0.23	0.082	0.268
1.01	0.173	1.09
9.9	1.172	10.1
15	1.646	14.4
25.7	2.788	24.8



Thank You

Comments and Questions?

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