Automation of Total Phosphorus (SM 4500-P F-2011)

BACWA Laboratory Committee

August 12, 2025

EBMUD

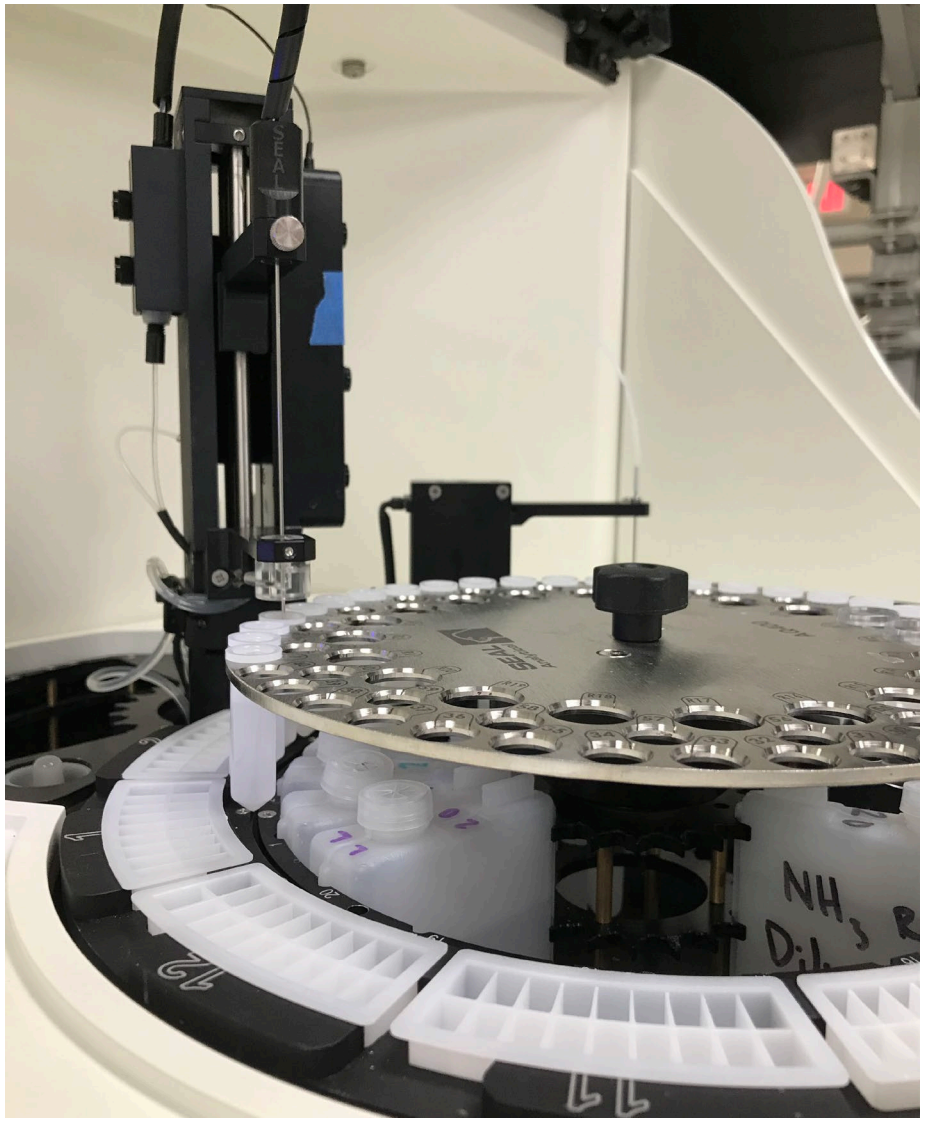
Outline

- Background
- SM 4500-P B
- SM 4500-P E
- SM 4500-P F
- Method Comparison
- Other Validated Methods
- Conclusion

Background

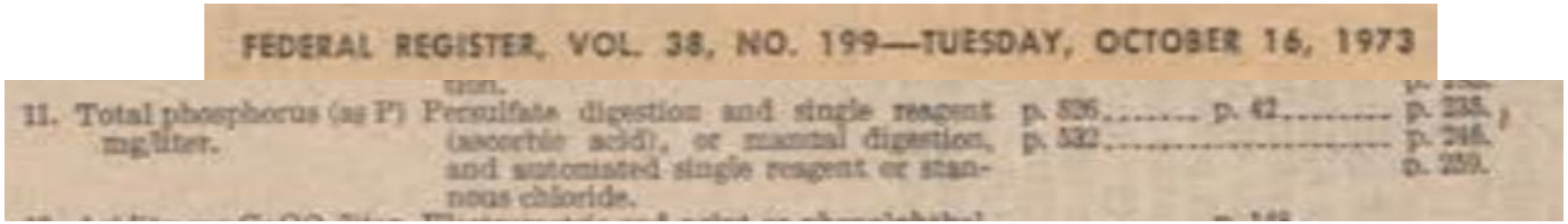
Why?

- Accredited for SM 4500-P E-2011
- Chemistry same
- SEAL AQ400 Discrete for BNR
- Improve efficiency & reduce injuries
- Reduce sample volume & reagents
- Validation/assessment required



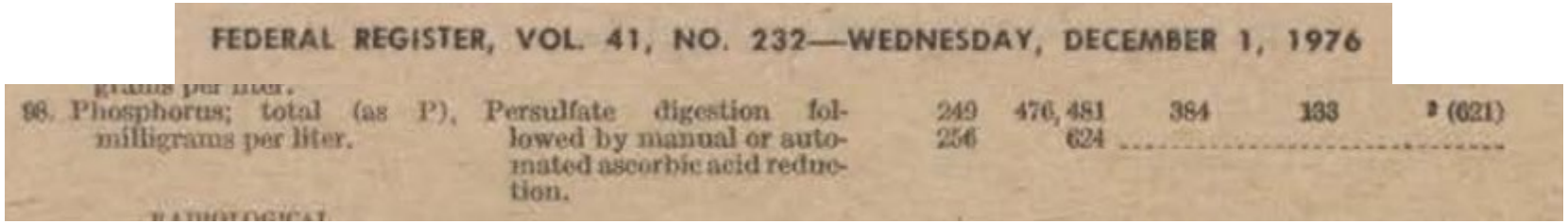
Background

Automated Phosphorus, Total (https://www.epa.gov/cwa-methods/cwa-methods-regulatory-history)



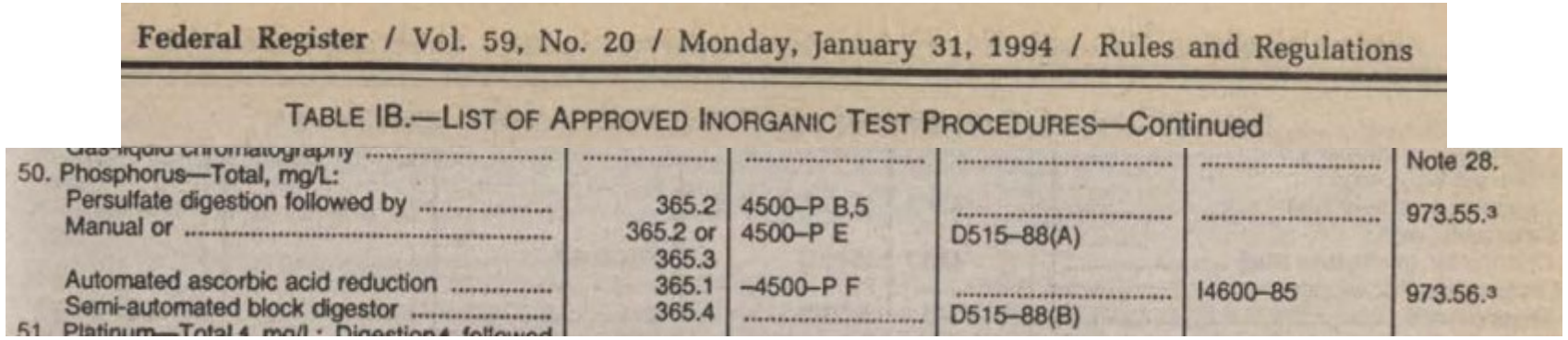
FEDERAL REGISTER, VOL. 38, NO. 199—TUESDAY, OCTOBER 16, 1973

11. Total phosphorus (as P) mg/liter.	Persulfate digestion and single reagent (ascorbic acid), or manual digestion, and automated single reagent or stannous chloride.	p. 535	p. 42		p. 235, p. 246, p. 252.



FEDERAL REGISTER, VOL. 41, NO. 232—WEDNESDAY, DECEMBER 1, 1976

98. Phosphorus; total (as P), milligrams per liter.	Persulfate digestion followed by manual or automated ascorbic acid reduction.	249 256	476, 481 624	384	133	3 (621)



Federal Register / Vol. 59, No. 20 / Monday, January 31, 1994 / Rules and Regulations

TABLE IB.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Gas-liquid chromatography					Note 28.
50. Phosphorus—Total, mg/L:					
Persulfate digestion followed by	365.2	4500–P B,5			973.55.[3]
Manual or	365.2 or 365.3	4500–P E	D515–88(A)		
Automated ascorbic acid reduction	365.1	–4500–P F		I4600–85	973.56.[3]
Semi-automated block digestor	365.4		D515–88(B)		
51. Platinum—Total 4, mg/L: Digestion4 followed					

SM 4500-P B

Persulfate Digestion

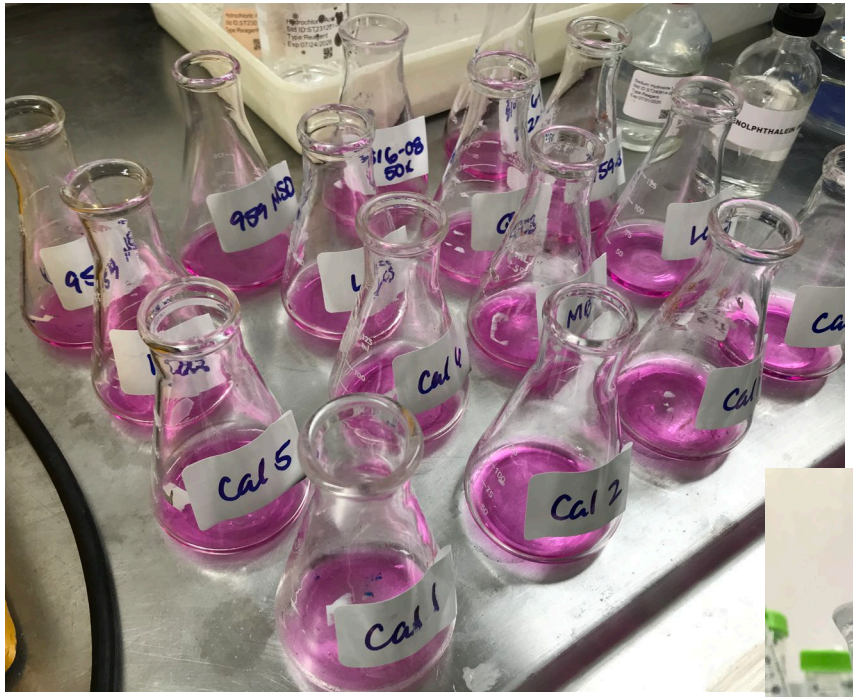
- 50 mL sample
- 0.5 g $K_2S_2O_8$
- 0.5 mL 11 N H_2SO_4
- Evaporate to ~10 mL

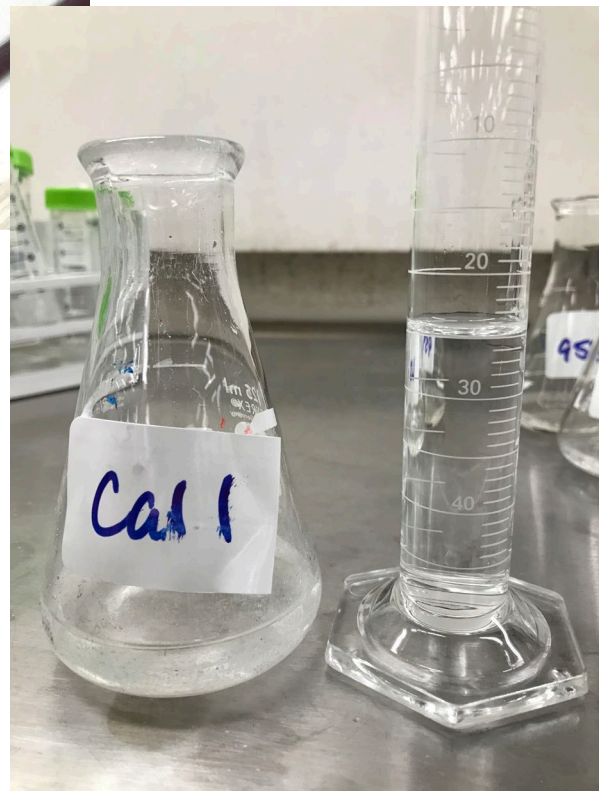
- ~2 hrs

SM 4500-P B

Persulfate Digestion

- pH adjust
- Bring to 50 mL
- Aliquot 25 mL for color development
- ~2 hrs

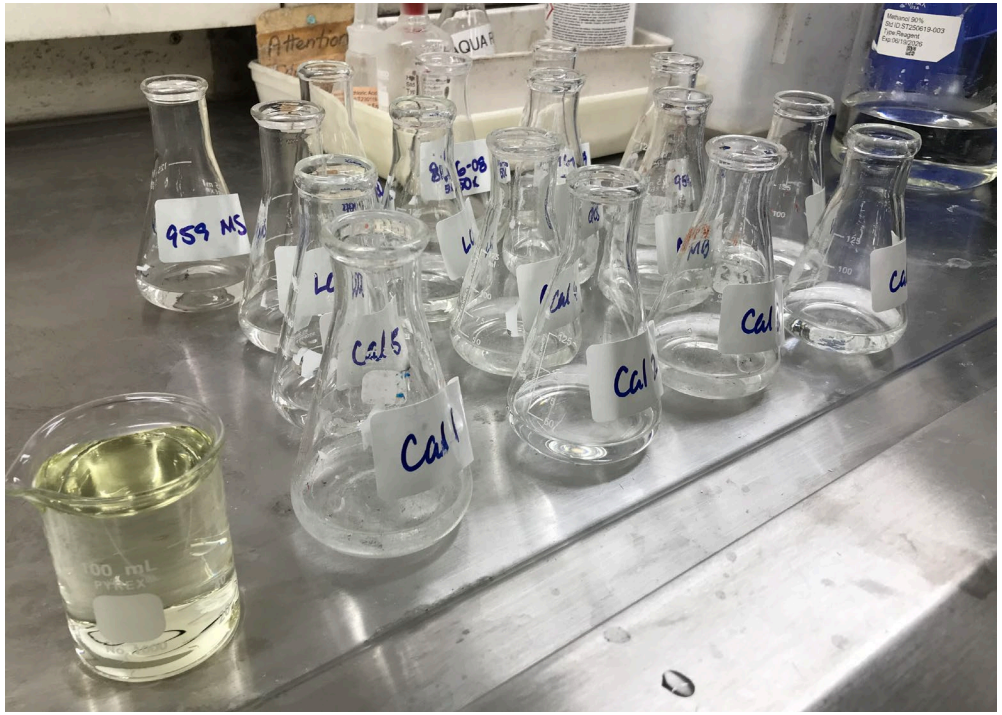




SM 4500-P E

Ascorbic Acid Method

- 25 mL digested sample
- 4 mL combined Color Reagent
- Read between 10-30 min @ 880nm



SM 4500-P F

Automated Ascorbic Acid Method

Method identified automation

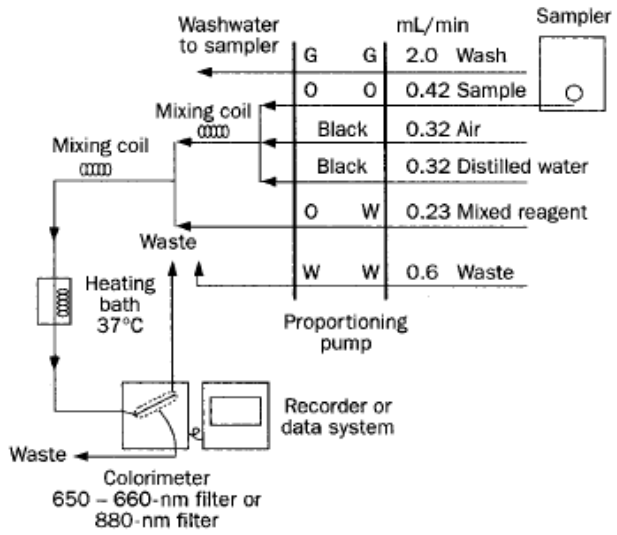


Figure 4500-P:2. Phosphate manifold for automated analytical system.

4. Procedure

Set up manifold as shown in Figure 4500-P:2 and follow the general procedure described by the manufacturer.

Add 0.05 mL (1 drop) phenolphthalein indicator solution to approximately 50 mL sample. If a red color develops, add H_2SO_4 (4500-P.F.3*e*) dropwise to just discharge the color.

40 CFR 136.6 (2007)

(b) *Method Modifications.*

(1) *Allowable Changes.* Except as set forth in paragraph (b)(3) of this section, an analyst may modify an approved test procedure (analytical method) provided that the chemistry of the method or the determinative technique is not changed, and provided that the requirements of paragraph (b)(2) of this section are met.

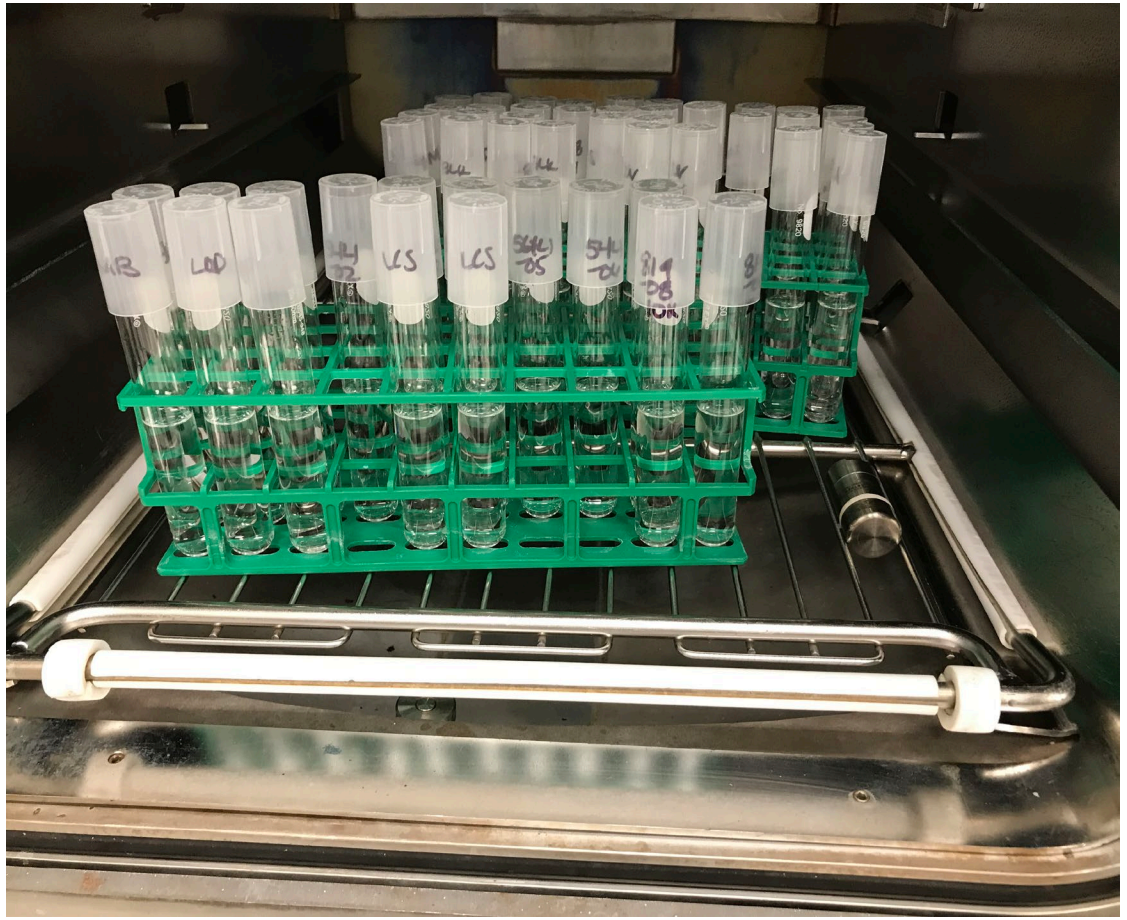
(i) Potentially acceptable modifications regardless of current method performance include changes between automated and manual discrete instrumentation; changes in the calibration range (provided that the modified range covers any relevant regulatory limit); changes in equipment such as using similar equipment from a vendor other than that mentioned in the method (*e.g.*, a purge-and-trap device from OIA rather than Tekmar), changes

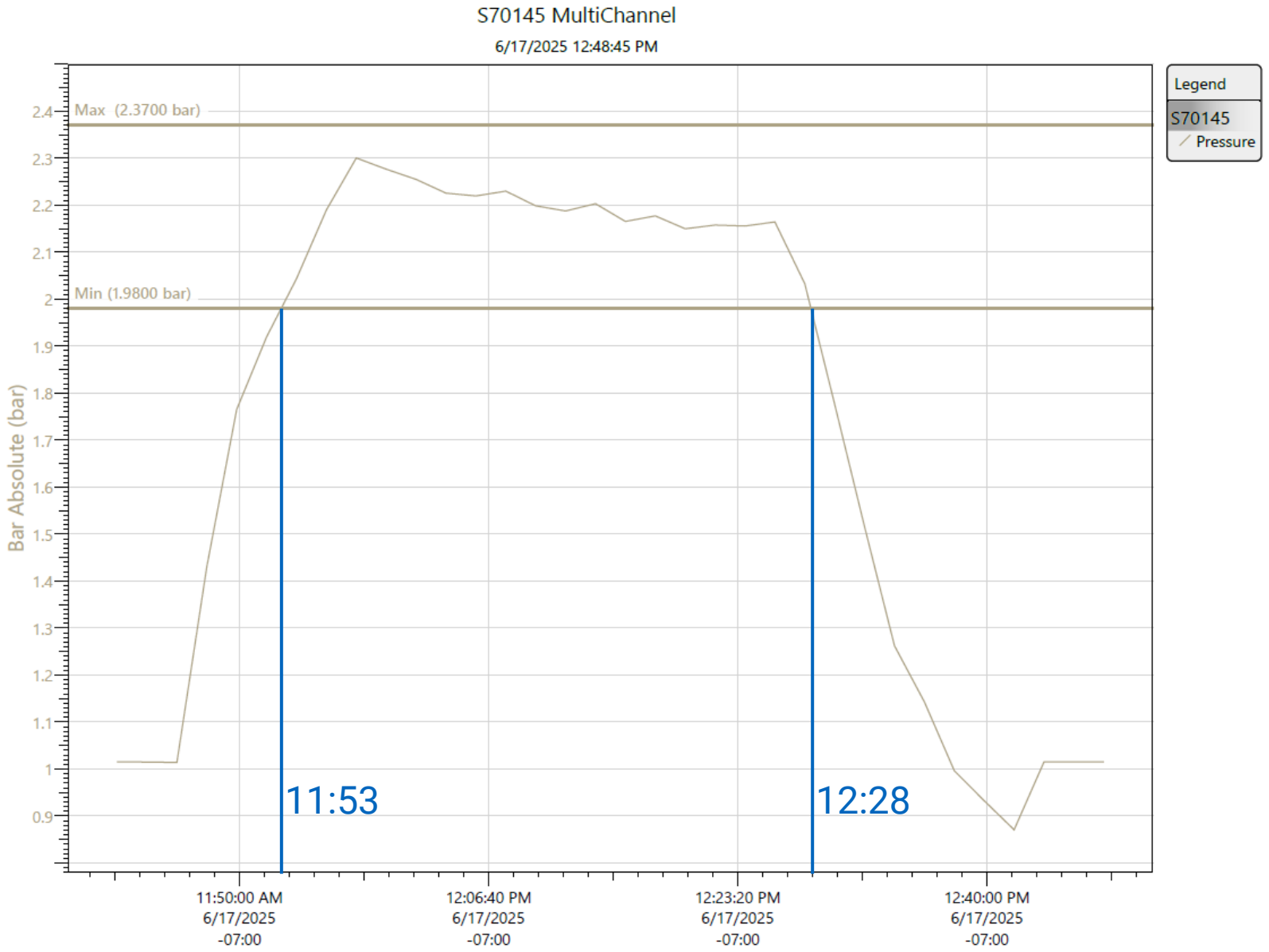
SM 4500-P F

Automated Ascorbic Acid Method

- SM 4500-P B still needed:
  - 10 mL sample
  - 5 mL Digestion Reagent

- Autoclave 30 min (98-137 kPa)



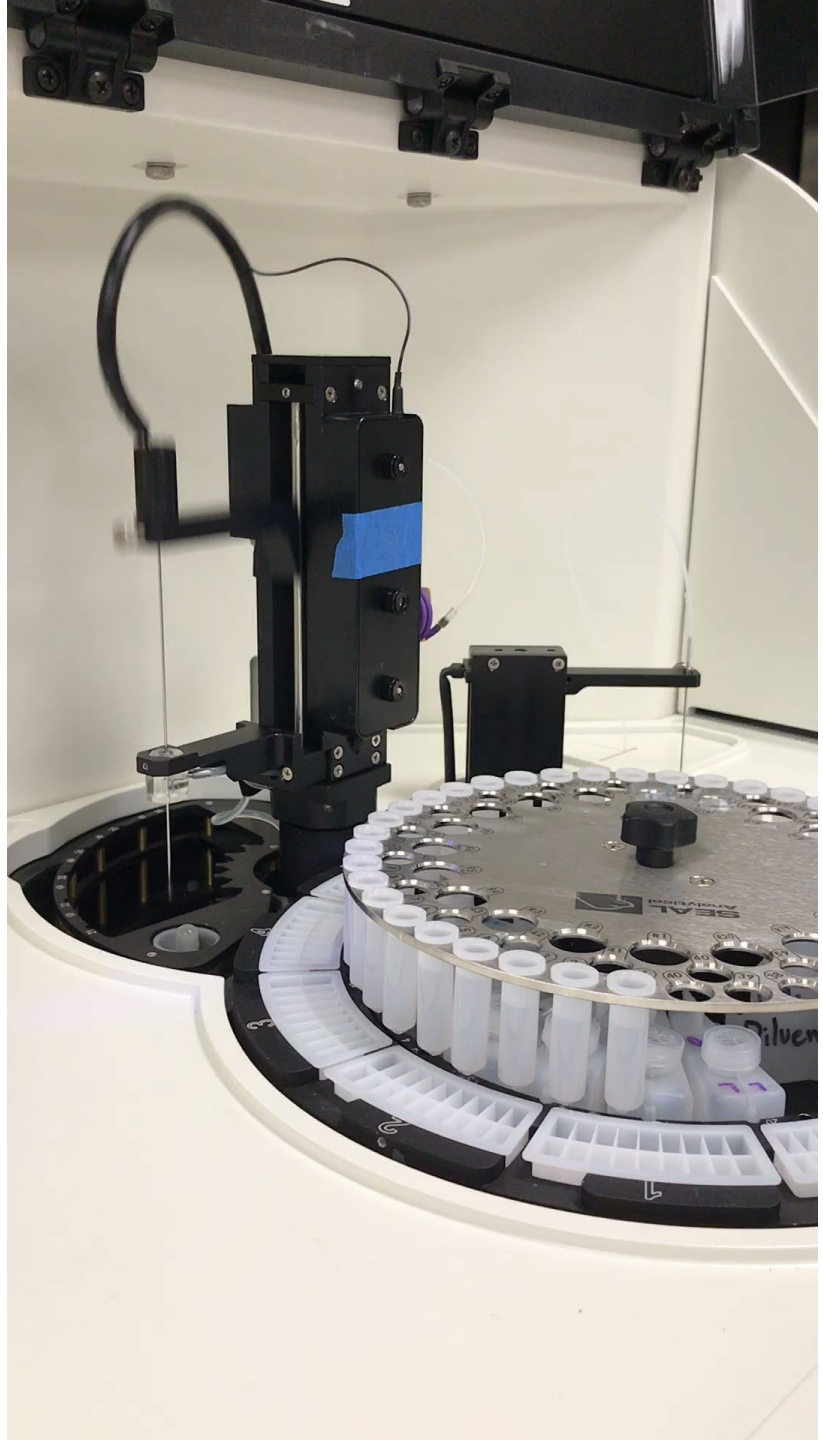


SM 4500-P F

Automated Ascorbic Acid Method

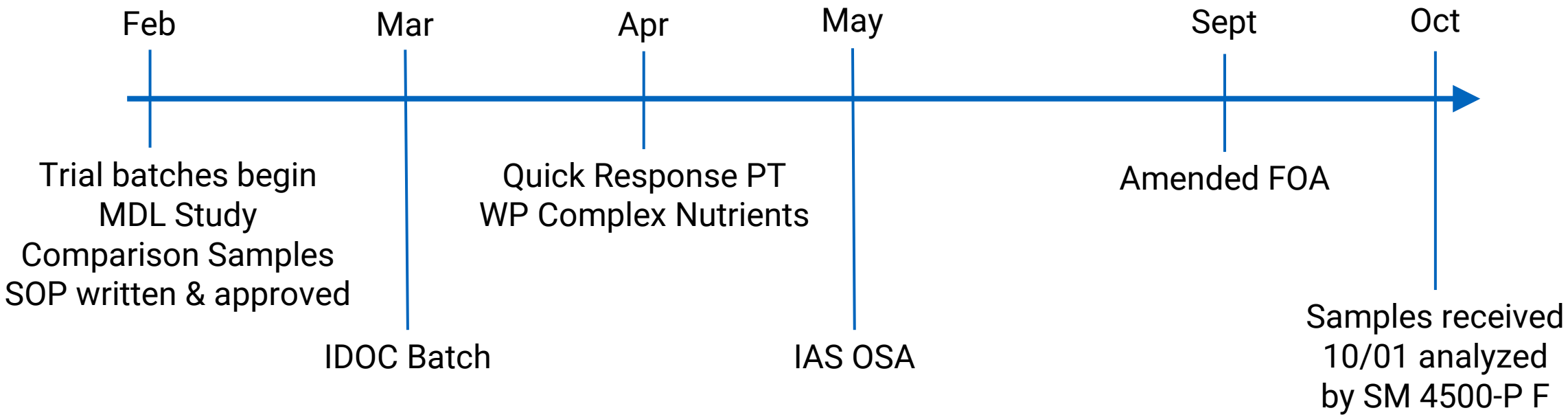
- Load autosampler

- Analyze



SM 4500-P F

Timeline for development (2024)



SM 4500-P F

Ammended FOA list 09/06/2024

East Bay Municipal Utility District

Certificate Number: 1060
Expiration Date: 12/31/2025

108.109	001	Chlorine, Total Residual	SM 4500-Cl F-2011
108.124	001	Cyanide, Total	SM 4500-CN- E-2016
108.125	001	Cyanide, Total	SM 4500-CN E-2011
108.137	001	Hydrogen Ion (pH)	SM 4500-H+ B-2011
108.139	001	Ammonia (as N)	SM 4500-NH3 C-2011
108.139	002	Kjeldahl Nitrogen, Total (as N)	SM 4500-NH3 C-2011
108.175	002	Phosphorus,Total	SM 4500-P E-2011
108.177	002	Phosphorus,Total	SM 4500-P F-2011

Method Comparison

SM 4500-P E-2011

- Persulfate Digestion
  - 50 mL sample
  - 0.5 g $K_2S_2O_8$ + 1.0 mL 11 N H_2SO_4
  - Evaporate to ~10 mL
  - pH adjust, bring to 50 mL
  - Pour off 25 mL
- React 25 mL
- Read within 10-30 min
- 1 batch/day

SM 4500-P F-2011

- Persulfate Digestion
  - 10 mL sample
  - 5 mL Digestion Reagent
  - Autoclave 30 min
- Load Discrete
- 1+ batch(es)/day

Method Comparison

SM 4500-P E-2011

- Cal range: 0.02 – 0.5 mg/L
- MDL: 0.007 mg/L
- QCS using 2nd source (Complex P)
- Documented elapsed time of color reagent

SM 4500-P F-2011

- Cal Range: 0.02 – 1.0 mg/L
- MDL: 0.012 mg/L
- LCS/MS/MSD using 2nd source (Complex P)
- No additional documentation needed

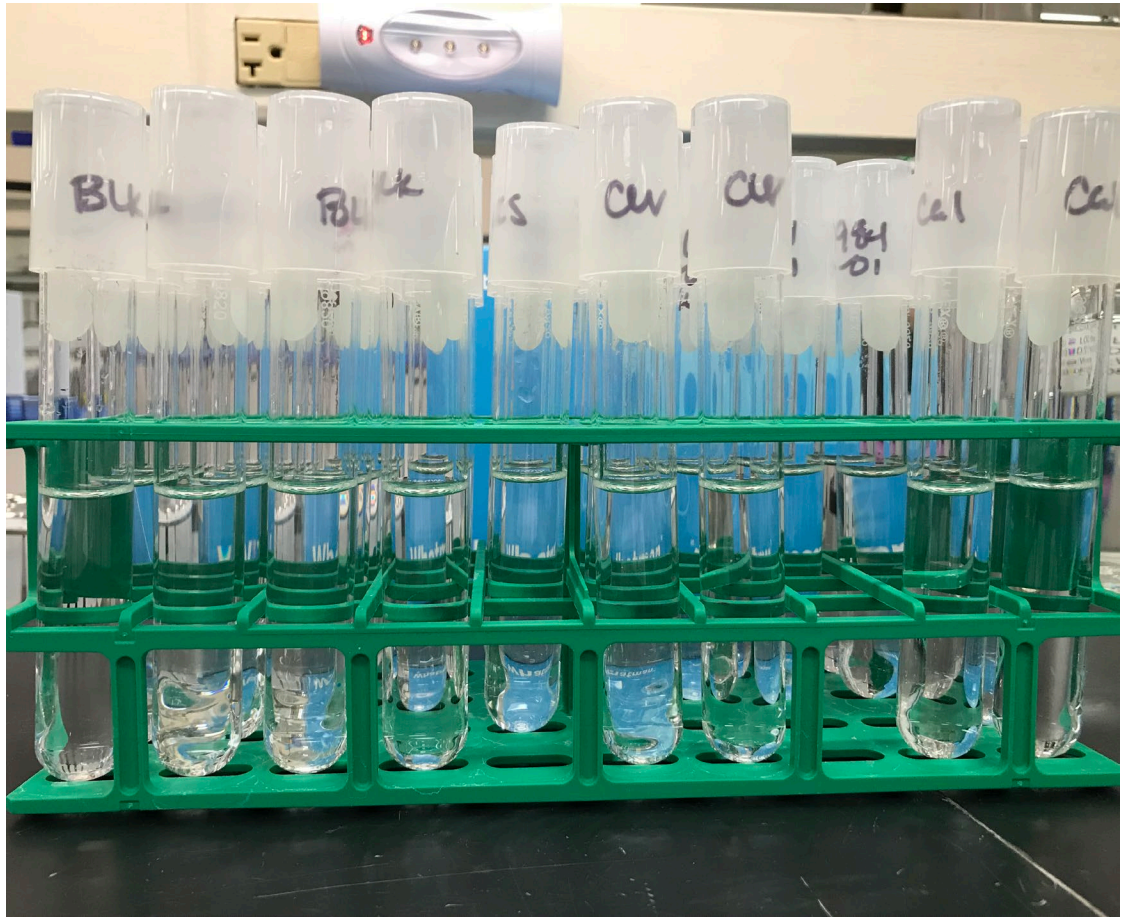
Other Methods on Discrete Analyzer

EBMUD Method	Comments	Status	Frequency Performed
Process Ammonia	For BNR Process Engineers	Complete	**3X / week**
Process Ammonia – LL	Not for compliance	Complete	**1X / month**
Process Ammonia – SW	For Bay monitoring	Complete	N/A
Process NO_3+NO_2	Could seek certification	Complete	N/A
Process NO_2	Could seek certification	Complete	N/A
Phosphorus, Total	**ELAP Certified**	Complete	**2X / month**
Hexavalent Chromium	**No change to ELAP Certificate**	Complete	**1X / month**
Process NO_2 – SW	For Bay monitoring	In Development	N/A
Process NO_3+NO_2 – SW	For Bay monitoring	In Development	N/A
Process o-PO_4	Could seek certification	In Development	N/A
Process o-PO_4 – SW	For Bay monitoring	In Development	N/A
Process TN/TP	For BNR Process Engineers	MDL study complete	N/A

Conclusion

Efficient Total Phosphorus Digestion and Analysis

- Full day analysis reduced to half day
- Reduced repetitive stress injuries
- More than 1 batch can be digested at a time = increased efficiency
- Faster clean-up



Thank you!

Questions?