# A New Method for Measuring Ammonia and TKN in Wastewater

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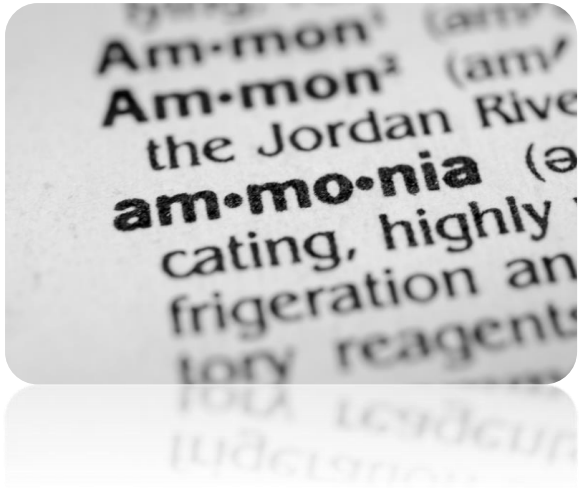

# HELLO!

**I am Dr. Ilkka Lahdesmaki**

Chief Scientist

You can find me at ilkka@flowinjection.com

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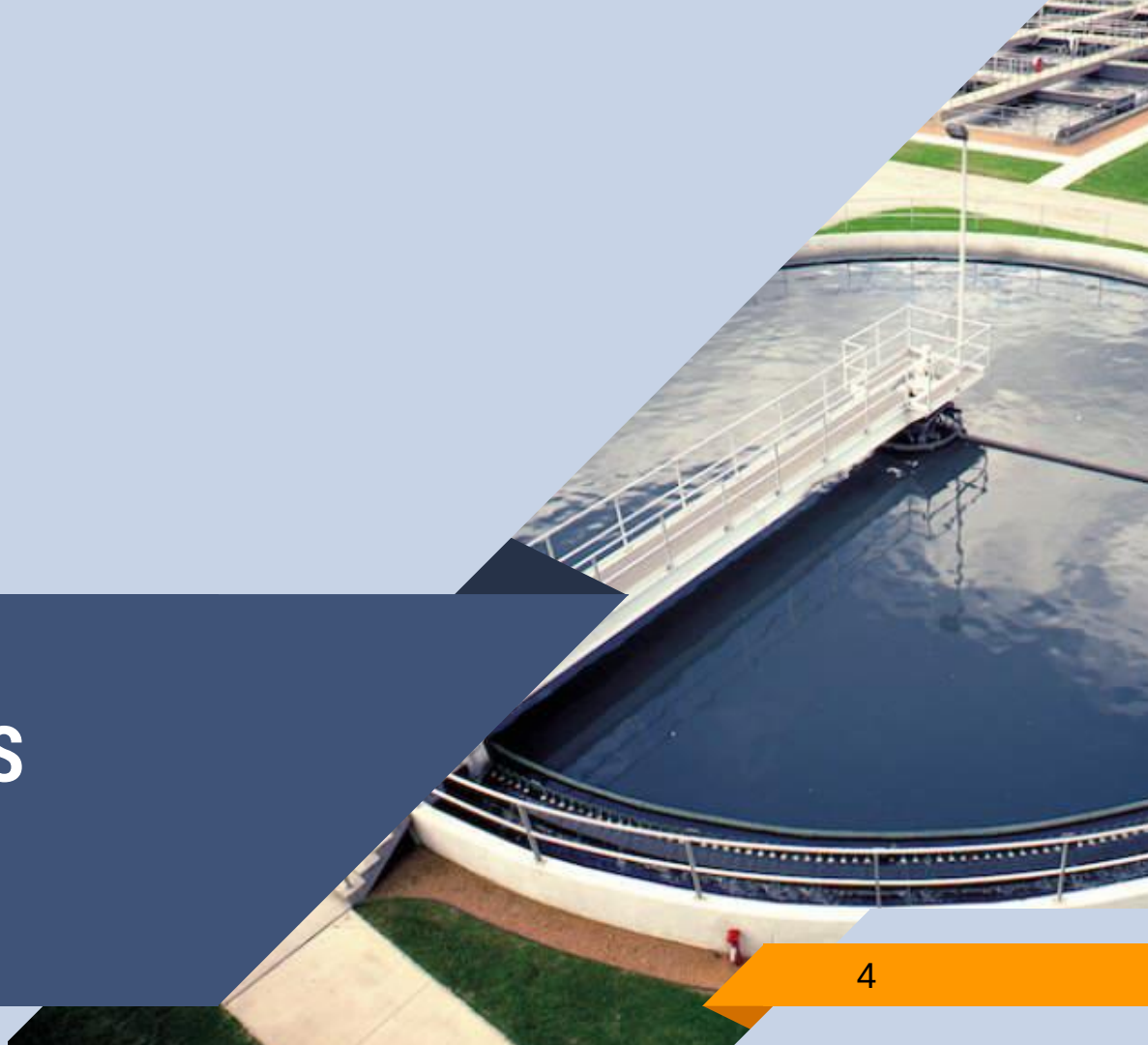
# 1

# CURRENT METHODS

## Automated methods for ammonia and TKN



# CURRENT METHODS

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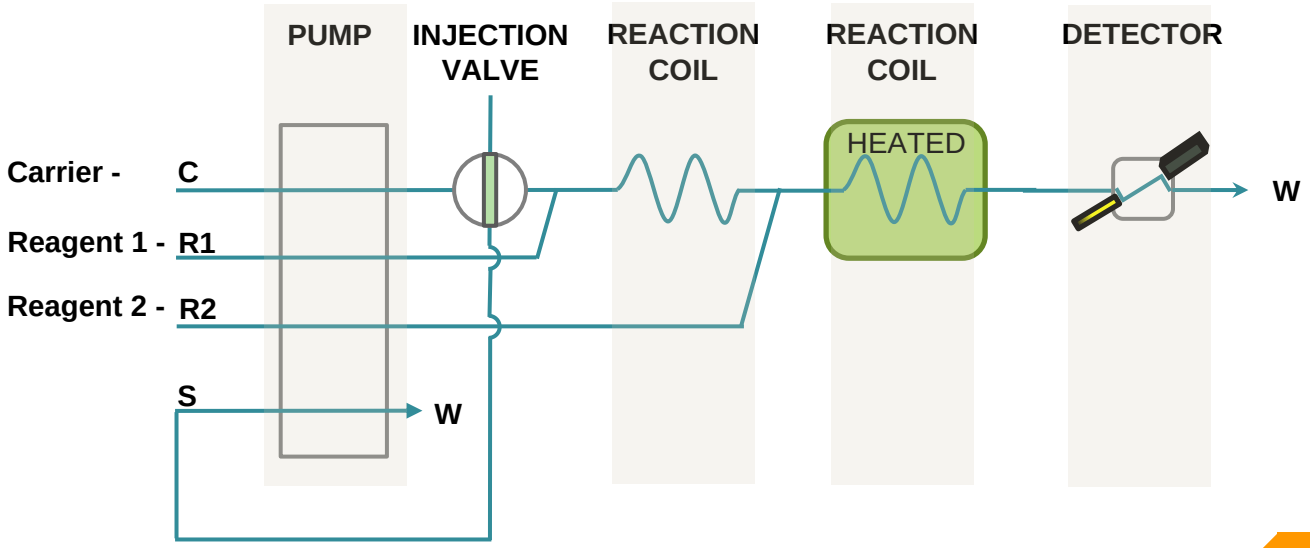
- Flow methods (FIA, SFA) achieve a high degree of automation



# CURRENT METHODS

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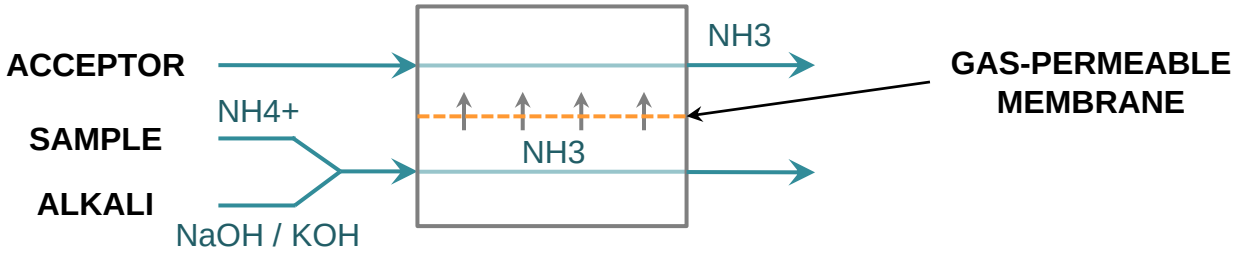
- Use of gas diffusion to replace distillation




- Detection of diffusion-separated ammonia
  - Phenolate / salicylate + photometric detection (EPA 351.2, SM 4500-$N_{org}$ D.)
  - Conductimetric detection (EPA Timberline-Ammonia-001)

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# 2

# NEW METHOD

What is the new method?

Why would a new method be needed?

# NEW METHOD – HOW DOES IT WORK?

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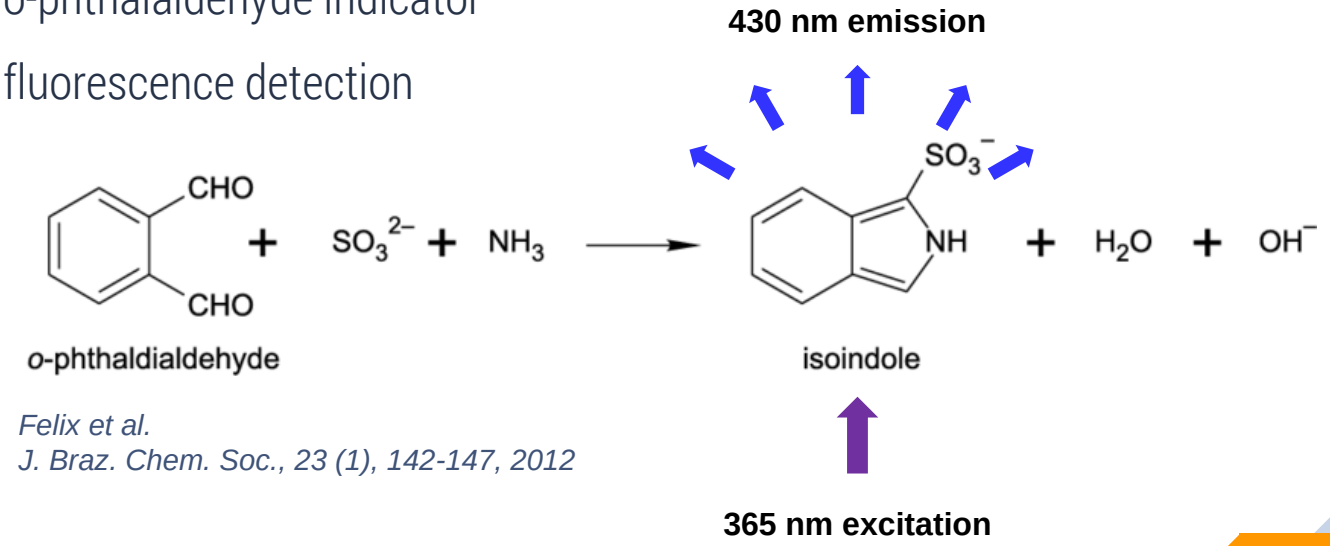
## Based on:

- o-phthalaldehyde indicator
- fluorescence detection




*Felix et al.*
*J. Braz. Chem. Soc., 23 (1), 142-147, 2012*

# NEW METHOD – HOW DOES IT WORK?

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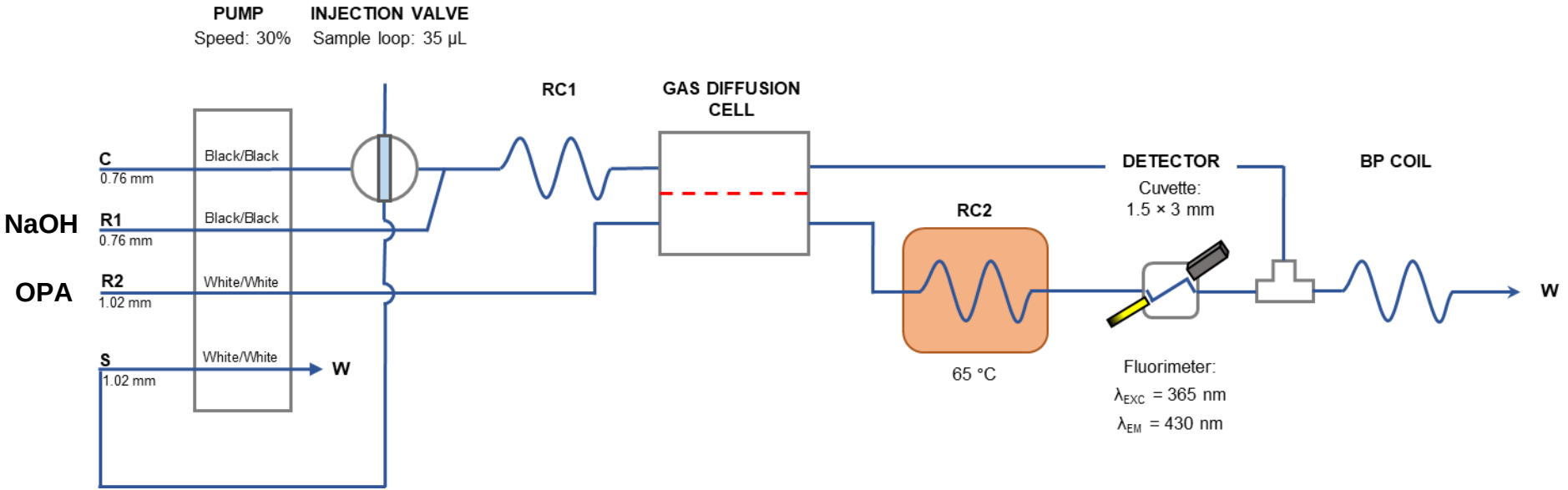

# NEW METHOD – WHY INTRODUCE IT?

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## Extensive prior use in oceanography

### 8.7 DETERMINATION OF AMMONIUM

#### 8.7.1 Overall Description of the Method

The fluorometric method offers many advantages over indophenol blue colorimetry: simplicity, very high sensitivity, stable reagents with low toxicity, no refractive index blank, mostly insignificant fluorescence blank from natural substances, almost unaltered by sample turbidity, and a low salt effect. Both methods produce equivalent results (Kérouel and Aminot, 1997). While a detection

*A. Aminot et al. in O. Wurl (ed.) "Practical Guidelines for the Analysis of Seawater", p. 166-169. CRC Press, Boca Raton, 2009.*

# NEW METHOD – WHY INTRODUCE IT?

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- Used by customers for **ammonia** and **TKN** measurements
  - Oceanography research groups
  - International environmental laboratories
  - Very positive feedback: no phenol, more sensitive, stable baseline, **consistent**

- Bring method available to accredited labs in the U.S.
  - EPA Alternative Test Procedure (ATP) application
  - Validation for use in wastewater analysis

# NEW METHOD – APPROVAL PROCESS

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## Recommendation letter from EPA – 10 Apr 2018

I have reviewed FIAlab Method 100 (ATP Case No. N15-0001), "Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Fluorescence Detector Analysis", and the supporting validation data in ATP Case No. N15-0001. I determined that this method meets all requirements for measurement of ammonia in wastewater and total Kjeldahl nitrogen (TKN) digestates. That is, the performance of this method is substantially similar to methods listed at 40 CFR Part 136 for measurement of ammonia in wastewater and TKN digestates.

## Inclusion in 2019 Methods Update Rule proposal – 11 Jun 2019

contained as supporting documents within the docket for this proposed rule. These proposed new methods include: FIAlab Method 100, "Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Fluorescence Detector Analysis," MACHEREY-NAGEL GmbH and

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# 3

# PRACTICAL USE

How to implement on FIA instrument?

Performance metrics

# PRACTICAL USE – INSTRUMENT CONFIGURATION

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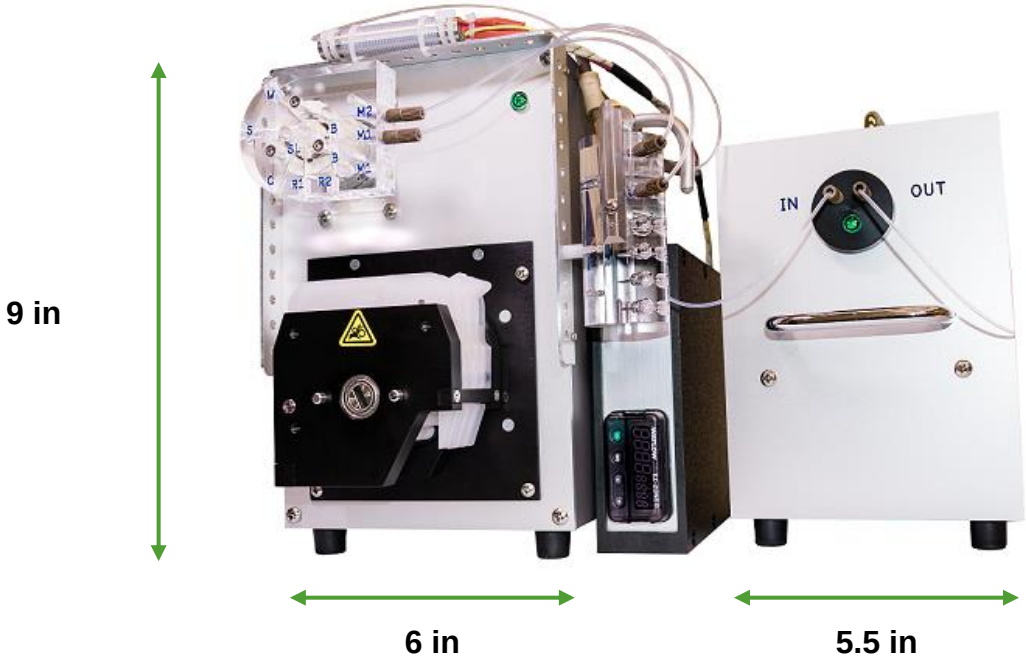


Pictured:

**FIAlyzer-1000 with PMT Detector**

# PRACTICAL USE – DATA OUTPUT

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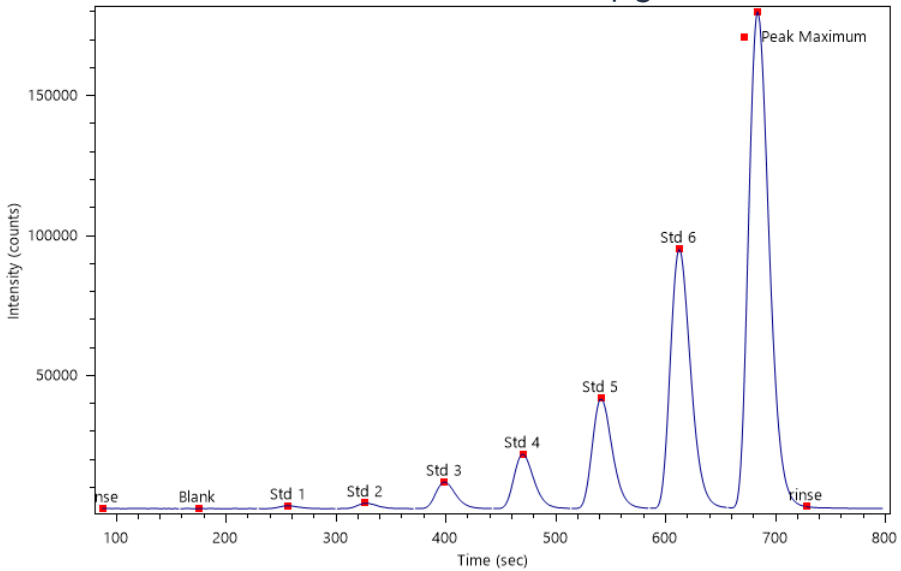
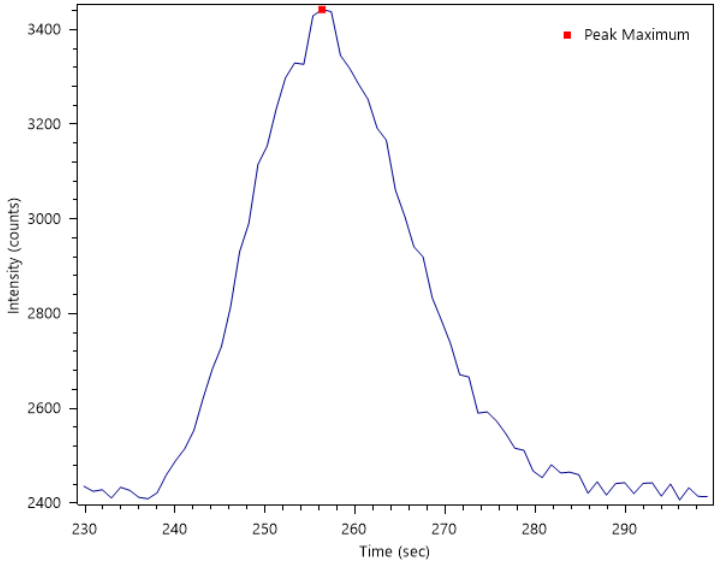
## Calibration 50 – 10,000 µg N / L




## Single injection 50 µg N / L



# PRACTICAL USE – DATA OUTPUT

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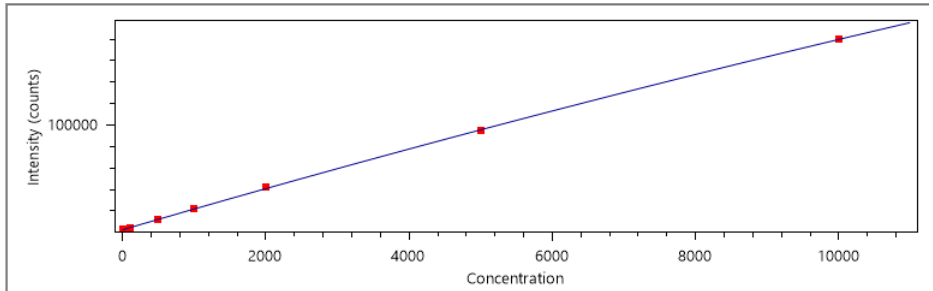
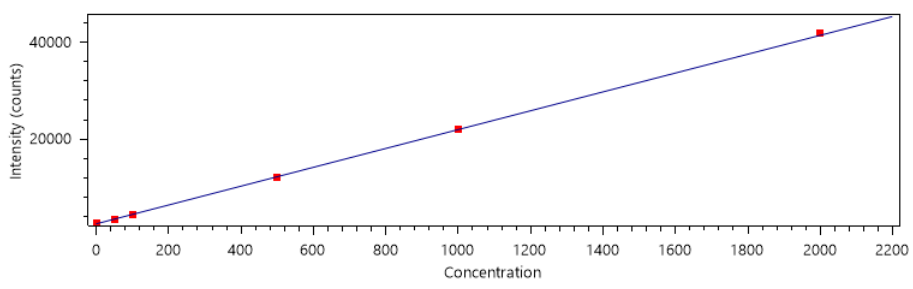



Fit model: 2nd order polynomial
Weighting: none
Coeff A: 2526.62741
Coeff B: 19.53941
Coeff C: -0.00018
$R^2$: 0.99995
RSE (%): 4.53106
Apply Drift Correction

| | Name | Peak Response | Known Concentration | Calculated Concentration | % Error | Enabled |
|---|---|---|---|---|---|---|
| ▶ | Blank | 2464.9000 | 0 | -3.159 | NA | ☑ |
| | Std 1 | 3442.4000 | 50 | 46.8881 | 6.22 | ☑ |
| | Std 2 | 4376.8000 | 100 | 94.7716 | 5.23 | ☑ |
| | Std 3 | 11951.6000 | 500 | 484.5086 | 3.10 | ☑ |
| | Std 4 | 21934.5000 | 1000 | 1002.4788 | 0.25 | ☑ |
| | Std 5 | 41811.5000 | 2000 | 2049.0256 | 2.45 | ☑ |
| | Std 6 | | | | | ☑ |
| | Std 7 | | | | | ☑ |

Relative Standard Error

## 2nd order fit 50 – 10,000 µg N / L




Fit model: 1st order polynomial
Weighting: 1/response^1/2
Coeff A: 2464.87341
Coeff B: 19.52027
Coeff C: 0
$R^2$: 0.99991
RSE (%): 2.06344
Apply Drift Correction

| | Name | Peak Response | Known Concentration | Calculated Concentration | % Error | Enabled |
|---|---|---|---|---|---|---|
| ▶ | Blank | 2464.9000 | 0 | 0.0014 | NA | ☑ |
| | Std 1 | 3442.4000 | 50 | 50.0775 | 0.16 | ☑ |
| | Std 2 | 4376.8000 | 100 | 97.9457 | 2.05 | ☑ |
| | Std 3 | 11951.6000 | 500 | 485.9936 | 2.80 | ☑ |
| | Std 4 | 21934.5000 | 1000 | 997.4056 | 0.26 | ☑ |
| | Std 5 | 41811.5000 | 2000 | 2015.6804 | 0.78 | ☑ |
| | Std 6 | 95201.4000 | 5000 | 4750.7809 | 4.98 | ☐ |
| | Std 7 | 180112.1000 | 10000 | 9100.6541 | 8.99 | ☐ |

## 1st order fit 50 – 2,000 µg N / L

# PRACTICAL USE – PERFORMANCE METRICS

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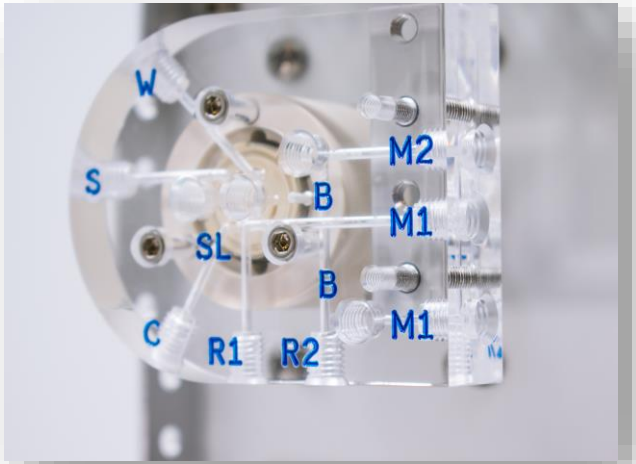
| | | |
|---|---|---|
| Detection Limit | 12 µg N/L | |
| Reporting Limit | 50 µg N/L | |
| Range Upper Limit | 10 000 µg N/L | |
| Spike recovery | 99.3% | POTW (Anaerobic digester sludge) |
| | 97.3% | Industrial discharge (Food process) |
| | 109% | Industrial discharge (Metal finish) |
| | 96.9% | River water |
| | 102% | POTW (Final effluent, pre-UV) |
| | 105% | POTW (Primary clarifier effluent) |
| Throughput | 50 samples / h | |

# PRACTICAL USE – PERFORMANCE METRICS

- Above performance with 35 µL sample loop
  - "Standard" size that works both for ammonia and TKN
  - Ability to adjust range by varying sample loop size



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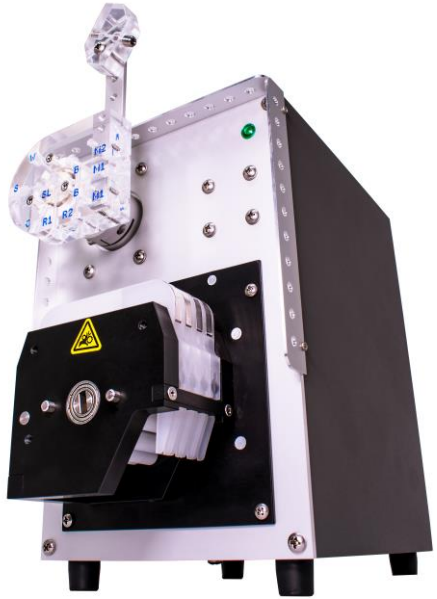
# 4

# CONCLUSIONS

What you should take home from this talk

# CONCLUSIONS

- New method for measuring **ammonia** and **TKN**
  - Applicable to wastewater and natural waters
  - Included in 2019 MUR, signed and being proposed
  - Pending inclusion in 40 CFR Part 136
- Method highlights
  - High sensitivity
  - Quick calibration and analysis
  - Robust – gas diffusion
  - Simple - one-reagent chemistry



**FIAlyzer-1000**

# CREDITS

- Askew Scientific Consulting
  - Dr. Ed Askew
- EPA Clean Water Act ATP Coordination Team
  - Lem Walker
  - Kevin Roberts
- Laboratories participating in the ATP validation experiments

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# THANKS!

**Any questions?**

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