

Variability of Low Phosphorus Analytical Measurement

Phosphorus measurements at very low concentrations have been tested and found to be unreliable.

Recent work (e.g., by Coeur d'Alene, ID, City of Spokane, WA, and the City of Las Vegas, NV) demonstrated that phosphorus analytical measurements at very low levels (20 µg/L) are highly variable. Stricter phosphorus discharge requirements are significantly challenging the capabilities of wastewater facilities and accredited laboratories to measure low phosphorus concentrations in the effluent. The major issue associated with low phosphorus measurements appears related to the sample matrix and the digestion methodologies. This WERF study determined the reliability of current phosphorus analysis methodologies, documents current certification programs, and describes enhanced monitoring and management of phosphorus removal at low levels.



This study provides important information on the capability of wastewater treatment facilities and commercial laboratories to measure low levels of phosphorus accurately and reliably.

The results of the study showed a significant variability in phosphorus measurements at concentrations ranging from 3 µg/L to 20 µg/L. Total phosphorus measurements in the 18 MΩ water quality samples and wastewater effluent samples and orthophosphate measurements in wastewater effluent samples, showed a large variability. However, orthophosphate measurements in the 18 MΩ water quality samples showed insignificant variability.

The results demonstrated that as the concentration of phosphorus increases, the variability decreases. A large variability in measurements of phosphorus at low level (< 50 µg/L) was observed even when laboratories followed standard procedures.

The digestion methods and the samples matrix seem to play a central role in the low phosphorus analytical measurements. The presence of some components or substances in the matrix and reagents may have caused negative and positive interferences in the results. Wastewater tertiary effluent and 18 MΩ deionized water were the matrices used in this study. The digestion methods used for total phosphorus determination include perchloric acid, nitric acid-sulfuric acid, and persulfate oxidation methods.

The ascorbic method is followed by all participating laboratories and was successfully used for the determination of orthophosphate.

This study provides important information regarding the capability of wastewater and commercial laboratories to accurately determine low phosphorus concentration (0-20 µg/L). The study findings raise important questions regarding how phosphorus permit limits are established and the ability of utilities to comply with them. Measurements to comply with very low limits (<20 µg/L TP) will inherently vary, making it challenging to determine both the environmental impact of the discharge stream and the performance of the utility.

BENEFITS

- Documents methods to analyze phosphorus in wastewater and associated detection limits.
- Shows high variability in total phosphorus measurements in treated effluent from datasets analyzing the accuracy of measuring orthophosphate and total phosphorus at very low concentrations in clean water and effluent.
- Verifies that high quality, consistent laboratory QA/QC protocol is fundamental to successful phosphorus (P) measurement at very low levels.
- Raises important questions about permit limits and the ability of utilities to comply with these low limits as measurements to very low limits (<20 µg/L TP) will inherently vary.

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Table 1 summarizes commonly used phosphorus analytical methods to measure total phosphorus (TP) and orthophosphate (OP), with the minimum detection limit (MDL) for each method.

Phosphorus Analysis Testing

Ten laboratories were selected to conduct TP and OP analysis in two different sample matrixes. Twelve samples (six duplicates) were prepared in the laboratory and shipped to all 10 laboratories for testing. Each laboratory used its preferred method. Samples were deionized water or effluent from the wastewater treatment plant. Some were spiked with phosphorus, and some diluted with filtered lake water to reduce effluent P concentrations.

As the phosphorus concentration went down, it became more difficult to reach the target or “true” value in the high quality DI water and in the wastewater tertiary effluent. These results were used to evaluate the performance of the laboratories as a group for OP analysis. Similar results were obtained with total phosphorus measurements.

Table 1. Summary of Commonly Used Phosphorus Analytical Methods.

Method	Total Phosphorus	Orthophosphate	MDL (µg/L)
Vanadomolybdophosphoric Acid	✓	✓	200
Stannous Chloride	✓	✓	3
Flow Injection Analysis Orthophosphate		✓	0.7
Manual Digestion & Flow Injection Analysis	✓		2
In-line UV/Persulfate Digestion & FIA	✓	✓	7
Persulfate Method for Determination of TP	✓		2
I-2601-90 (Automated-segmented flow)		✓	10
Kjeldahl Digestion Method	✓		10

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