Determination of Total Phosphorus in Precipitation Samples by Inductively Coupled Plasma-Optical Emission Spectroscopy

Tracy Dombek and Karen Harlin,
Central Analytical Laboratory
National Atmospheric Deposition Program,
Illinois State Water Survey, Champaign
Illinois, 61820, USA

Abstract

The aim of this study was to determine if total phosphorus in precipitation samples could be measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The CAL measures soluble orthophosphate, commonly referred to as "reactive phosphorus" in filtered (0.45 um) samples for the NTN and in unfiltered samples for the AIRMoN. Orthophosphate is measured colormetrically using the Berthelot reaction method by flow injection analysis (FIA). Total phosphorus measurements require a predigestion step that greatly increases analysis time. Traditionally, the colorimetric method for orthophosphate provides lower detection levels than ICP-OES methods; however, the high temperature of the argon plasma used in ICP-OES could eliminate the need to hydrolyze and digest samples prior to colorimetric analysis. In order to enhance ICP-OES sensitivity, a "polyboost" setting that purges the optics with argon gas at about twice the rate for normal analysis to minimize spectral interferences in the UV region was used. A method was developed which yielded a detection limit of 0.009 mg/L for phosphorus, which is consistent with FIA method detection limits. Calcium and sodium have been reported to interfere with phosphorus measurements with ICP-OES. Matrix spikes at the 25th, 75th, and greater than 99th percentile levels of these analytes in precipitation samples were performed and no interferences were observed.

Introduction

Conventional methods for the determination of total phosphorus are difficult and lengthy processes. Heating acidified solutions to high temperatures in order to convert the total dissolved phosphorus into orthophosphate is a specific concern. While these methods offer great sensitivity and a certain degree of flexibility in linear ranges, it is necessary to explore new methods for a faster, easier analysis. Analysis of total phosphorus by ICP-OES is a fresh approach that is attracting more attention particularly for low-level analysis. The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) has been monitoring wet deposition for the last 25 years. The Central Analytical Laboratory (CAL) quantifies how much orthophosphate is in the samples, but does not really exploit how much additional phosphorus is in the samples. This is important when considering that phosphorus is the nutrient that limits the productivity in water bodies. It would be very helpful to quantify how much additional phosphorus is being contributed from wet deposition. While there are many questions that need to be answered, this study was done to measure the sensitivity of the ICP-OES as well as explore possible interferences.

Experimental

Research by Boer et al., suggested that strong matrix effects exist in the presence of calcium and sodium for total phosphorus measurements. This was studied by using existing quality control solutions that contain ion concentrations for sodium and calcium at the 25th percentile, 75th percentile and greater than 99th percentile and spiking them in duplicate with known concentrations of phosphorus and phosphate. Deionized water samples were also spiked in duplicate with the same phosphorus and phosphate standards. Additionally, four NADP/NTN samples were spiked in duplicate with the same stock solutions. All the samples were measured twice on the Varian Vista Pro ICP-OES on different days. This study was carried out using 177.434 nm and 213.618 nm for phosphorus. Yttrium at 2ppm was used as the internal standard. Cesium chloride was used in addition to yttrium only for the first analysis of all of the samples.

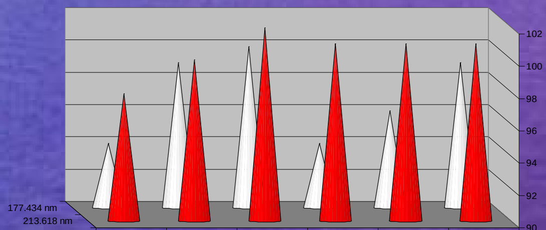
Instrument set-up

Power 1.4kw
Plasma flow 15.0
Auxiliary flow 0.75
Nebulizer flow 0.75
Replicate Read Time: 10 seconds
Instrument stabilization Time: 25 seconds
Sample uptake: 25 seconds
Pump rate 15 rpm
Rinse 40 seconds
Replicates 3

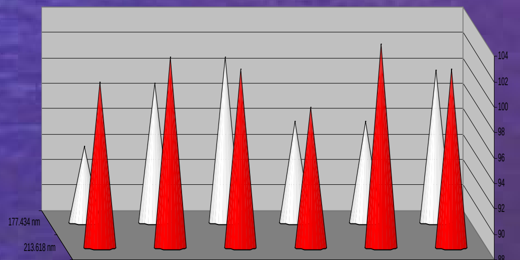
Acknowledgements:
Pam Bedient

References:
De Boer Jan L. M.; Kohlmeyer U.; Breugem P.M.; Van Der Velde-Koerts T. *Fresenius J Anal Chem.* **1998**, 360: 132-136.

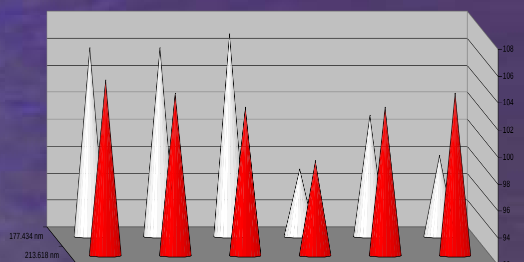
Phosphorus recovery in percentages from samples containing sodium and calcium



	25th percentile	25th percentile	25th percentile	25th percentile	25th percentile	25th percentile
213.618 nm	97.9	100	102	101	101	101
177.434 nm	94	99	100	94	96	99



	75th percentile	75th percentile	75th percentile	75th percentile	75th percentile	75th percentile
213.618 nm	101	103	102	99	104	102
177.434 nm	94	99	101	96	96	100



	> 99th percentile	> 99th percentile	> 99th percentile	> 99th percentile	> 99th percentile	> 99th percentile
213.618 nm	105	104	103	99	103	104
177.434 nm	106	106	107	97	101	98

Results

Minimum detection limits were 9 ppb for both wavelengths studied.

There is no evidence of matrix effects present for the 25th, 75th or greater than 99th percentile concentrations of both sodium and calcium

There were no distinguishable differences when analyzing the samples with the cesium chloride compared to those analyzed without the cesium chloride.

Conclusions

The minimum detection limit determined for the analysis of phosphorus by ICP-OES compares fairly well with the CAL's detection limit for orthophosphate by FIA. However, it will be difficult to detect very small differences in samples where the total phosphorus is only slightly higher in concentration than the reactive phosphorus. When converting a result measured for orthophosphate to a phosphorus value, orthophosphate is slightly over three times greater. If a result has 9 ppb of orthophosphate (right at the detection limit), this same result measured by ICP-OES would be 3 ppb (below the detection limit).

In order to detect measurable differences, samples containing levels greater than the detection limit of orthophosphate need to be analyzed. These samples will very likely be contaminated samples. Samples collected from AIRMoN will be studied further to determine if there are measurable differences between reactive and total phosphorus. A study will be completed that compares undigested samples analyzed by ICP-OES with samples digested and analyzed by FIA.