Application of the FIAlyzer for Nutrient Analysis

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August 12, 2025

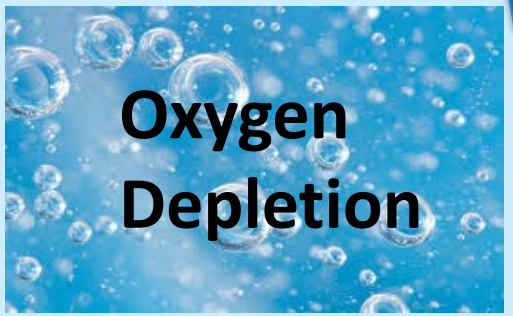
CITY OF SAN JOSE
CAPITAL OF SILICON VALLEY

Environmental Services

Delivering world class utility services and programs to improve our health, environment, and economy.

Addressing Nutrient Pollution in Wastewater

Nitrogen & Phosphorus in Wastewater



Nutrient Management in Wastewater Treatment

- **Biological Nutrient Removal process:**

Nitrification: Under aerobic conditions by Nitrifying bacteria

$$NH_3 \rightarrow NO_2^- \rightarrow NO_3^-$$

Denitrification: Under anerobic conditions by Denitrifying bacteria

$$NO_3^- \rightarrow N_2$$

NPDES and Nutrient Permits

- **Effluent Limitations for NH_3, Total:**
  Average Monthly = 3.0 mg/L
  Maximum Daily = 8.0 mg/L

		Parameter	
		Total NH_3	TKN
Sampling Frequency	Effluent	2/Month	NA
	Influent	1/Quarter	

NH_3 Analysis for Process & Struvite Monitoring

Location	Process Monitoring	Struvite Monitoring
Raw Sewage	Daily	
Primary Effluent		
Settled Sewage		
Nitrification Influent		
Nitrification Effluent		
Secondary Effluent		
Filter Influent		
Final Effluent		
Recycled Water	Once a Month	
Digesters		Twice a Week
Sludges		

Instruments Used for NH_3 Analysis in Our Laboratory in the Past

- **Segmented Flow Analyzer**

  - **Segmented flow with air bubbles**
  - **Good Sensitivity**
  - **Colorimetric detection based on phenolate chemistry**
  - **Longer Analysis times**
  - **Requires distillation for complex sample matrices**

Instruments Used for NH_3 Analysis in Our Laboratory in the Past

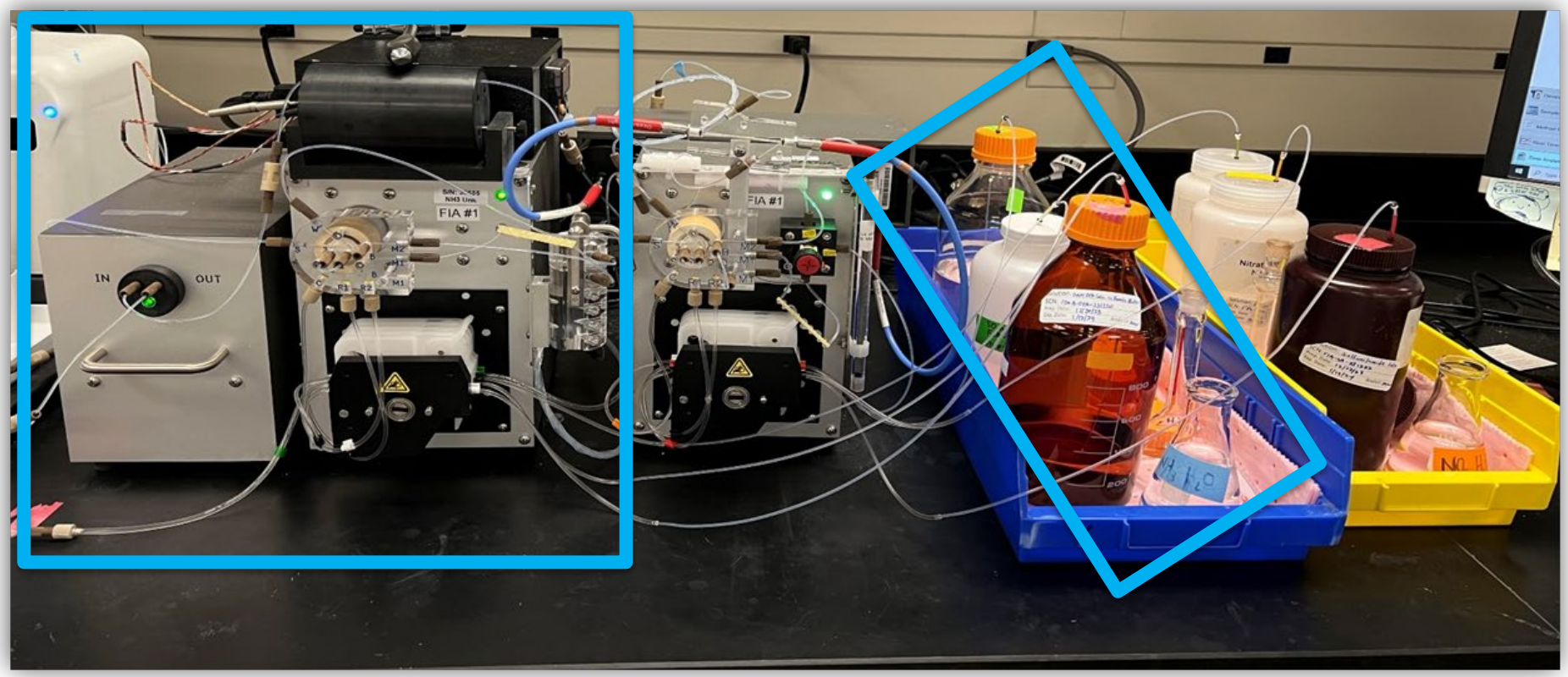
- Discrete Analyzer

  - Standards/Samples and Reagents mixed using Robotics
  - Good Sensitivity
  - Colorimetric detection based on phenolate chemistry
  - Longer Analysis times
  - Requires distillation for complex sample matrices

Advantages of Using Flow Injection Analysis with Gas Diffusion & Fluorescence Detection

- **Elimination of matrix effects** due to gas diffusion technology – **Saves Time & Resources**
- **High sensitivity** due to fluorescence detection
- **High selectivity** due to OPA/sulfite reagent chemistry
- **Excellent reagent stability**

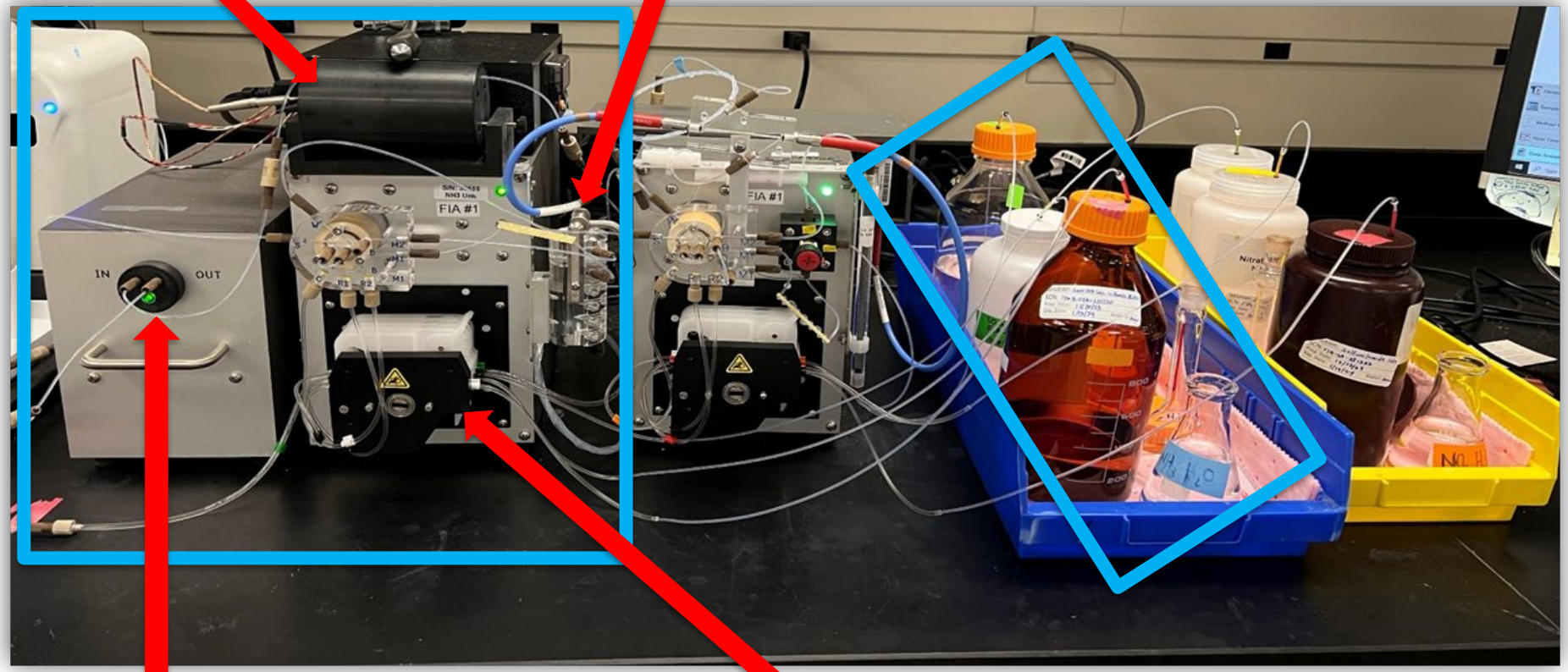
Flow Injection Analysis: NH_3 & TKN



Flow Injection Analysis: NH_3 & TKN

Heater

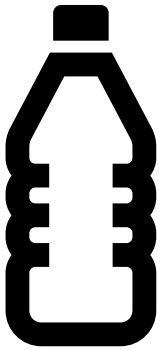
Gas Diffusion Unit (Sandwich Membrane Cell)



PMT Fluorescence Detector

Peristaltic Pump

Flow Injection Analysis: NH_3 by EPA FIAlab 100

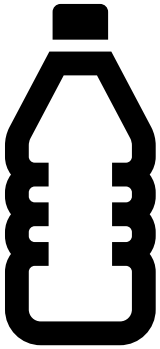


Preservation check: pH <2

Oxidizer Check

Centrifuge: 2000 rpm, 20 min

Flow Injection Analysis: TKN by EPA FIAlab 100



TKN = Organic Nitrogen + NH_3

Digestion

Free NH_3 &
Organic Nitrogen

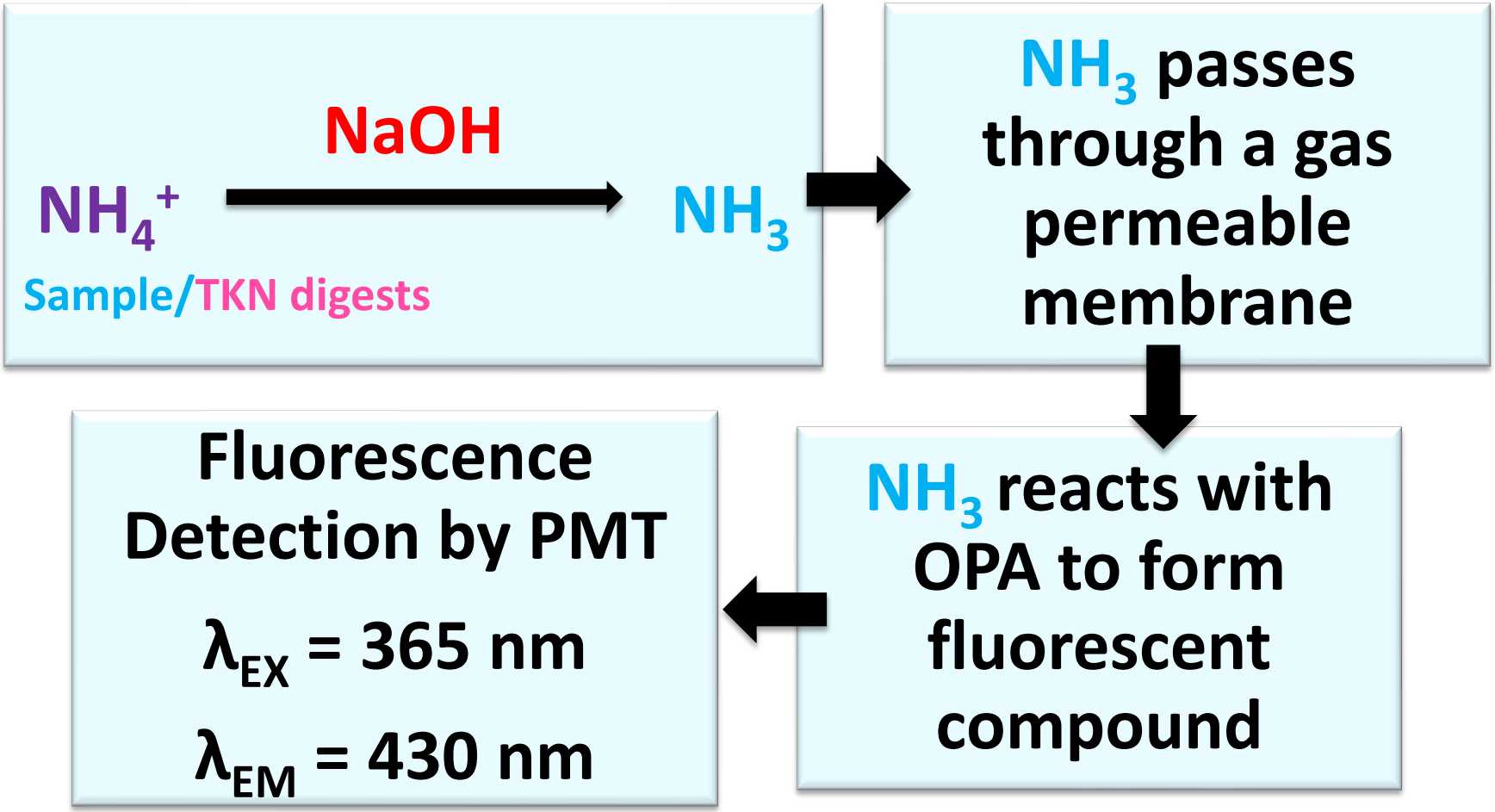
H_2SO_4, K_2SO_4 , $CuSO_4$

160 °C, 1 h

380 °C, 30 min

NH_4^+

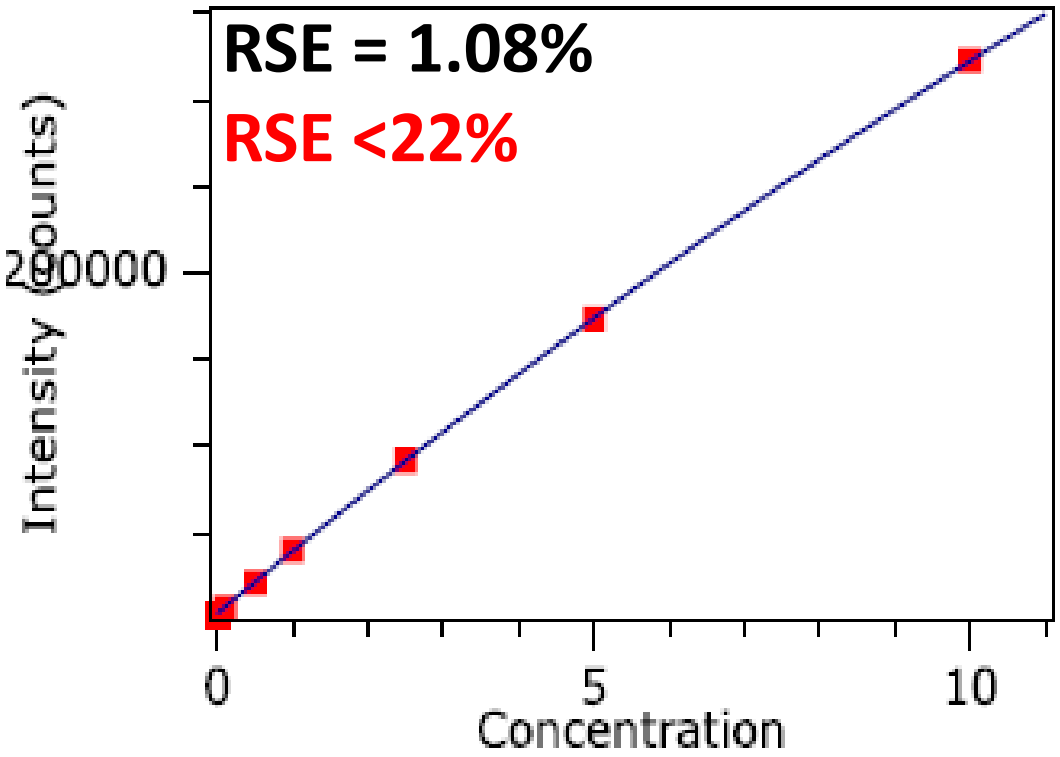
Flow Injection Analysis: NH_3 & TKN by EPA FIAlab 100



Setting up the Method

- **Objective: Validate EPA method FIAlab 100 as an effective and sustainable approach to analyze ammonia in diverse water matrices.**
  - **Determine a Calibration Range**
  - **Conduct a Method Detection Limit Study**
  - **Perform Initial Demonstration of Capability**
  - **Analyze PT samples**
  - **Set up an audit**

Flow Injection Analysis: NH_3 by EPA FIAlab 100



MDL = 0.02 mg/L

RL = 0.1 mg/L

Initial MDL: NH_3

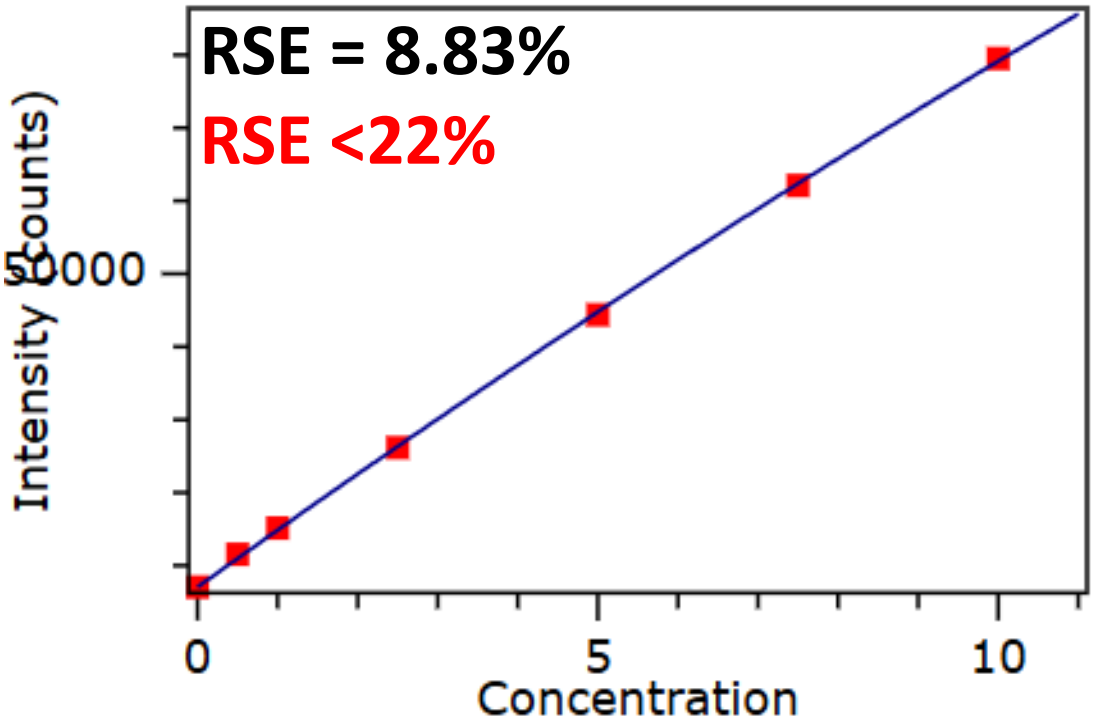
Analysis Date	MDL_b	MDLs	Replicate No.
5/18/2023	-0.0046	0.0765	1
5/18/2023	-0.0045	0.0959	2
5/18/2023	-0.0027	0.0584	3
5/19/2023	0.0001	0.1011	4
5/19/2023	0.0002	0.0994	5
5/19/2023	0.0006	0.0997	6
5/22/2023	0.002	0.1053	7
5/22/2023	0.0007	0.1015	8
5/22/2023	0.0001	0.0907	9
8/2/2023	0.0016	0.1002	10
8/2/2023	0.0018	0.1089	11
8/2/2023	0.0009	0.1013	12
8/3/2023	0.0007	0.1005	13
8/3/2023	-0.0002	0.0995	14
8/3/2023	-0.0007	0.1	15
8/4/2023	0.0044	0.1019	16
8/4/2023	0.0044	0.1029	17
8/4/2023	0.0043	0.1003	18
Average	0.0005	0.0992	
Standard Deviation	0.0026	0.0069	
n	18	17	
n-1	17	16	
t(n-1,1-α =0.999)	2.567	2.583	
MDL	0.0071	0.0179	

$$MDL_s = t_{(n-1,\ 1-\alpha=0.99)} S_s$$

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)} S_b$$

Initial MDL: 0.02 mg/L

Flow Injection Analysis: TKN by EPA FIAlab 100



MDL = 0.16 mg/L

RL = 0.5 mg/L

Initial MDL: TKN

Analysis Date	MDL_b	MDLs	Replicate No.
8/14/2023	0.0740	0.5412	1
8/14/2023	0.0256	0.5256	2
8/14/2023	0.0349	0.5451	3
8/16/2023	0.0461	0.5263	4
8/16/2023	0.0328	0.4624	5
8/16/2023	0.0302	0.4159	6
8/17/2023	0.0029	0.5446	7
Average	0.0352	0.5087	
Standard Deviation	0.0216	0.0500	
n	7	7	
n-1	6	6	
t(n-1,1-α =0.999)	3.143	3.143	
MDL	0.1030	0.1573	

$$MDL_s = t_{(n-1,\ 1-\alpha=0.99)} S_s$$

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)} S_b$$

Initial MDL: 0.16 mg/L

Demonstration of Capability

Source (NH3)	Result	Certified Value	Recovery(%)
LCS 1	1.9378	2	96.89%
LCS 2	2.0048	2	100.24%
LCS 3	2.0139	2	100.695%
LCS 4	2.0212	2	101.06%
		Acceptance Range:	90-110%
		Average Rec. %:	100%
		Acceptance Range (RSD%):	10.00%
		Calculated RSD %:	1.92%

Source (TKN)	Result	Certified Value	Recovery(%)
LCS 1	2.5317	2.5	101.268%
LCS 2	2.4339	2.5	97.356%
LCS 3	2.6777	2.5	107.108%
LCS 4	2.3956	2.5	95.824%
		Acceptance Range:	85-115%
		Average Rec. %:	100%
		Acceptance Range (RSD%):	10.00%
		Calculated RSD %:	5.01%

Accuracy

Precision

Proficiency Testing

Samples	Result	True Value	Acceptance Range	% Recovery
NH3 ERA	3.73	3.72	3.18-4.24	100.3
NH3 ERA	18.0	16.9	13.6 - 20.1	106.5
NH3 ERA	8.61	8.34	6.60 - 10.1	103.2
NH3 PT	4.42	4.3	3.30 - 5.35	102.8
TKN PT	30.5	29.9	22.6 - 35.9	102.0

1 PT sample per Year

Matrix and Comparison Studies

Spike Recovery in Various Matrices

Samples	Sample Result (mg/L)	Spiked Sample Result	Spike Recovery (%)
Industrial Waste (2X)	4.50	8.59	102.2
Industrial Waste (2X)	1.95	6.01	101.5
Industrial Waste (2X)	3.96	8.25	107.2
Estuarine	0.17	2.22	102.5
Estuarine	0.19	2.23	102.0
Estuarine	0.36	2.35	99.5

FIA vs Previous Distilled Method

Samples	Distilled Method (mg/L)	FIA w/ Gas Diffusion (mg/L)	RPD
Industrial Waste	1.72	1.62	5.99
Industrial Waste	8.72	9.44	7.93
Industrial Waste	0.66	0.72	8.70
Industrial Waste	2.56	2.70	5.32
Industrial Waste	3.07	3.08	0.33
Plant Effluent	0.40	0.38	5.13
Plant Effluent	1.69	1.65	2.40

Typical Sample Data

Sample	NH_3 (mg/L)
Final Effluent	0.398
Raw Sewage	30.0
Recycled Water	1.73
Industrial Waste	39.9
South Bay Water	0.301

Sample	TKN (mg/L)
Raw Sewage	46.8

EPA FIAlab 100 Quality Control

QC / Method	ICV	ICB/CCB	MB	LCS	MS/MSD	RPD	CCV
EPA FIAlab 100 (NH_3/TKN)	N/A	✓	✓	✓	✓	✓	✓
In-House Control Limits	90-110%	≤½ RL	≤½ RL	90-110% 85-115%	85-115% 80-120%	≤15 %	90-110%

FIAlyzer Troubleshooting: Do's and Don'ts

Do's	Don'ts
Perform routine maintenance (daily, monthly, etc.)	Neglect to perform routine maintenance
Start with basics: Inspect reagent levels, air bubbles, connections, leaks	Ignore the basics
Inspect pump tubing	Assume pump tubing are in good condition
Refer to the instrument manual	Neglect to refer to the manual
Contact FIAlab technical support	Fail to get help from Technical support

How to Get Certified?

4. Ammonia (as N), mg/L	Manual distillation [6] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993)	4500-NH_3 B-2011		973.49.[3]
	Nesslerization			D1426-15 (A)	973.49,[3] I-3520-85.[2]
	Titration		4500-NH_3 C-2011.		
	Electrode		4500-NH_3 D-2011 or E-2011	D1426-15 (B).	
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction-based methods		4500-NH_3 F-2011		See footnote.[60]
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction-based methods	350.1,[30] Rev. 2.0 (1993)	4500-NH_3 G-2011 4500-NH_3 H-2011		I-4523-85,[2] I-2522-90.[80]
	Automated electrode				See footnote.[7]
	Ion Chromatography			D6919-17.	
	Automated gas diffusion, followed by conductivity cell analysis				Timberline Ammonia-001.[74]
	Automated gas diffusion followed by fluorescence detector analysis				FIAlab100.[82]

- **Contact the Waterboard QAO regarding addition to the FOA table since approved in 40CFR**

- **“FIALab100 was requested to be added to ELAP's accreditation offerings as part of the MUR 2021 and will be added as soon as ELAP completes their process.”**

Scheduling Your Audit

- **Things to consider**
  - **Where are you on your accreditation cycle? Amendment? Renewal? Are there any other methods?**
  - **Consider your budgetary options to determine need**
  - **Things to consider**

- **Inform you assessor, especially with a new method**
  - **SOP must be in place**
  - **Complete your IDOC and PTs ahead of time**
  - **MDL study must be completed**

Post Audit Response

- Email the assessor the table

Subgroup Code	Analyte Code	Method	Analyte	Technology	Enter Y for Selection
108.345	001	FIAlab 100	Ammonia (as N)	Auto Gas Diffusion w/ Conductivity Cell	Y
108.345	002	FIAlab 100	Kjeldahl Nitrogen, Total (as N)	Auto Gas Diffusion w/ Conductivity Cell	Y
108.033	002	EPA 353.2	Nitrite (as N)	Automated Cd Reduction	Y

- Don’t forget to have all the documents from assessors (especially Conflict of Interest form)

Conclusions

- **Ammonia Analysis via EPA FIAlab 100**
- **EPA FIAlab 100 Method Validation**
- **Accreditation**