

# Continuous Flow Analysis of ppb-Level Total Phosphorus in Natural Waters Following Manual Persulfate Digests as an Alternative to Kjeldahl Methodologies

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## INTRODUCTION

The influx of nutrient pollutants from agriculture and other human activities is one of the major factors causing impairment of surface waters within the U.S <sup>(1)</sup>. Excess levels of phosphorus can cause algal blooms and eutrophication of natural water ecosystems. U.S. Environmental Protection Agency (USEPA) regulations call for states to develop nutrient water quality standards for lakes, rivers, wetlands, estuaries, and coastal waters <sup>(2)</sup>. Nutrient discharges from point sources such as wastewater treatment facilities and large animal feed operations are controlled through National Pollutant Discharge Elimination System Permits (NPDES). USEPA Methods 365.1 – 365.4 <sup>(3)</sup> used for monitoring and enforcing typical NPDES permit levels of 0.1 ppm to several hundred ppm Total Phosphorus are not always sensitive enough for the measurements necessary to establish ambient numeric criteria for some natural water ecosystems. This poster presents an automated continuous flow analysis method suitable for measurement of phosphorus at low ppb-levels in natural water samples.

## EXPERIMENTAL

Instrumentation used for this study was an OI Analytical FS 3100 Automated Ion Analyzer consisting of an autosampler, peristaltic pump, valve module with heater, a reaction manifold, and a photometric detector, (Figure 1 and Figure 2). The valve module was equipped with a 200-μL injection loop. The photometric detector was fitted with a 10-mm flow cell and 880-nm filter, as this is the known maximum wavelength value for the molybdenum-blue reaction <sup>(4)</sup>.

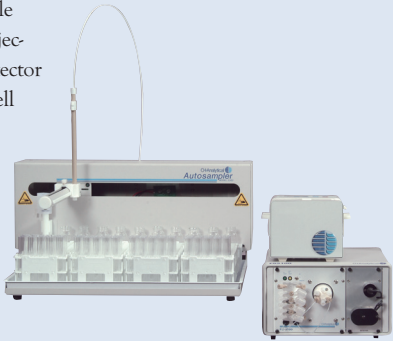


Figure 1. OI Analytical FS 3100 Automated Ion Analyzer

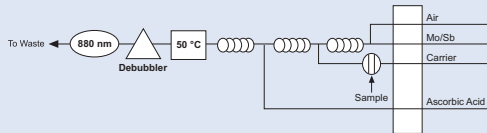


Figure 2. General Flow Diagram of the iSFA System

## RESULTS & DISCUSSION

### Methodology

Phosphorous measurements were performed spectrophotometrically utilizing the reagents and mixtures defined in USEPA Method 365.1 for Total Phosphorus <sup>(2)</sup>. The reagents and procedures detailed in this manual method provide the basis for a continuous flow methodology capable of ppb-level analyses. Optimizations were achieved through modification of experimental parameters such as reaction temperature, pH, reaction kinetics, detector cell path length, and reaction wavelength. Standards and representative samples were analyzed by conducting the molybdenum-blue colorimetric reaction chemistry defined in USEPA Method 365.1 on the FS 3100 continuous flow analyzer. Standards were prepared from potassium phosphate, monobasic solid at concentrations ranging from 5.0–200.0 ppb in a simulated digestion matrix, (Figures 3 and 4). Samples consisted of various phosphorus-containing compounds, and were digested using ammonium persulfate and sulfuric acid on a hot plate for 30 – 40 minutes. This digestion step converts each compound of interest into measurable orthophosphates.

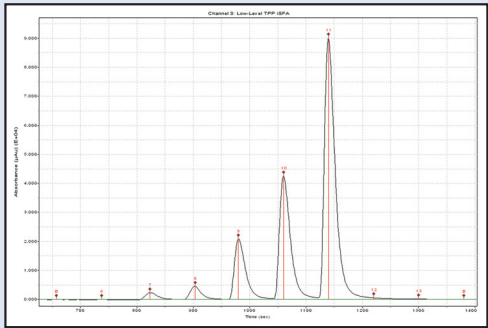


Figure 3. Calibration Peak Response

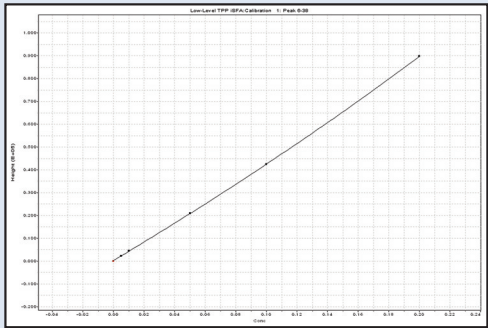


Figure 4. Calibration Curve

The resulting method can be used to analyze for the presence of phosphorus over a range of 5.0–200 ppb, (Table 1). The use of an iSFA format proved essential to facilitate this low-level analysis. In conventional Flow Injection Analysis (FIA) samples can disperse in the carrier stream, inhibiting analysis below certain levels. Conversely, standard Segmented Flow Analysis (SFA) can be subject to high signal-to-noise ratios at certain sample volumes, decreasing the confidence of low-level analyses. Combining the two techniques allowed sufficient sample volumes to be introduced for optimal signal intensity, while conserving the highly efficient mixing conditions needed for ppb-level measurements.

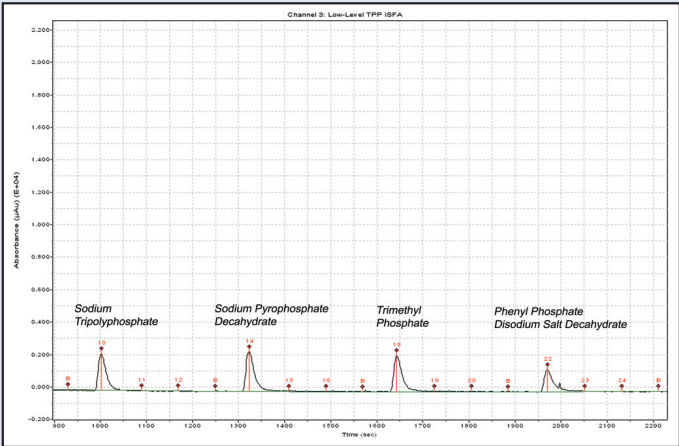


Figure 5. Representative Sample Analyses

Table 2. Representative Sample Data

Analyte	Actual Concentration (Phosphorus)	Calculated Concentration (Phosphorus)	%Accuracy
Sodium Tripolyphosphate	10.0 ppb	10.6 ppb	106
Sodium Pyrophosphate Decahydrate	10.0 ppb	11.4 ppb	114
Trimethyl Phosphate	10.0 ppb	10.5 ppb	105
Phenyl Phosphate Disodium Salt Dihydrate	10.0 ppb	6.7 ppb	68

Table 1. Calibration, MDL, and QC Data

Analyte	Actual Concentration	Calculated Concentration	%RSD	%Accuracy	Correlation (R-Value)
Standard 1	0.00 ppb P	0.00 ppb P	—	—	0.99998
Standard 2	5.00 ppb P	5.13 ppb P	—	—	0.99998
Standard 3	10.0 ppb P	10.7 ppb P	2.13	—	0.99998
Standard 4	50.0 ppb P	49.6 ppb P	—	—	0.99998
Standard 5	100.0 ppb P	100.1 ppb P	0.91	—	0.99998
Standard 6	200.0 ppb P	200.0 ppb P	—	—	0.99998
MDL	—	3.5 ppb P	1.71	—	—
QC	50.0 ppb P	47.7 ppb P	0.47	94.21	—

The optimized iSFA system allowed samples to be analyzed immediately following digestion, ensuring better accuracy. Each sample produced significant peak intensities relative to the noise level at the expected 10.0–ppb level, (Figure 5). Inorganic and polyphosphates were effectively oxidized to measureable orthophosphates. Increased levels of acidity in the sample loop and mixing manifold ensured that the viscosity of the persulfate present in each sample matrix could be effectively mitigated, allowing for quick and efficient sample analyses, (Table 2).

## SUMMARY & CONCLUSIONS

There is a need for a reliable, highly-sensitive (low-ppb) analytical method for testing ambient levels of phosphorus in natural waters. The low-level Total Phosphorus method described in this poster can be used effectively to meet USEPA requirements for low-level nutrient monitoring. The iSFA technique used to develop this method provided the thorough sample-reagent mixing, high peak intensities, and low signal-to-noise ratio necessary for low-ppb level phosphorus analysis.

### REFERENCES

1. Draft Nutrient Criteria Technical Guidance Manual, USEPA, EPA-823-B-05-003, December 2006
2. Federal Register, Vol. 63, No. 122, June 25, 1998.
3. Phosphorus, All Forms. *Methods for Chemical Analysis of Water and Wastewater*; EPA-600/4-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993; Method 365.1–365.4
4. Murphy, J., and Riley, J.P. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Analytical Chemical Act*; 1962, 27, pp 31-36.