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**ORTHO-PHOSPHORUS AND TOTAL PHOSPHORUS DETERMINATION BY THE
ALPKEM CONTINUOUS FLOW ANALYZER
A303-S203**

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Summary of Method

Ortho Phosphate reacts with molybdenum(VI) and antimony(III) in an acid medium to form a phosphoantimonymolybdenum complex. This complex is subsequently reduced by ascorbic acid to a heteropolyblue with an absorbance maximum at 880nm.

Interfering Substances

Ferric iron up to 70mg/L, copper up to 10mg/L and silica up to 10mg/L do not interfere. Filter turbid samples prior to analysis (1).

Sample Handling and Preservation

Analyze samples as soon as possible. Samples may be held for 48 hours if refrigerated at 4°C (2). Or frozen for 2 months.

Reagents

Levor IV
Stock Sulfuric Acid, 5N (500mL)
Sulfuric Acid (conc): 70mL H₂SO₄ (FW 98.08)
Deionized Water

Cautiously add 70mL of concentrated sulfuric acid to 300mL of deionized water contained in a 1000mL volumetric flask. Cool to room temperature and transfer to a 500mL volumetric flask. Dilute to the mark with deionized water.

Caution: The dilution of sulfuric acid in water generates a great amount of heat.

Stock Antimony Potassium Tartrate (100mL) (APT)
Antimony Potassium Tartrate: 0.3 g K(SbO)C₄H₄O₆·1/2H₂O (FW 333.94)
Deionized Water

Dissolve 0.3 g of antimony potassium tartrate in 80mL of deionized water contained in a 100mL volumetric flask. Dilute to the mark with deionized water. Store at 4°C in the dark.

Stock Ammonium Molybdate (100mL) (AMMO)
Ammonium Molybdate: 4 g (NH₄)₆MO₇O₂₄ * 4H₂O (FW 1235.95)
Deionized Water

Dissolve 4 g of ammonium molybdate in 70mL of deionized water contained in a 100mL volumetric flask. Dilute to the mark with deionized water. Store at 4°C in a polyethylene bottle.

Stock Ascorbic Acid (100mL) (AA)

Ascorbic Acid: 1.8 g C₆H₈O₆ (FW 176.13)

Deionized Water

Dissolve 1.8 g of ascorbic acid in 70mL of deionized water contained in a 100mL volumetric flask. Dilute to the mark with deionized water. Stable for 1 week if stored at 4°C.

Working Reagent (100mL)

Stock Sulfuric Acid, 5N 50mL

Stock Antimony Potassium Tartrate 5mL

Stock Ammonium Molybdate 15mL

Stock Ascorbic Acid 30mL

Add reagents in the order stated and mix after each addition. Prepare reagent daily.

Alternate Working Reagents (Prevents excessive baseline drift and improves resolution)

Ascorbic Acid Reagent: Dissolve 0.54 g of ascorbic acid in 100ml of deionized water in a 100ml volumetric flask. Transfer to a 125ml erlenmeyer flask, add two-six drops of Levor IV and mix.

Alternate Combined Reagent: Combine and mix in this order. 45ml 5N H₂SO₄, 15ml DI, 5ml APT, 15ml AMMO.

Calibrants

Stock 100 mg P/L (1L)

Potassium Dihydrogen Phosphate: 0.4393 g KH₂PO₄ (FW 136.09)

Deionized Water

Dissolve .4393 g of dry potassium dihydrogen phosphate in approximately 900mL of deionized water contained in a 1L volumetric flask. Dilute the solution to the mark with deionized water.

Stock 1000mg P/L (1L)

Purchase a 1000mg P/L certified reference standard (CRS).

Working Calibrants

Prepare a 10 mg/L P standard by making a 10 ml to 100 ml dilution of the 100 mg/L stock or a 1 ml to 100 ml dilution of the 1000 mg/L stock in a volumetric flask with DI water. Then prepare the following standards.

Use adjustable, microliter pipets to add the designated volumes of stock calibrant, tabulated below, to the required number of volumetric flasks that each contain approximately 85mL of deionized water and mix it well. Keep these solutions tightly sealed. If samples are preserved with sulfuric acid, add acid in the same proportion to each volumetric flask.

Prepare calibrants in the desired range as suggested by the table below.

Calibration

Run the standards from the highest to the lowest. Include deionized water as the lowest concentration and assign it a value of 0.0 mg/L. The correlation coefficient for the curve should be > 0.995 and > 0.999 is preferred.

Running Samples

After calibrating, the initial QC samples should be run as a check of the calibration curve. If the curve is found to meet the QC criteria the sample run can begin. Refer to the Alpkem RFA 300 analytical methods notebook found in the laboratory for more specifics about the analysis. All samples should be within the range of the standards. Samples that are off scale should be diluted and rerun. Make a note of the dilution factor.

Quality Assurance

At the beginning and end of each run, run a QC sample (NIST traceable) with known concentration, a calibration standard and a blank. Sample duplicates, sample spikes, a calibration standard and blanks should be run at a frequency of 10%. Blanks should read no greater than two times the detection limit. Other values should meet the criteria as set forth in the specific project QAPP. If a value is not acceptable, the problem should be resolved and samples rerun from the point where the QC's were found to be in control. The detection limit is about 0.003mg/L.

Nominal Concentration (mg L ⁻¹)	Stock Calibrant Volume (mL) of 10.0mg/L
0.003	1.0mL@0.3mg/L/100ml DI
0.01	0.2ml/200ml DI
0.05	1.0mL/200ml DI

Notes:

This SOP has described the general operation and procedures for the ALPKEM RFA 300 system. Manuals and notebooks in the laboratory contain more information about the analysis and should be referred to by the analyst.

References

1. Standard Methods for the Examination of Water and Wastewater, 14th Ed. 1975, p. 625.
2. Methods for Chemical Analysis of Water and Wastewater, March 1984, EPA-600/4-79-020, "Sample Preservation", p. xvii, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH. 45286.
3. Methods for Chemical Analysis of Water and Wastewater, March 1984, EPA-600/4-79-020, "Phosphorous, All Forms", Method 365.1 (Colorimetric, Automated Ascorbic Acid).
4. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Samples, November 1992, EPA/600/R-92/121, Method 365.5.
5. Methods for the Determination of Chemical Substances in Environmental Samples, August 1993, EPA/600/R-93/100, "Determination of phosphorus by Automated Colorimetry, Method 365.1.
6. Nutrient Analytical Services Laboratory, Chesapeake Biological Laboratory, University of Maryland, Center for Environmental Science, Solomons, Maryland 20688-0038, Standard Operating Procedures, Technical Series No. 158-97.
7. RFA 300 Operation Manual, Revised 1/91. ALPKEM Corp., Clackamas, OR 97015.
8. SoftPac Plus User's Guide, Revision 7/90. ALPKEM Corp., Clackamas, OR 97015.