Low Level Phosphorus: A Method Comparison Study

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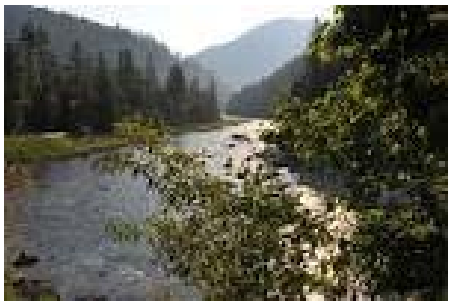
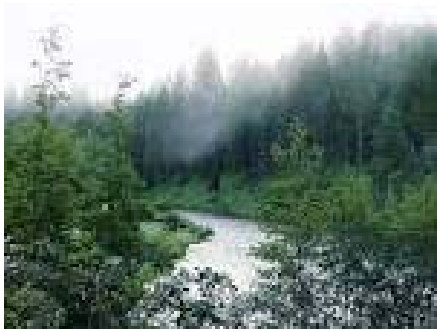
Goal: 1 µg/L Total P Quantitation

Why?



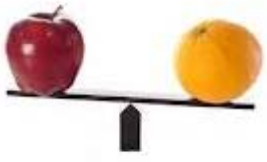


Another consideration…

Compliance Monitoring must be done using a CWA approved method; otherwise an ATP is required

Various analytical methods to try:

- **Standard Methods 4500-P E(3) (Colorimetric)** — Approved
  - manual UV/Vis,10 cm cell
- **EPA Method 365.1 (Colorimetric, Flow-Injection)** — Approved
  - "standard" manifold
  - "low level" manifold
  - in-line UV digestion manifold
- **Method 200.8 (ICPMS)** — ATP
  - Perkin Elmer, with and without reaction cell
  - Agilent, with and without collision cell



What do we call Quantitation?

MDL

- 7 low level standards
- 3.14 X Std. Dev.
- 95% confidence of non-zero result

VS

Reporting Limit

- 7 standards at the Reporting Limit concentration
- 70-130% recovery

Roadblock: Contamination

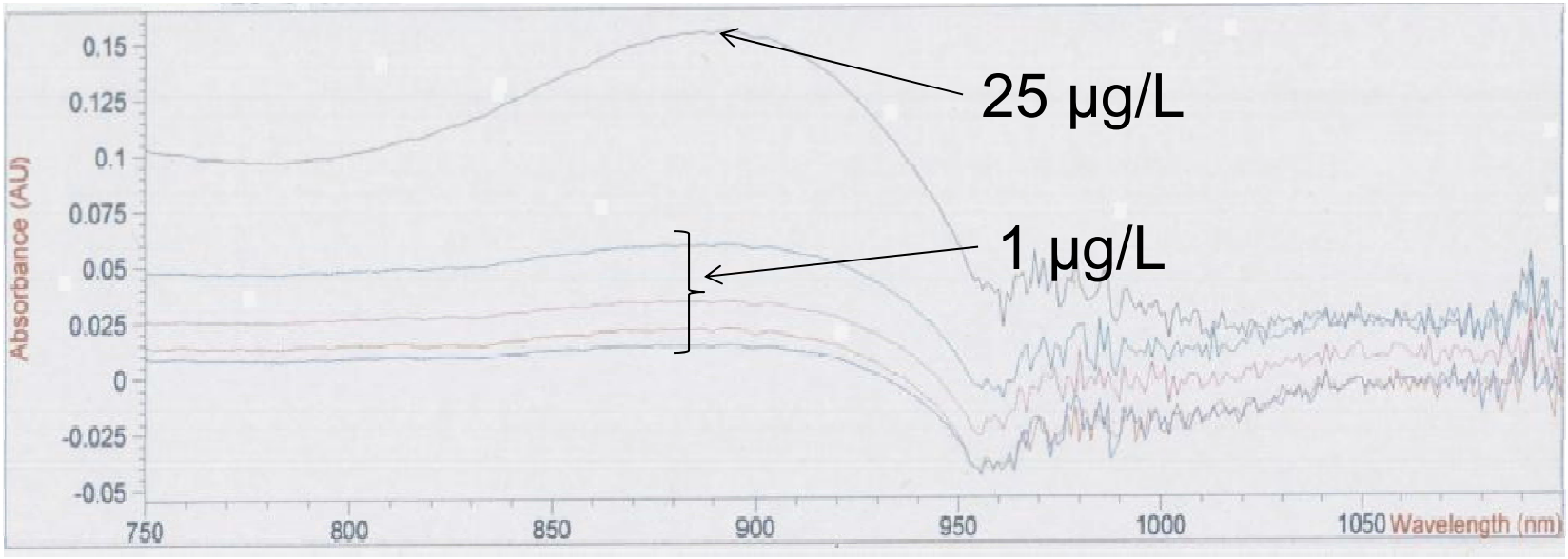
- Soak everything in HCl solution: (autosampler tubes, cuvettes, digestion tubes, volumetric flasks)
- Dedicated glassware
- Long rinse times
- Embedded in some plastics?

Standard Methods 4500-P E(3) (Manual UV/Vis)

- Colorimetric, based on Ascorbic Acid/Molybdate Chemistry
- Advantage: Can employ 10 cm cell
- Method for *orthophosphorus*, so samples must be digested (sulfuric acid/persulfate), then pH adjusted before analysis

Manual UV/Vis

Digested (then pH adjusted) standards:



Manual UV/Vis, Continued

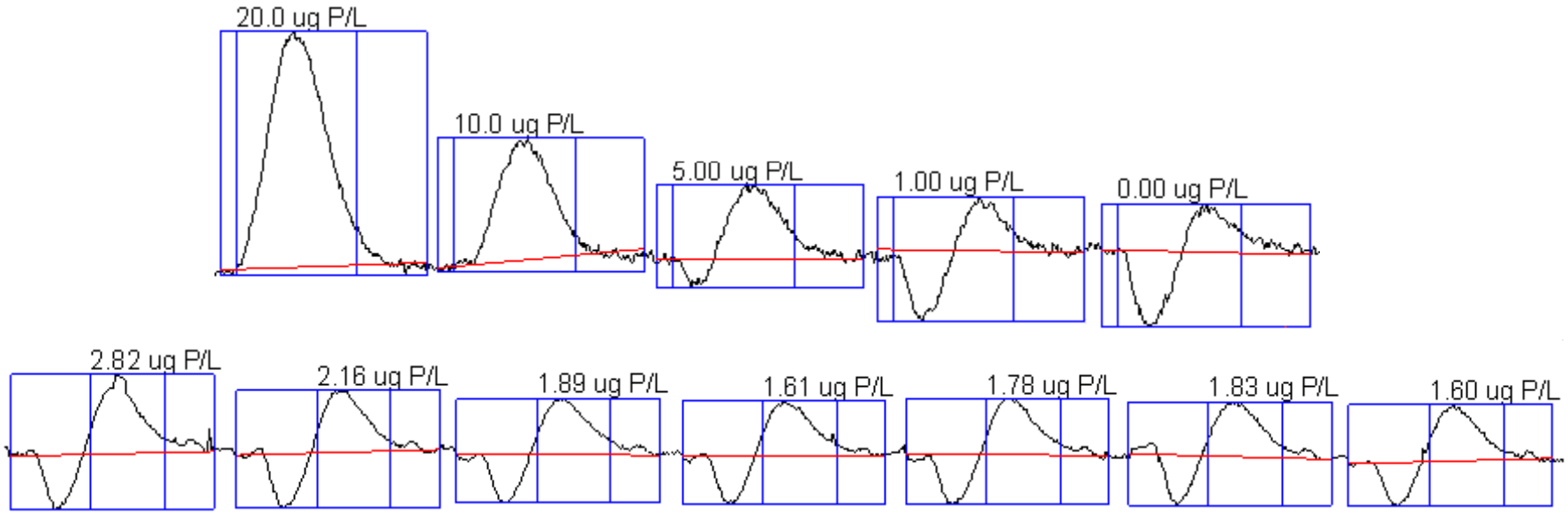
7 Replicates 1 µg/L Standard (µg/L)

0.551
0.556
-2.144
1.968
1.119
.3655
1.797

MDL = 4.3 µg/L
Not 70-130% recovery

Flow Injection Analysis (FIA)

FIA – Standard Manifold



MDL = 1.1 µg/L

Not 70-130% recovery

FIA:
Low-Level vs. Standard Manifold

Sample Loop:

350 cm x 1.02 mm vs. 100 cm x 0.8mm

Heater:

60° C w/ 1200 cm coil vs. 37° C w/ 175 cm coil

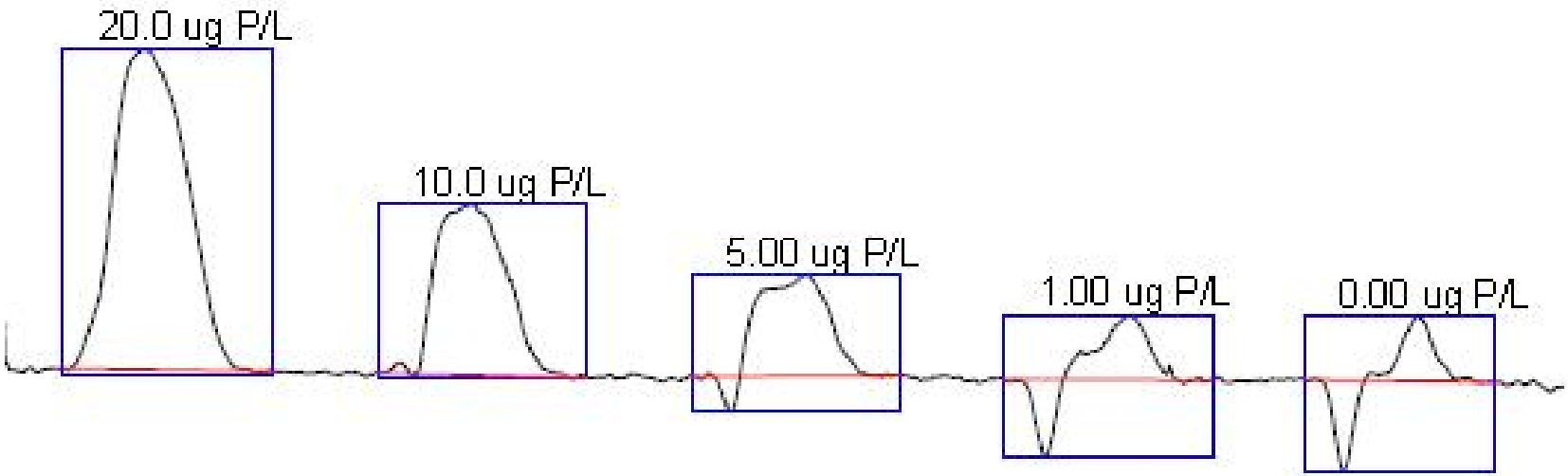
Post Heating:

Two 255 cm alternating coils vs. None

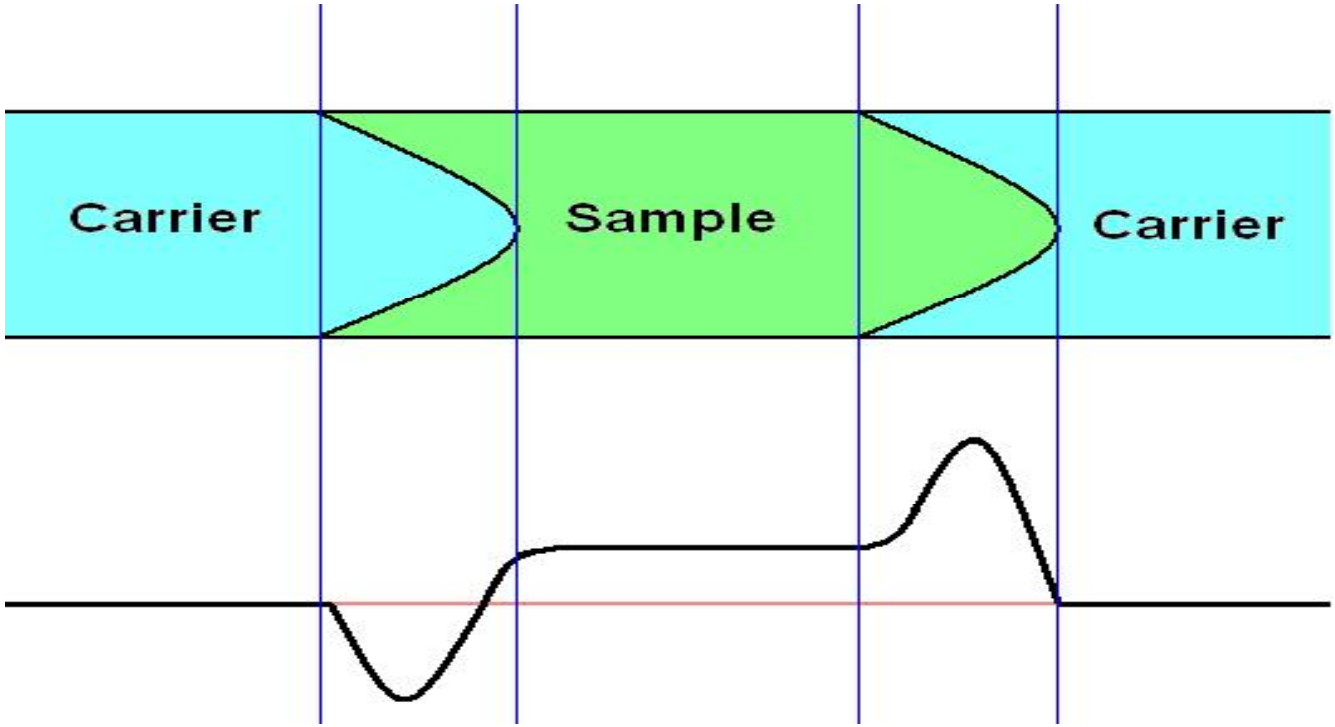
Pathlength:

2 cm flowthrough cell vs. 1 cm

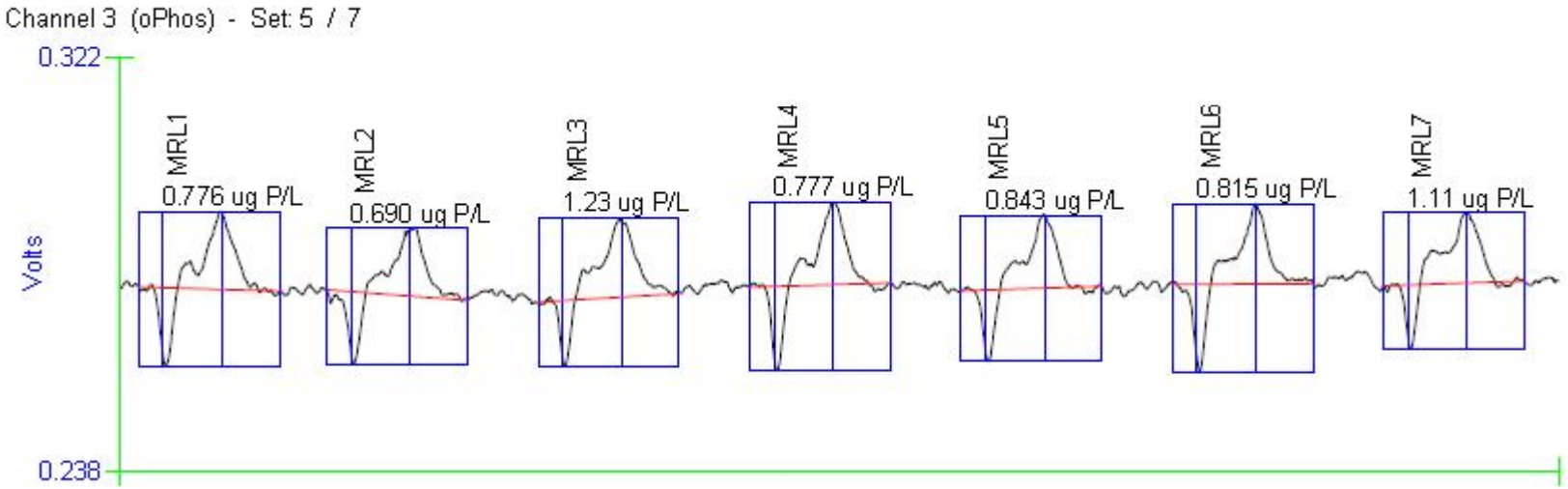
Low-Level FIA - Spectrum



Refractive Index in FIA



Low Level Manifold- 1 µg/L standards



MDL = 0.63 µg/L

Almost 70-130% recovery

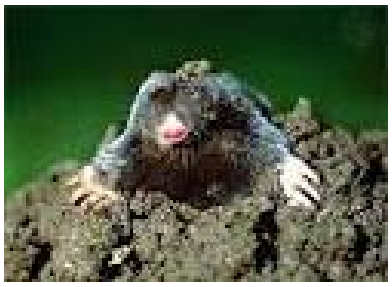
FIA – In Line Digestion

- UV irradiation used to convert all P to Ortho
- Separate manifold from Low Level P, but similar features
- Potentially Cleaner!
- Easier!

- As effective? Work in Progress…

ICP-MS: Why is P a Challenge?

- Ion is ^{31}P, interferences are $^{15}N^{16}O$, $^{14}N^{16}O^{1}H$
- Nitrogen is impossible to eliminate
  - From atmosphere
  - In samples
  - HNO_3 frequently used

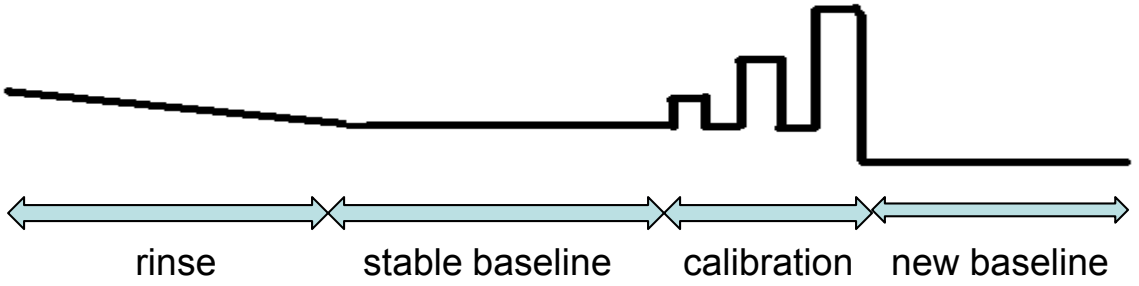


ICP/MS – Collision Cell vs. Reaction Cell

- Reaction Cell (Perkin Elmer)
  - Reactive gases; reacts with interferants, changing m/z^+
  - OR reacts with analyte, changing m/z^+ of measurement
  - With O_2 gas, $^{31}P \rightarrow {}^{31}P^{16}O$, m/z^+ 47
- Collision Cell (Agilent)
  - Gas (He or H_2) collides with all ions, but collides with larger polyatomic ions more frequently
- Both may be run in "No Gas" mode

Roadblock: Baseline

- Carryover
- Shifting baseline
- Exacerbated by presence of HNO_3



Perkin Elmer, “No Gas” Results

- Not useable, as expected (nitrogen interference)
- Background counts: 265000 cps
- 1 µg/L P is about 100 cps

Perkin Elmer, O_2 Reaction Gas Mode

(Background reduced to ~1000 cps)

Undigested 1 µg/L	Digested 1 µg/L
0.936	1.57
0.996	1.39
0.825	1.25
0.947	1.42
1.06	1.20
0.922	1.06
0.992	1.09
MDL = 0.23	MDL = 0.59
70-130% recovery	Not 70-130% recovery

Agilent, 1 µg/L Standards

Collision Gas Modes		"No Gas" Mode
He	H_2	
4.75	2.15	1.10
3.75	4.78	0.938
2.59	4.72	0.992
5.55	3.50	1.25
2.80	2.49	1.03
4.67	3.01	1.00
3.15	0.906	1.01
MDL = 3.5 Not 70-130% recovery	MDL = 4.4 Not 70-130% recovery	MDL = 0.32 70-130% recovery

Phase 2: Real Samples

Most Promising Methods

FIA, Low Level P manifold

ICPMS, PE, O_2 Reaction Gas

ICPMS, Agilent, No Gas Mode

FIA, in-line digestion?

Matrices

- Surface Waters
- WWTP Effluents

Surface Water : Coeur D'Alene Lake

All results in µg/L			
Sample	Agilent, No Gas Average Result	Low Level FIA Average Result	Perkin Elmer, O_2 Average Result
Lake sample 1	**3.7** (32% RPD)	**12.0** (RPD: N/A)	**139** (1.4% RPD)
Fortified sample 1, N=6	102% (2.8% SD)	117% (3.4% SD)	--
Lake sample 2	**3.5** (5.7% RPD)	**9.7** (RPD: N/A)	**140** (2.2% RPD)
Fortified sample 2, N=6	107% (2.8% SD)	140% (11% SD)	--
Lake sample 3	**5.8** (1.7% RPD)	**8.6** (8.2% RPD)	**130** (2.6% SD)
Fortified sample 3, N=6	104% (2.8% SD)	122% (3.4%SD)	100% (1.7% SD)
Fortifications: Agilent 10 µg/L, FIA 5 µg/L, PE 25µg/L on 5x diluted sample			

Possible Interferences?

- Ca 5 mg/L
- Fe 0.1 mg/L
- Mg 1.5 mg/L
- Na 2 mg/L
- Si 5 mg/L

$^{30}Si^{16}O^{1}H$
$^{28}Si^{18}O^{1}H$

May also bias colorimetric results

Conclusions

- Control blanks and baseline
- Minimize sample manipulation

- Method 200.8, using Agilent, “no gas” mode, shows promise
- Method 365.1, FIA using “low level P” manifold, has low detection limits but may be biased
- Method 200.8, using Perkin Elmer, O_2 reaction gas, exhibits a strong interference from Si, which may limit its usefulness

Yet to come…

- More investigation of In-line digestion FIA
- Continued evaluation of Surface Water; investigation of sources of bias
- Waste Water Treatment Plant Effluent

Acknowledgements

- Theresa McBride, Stephanie Le, Tom Pearson

Any Questions?