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ChemScan® Method Summary #40 Ortho-Phosphorous in Water or Wastewater

Phosphorus Analysis Classifications

Phosphorous analysis can be classified by the type of preprocessing performed on a sample. Phosphorous may be found in several forms in water or wastewater, including dissolved form (orthophosphate), inorganic form (reactive plus condensed or acid hydrolyzable phosphate) and organically bound forms. Total Phosphorous is the sum of reactive, condensed and organic phosphate.

Total Phosphorous (TP) is the form of analysis typically cited as an effluent parameter for municipal and industrial wastewater treatment plants. Total Phosphorous in effluent is a measure of the remaining dissolved phosphate plus any insoluble phosphate carried over into the effluent in the form of precipitates or within microbes. Following digestion, all phosphorous is converted into dissolved phosphate for analysis. This is not, however, the form of analysis that is the most useful for process monitoring or control purposes because the Total Phosphorous analysis does not identify the original source of the effluent phosphorous. The most basic form of analysis for process control is reactive phosphorous (orthophosphate), which can indicate the amount of phosphorous that is available to participate in chemical reactions or biological activity. This concentration can be measured before and after chemical precipitation or biological assimilation and settling. Measurement of dissolved reactive phosphorous requires filtration of the sample at 0.45 micron prior to analysis.

ChemScan Analytical Method

The standard ChemScan method for orthophosphate analysis is based on the Vanadomolybdo- phosphoric Acid Method (Standard Method 4500-PC.). Ammonium molybdate reacts under acid conditions with orthophosphate to produce molybdophosphoric acid. Further reaction with vanadium produces Vanadomolybdophosphoric acid, which has strong absorbance spectra in the ultraviolet and visible wavelength range. Dissolved orthophosphate analysis is performed on a filtered sample. If the sample is not filtered (0.45 micron or less) prior to analysis, any acid hydrolyzable phosphate precipitates or particulates in the sample may be redissolved and detected.

On-line orthophosphate analysis using ChemScan can also be performed based on the precipitation of orthophosphate with a known concentration of iron salt followed by measurement of the residual dissolved iron. Liquid ferrous chloride is the reagent of choice, particularly in wastewater with pH of 7 to 8. Lower pH samples may use liquid ferric chloride. Higher pH samples may require buffering with acid in the iron salt solution.

The reaction between ferrous chloride and phosphate can be approximated by the following:

$$3FeCl_2 + 2PO_4^{3-} \text{---> } Fe_3(PO_4)_2 + 6Cl$$

The ChemScan Process Analyzer must be set up to characterize any background iron concentration in the sample prior to introduction of the ferrous reagent. The analyzer must also be calibrated to compensate for the effects of variable sample turbidity and possible interference from nitrate, sulfate, chloride, bromide, organic matter and other metals. The ChemScan multiple wavelength detection and pattern recognition software is fully capable of this analysis and the necessary background correction.

Monitoring System Requirements

Sample extraction points are a function of the phosphate removal process (chemical, biological or combined). (See ChemScan Application Summaries #91, Chemical Phosphorous Removal and #92, Biological Phosphorous Removal.) Chemical precipitation processes typically use aluminum or iron salts, applied upstream of the primary clarifier, in the aeration basin or immediately after the aeration basin. Some designs have multiple addition points. Another option is the use of separate tertiary chemical precipitation tank as a polishing step following the chemical or biological treatment.

The ChemScan Process Analyzer can accommodate samples with up to 150 mg/l of total suspended solids and turbidity of up to 60 NTU. Samples extracted from points in the treatment process ahead of secondary clarification will typically exceed these solids or turbidity specifications. These samples will require filtration or settling prior to analysis to produce a sample meeting ChemScan solids and turbidity requirements. ChemScan has cross flow membrane filters and porous plastic cyclic filters available for use with on-line analyzer systems. Sample points should be selected to assure that fat, oil and grease (FOG) will be low enough not to interfere with the sample filtration method selected for the analyzer system. Raw wastewater samples (especially prior to screens, grit removal, FOG removal and primary clarification) are difficult to analyze and are of questionable value. Much of the Total Phosphorous load on the process is the sum of the soluble phosphate contributed by the incoming wastewater plus the phosphorous from the organic fraction contributed by the Return Activated Sludge plus the phosphorous of any recirculation flow back from the later stages of the treatment process. The ideal initial sample point is after RAS and recirculation addition to the primary effluent.