ANALYSIS OF ORTHO PHOSPHATE USING THE BRAN+LUEBBE SEGMENTED FLOW ANALYZER

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1. SCOPE AND APPLICATION

1.1. Concentrations of orthophosphate (PO_4^{3-}) in aqueous samples (surface, ground, effluents, influents and saline waters) and solid samples (soils and sediments) are determined using a Bran+Luebbe segmented flow analyzer. The calibration range is from 0.005 mg P/L to 0.30 mg P/L. Samples containing PO_4^{3-} levels higher than 0.30 mg P/L are diluted prior to analysis. The Method Detection limit (MDL) is 0.004 mg P/L. The Practical Quantitation Limit (PQL) is 0.010 mg P/L.

1.2. The aqueous sample tests covered by this SOP are W-PO4 and W-PO4-F.

1.3. For solid matrices, an aqueous extraction is performed (see DEP SOP NU-044) and the resulting extract is analyzed as an aqueous sample. The solid test covered by this SOP is S-PO4. The MDL is 0.40 mg P/kg. The PQL is 1.0 mg P/kg.

2. SUMMARY OF THE METHOD

2.1. The described procedure is based on EPA Method 365.1, Rev. 2.0 (1993) and the Bran+Lubbe method G-146-95 Rev. 3.

2.2. Orthophosphate reacts with molybdenum (VI) and antimony (III) in an acid medium to form an antimony-phospho-molybdate complex. The complex is reduced with ascorbic acid to form a blue complex that absorbs at 880 nm.

2.3. Interferences: High concentrations of iron may cause precipitation of phosphorous. Samples with background absorbance at the analytical wavelength may interfere. Color correction is used to eliminate sample background interference. High conductivity samples can cause interferences in matrix spike recoveries of orthophosphate. If necessary, samples may be diluted with de-ionized (DI) water prior to analysis to minimize interference effects.

3. EQUIPMENT AND SUPPLIES

3.1. Bran+Luebbe segmented flow analysis system:

3.1.1. Bran+Luebbe XY-3 autosampler - sample time/wash time 36/36 (set using software).

3.1.2. AA3 pump control via the AACE software. The red switch must be in position “Run” and the black switch in position “Normal”.

3.1.3. AA3 analytical manifold, heater temperature at 37 ^{o}C, (see Bran+Luebbe Method for MT-16 manifold setup).

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3.1.4. AA3 Digital Colorimetric detector. The AA3 Digital Colorimetric detector contains a 10 mm flow cell and 880 nm wavelength filter.

3.1.5. Pump tubing:

Orthophosphate (channel 1) -

1.	Blk/Blk (0.76 mm)	Air
2.	Red/Red (1.14 mm)	Color Reagent (4.2.2.)
3.	Wht/Org (0.64 mm)	Sample
4.	Wht/Org (0.64 mm)	Ascorbic acid (4.2.3.)
5.	Wht/Org (0.64 mm)	DI water

Color correction (channel 2) -

1.	Blk/Blk (0.76 mm)	Air
2.	Red/Red (1.14 mm)	Acid Reagent (4.2.1.)
3.	Wht/Org (0.64 mm)	Sample
4.	Wht/Org (0.64 mm)	Ascorbic acid (4.2.3.)
5.	Wht/Org (0.64 mm)	DI water

Sampler wash line -

1.	Grn/Grn (1.85 mm)	DI water

3.1.6. Glassware and pipettes – Assorted Class A type volumetric glassware, glass beakers, and variable Eppendorf pipettes.

3.1.7. Assorted clear and brown Nalgene bottles for reagent storage.

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 and NU-042)

Note: Wash all glassware with 1:2 HCl and rinse at least three times with DI water.

Note: All reagent preparations must be documented in the Reagent and Standard Logsheet for Ortho Phosphate analysis (NU-RGTSTD_PO4). This excel sheet is located at \\FLDEP1\DEAR\LABS\Lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\PO4\. It needs to be updated whenever a reagent is newly prepared. For every analysis file print the Reagent and Standard Logsheet and place it into the analysis folder.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in the reagent and standard logsheet submitted with each analysis folder. The Certificate of

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Analysis for the standard reference material (4.1.9.) is kept in a binder in C307. If available, a Certificate of Analysis for each purchased reagent is maintained in the REAGENT_PREP\PO4\ folder. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

4.1. Chemicals:

4.1.1. Ammonium Molybdate, $(NH_3)_6Mo_7O_{24}*4H_2O$

4.1.2. Antimony Potassium Tartrate, $K(SbO)C_4H_4O_6*1/2\ H_2O$

4.1.3. Ascorbic Acid, $C_6H_8O_6$

4.1.4. Sulfuric Acid, concentrated H_2SO_4

4.1.5. Potassium Dihydrogen Phosphate, KH_2PO_4

4.1.6. Sodium Dodecylsulfate (SDS), $C_{12}H_{25}NaO_4S$

4.1.7. Sodium Hypochlorite, NaOCl (Generic bleach, no additives)

4.1.8. Copper Sulfate, $CuSO_4*5H_2O$

4.1.9. Standard Reference Material (ALTQC) from Environmental Resource Associates (ERA)

4.1.10. Hydrochloric Acid, concentrated HCL

4.1.11. Sodium Hydroxide pellets, NaOH

4.2. Reagents:

4.2.1. Acid Reagent (5 N H_2SO_4) - To a 1 L flask containing approx. 600 mL DI water, add 22 mL of concentrated H_2SO_4 (4.1.4.) while stirring. Cool flask in a water bath and bring to volume. Add 2 g of SDS (4.1.6.) and mix thoroughly. Store in a refrigerator. Holding time, 5 days with SDS.

4.2.2. Color Reagent - To a 1 L flask containing approximately 600 mL DI water, first add 0.10 g of antimony potassium tartrate (4.1.2.) followed by 2.4 g ammonium molybdate (4.1.1.). Slowly, with swirling, cautiously add 22 mL of concentrated sulfuric acid (4.1.4). Add 2 g of SDS (4.1.6.) and mix well. <u>The order in which the reagents are added is important.</u>

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Bring to volume with DI water. Store in a refrigerator using an airtight amber container. Holding time, 5 days.

4.2.3. Ascorbic Acid Reagent - To a 1 L flask containing approx. 500 mL DI water add 11.0 g L-ascorbic acid (4.1.3.). Bring to volume with DI water. Store in a dark bottle in a refrigerator. Holding time, 5 days.

4.2.4. Bleach Cleaning Solution - Prepare a 1 % v/v bleach solution by adding 1 mL Bleach (4.1.7.) to 100 mL DI water. Invert to mix. The bleach solution is made fresh daily.

4.2.5. Sodium Dodecylsulfate solution - Add 2 g of SDS (4.1.6.) to 1 L DI water. Holding time, 180 days.

4.2.6. Copper Sulfate (Color Correction Reagent) - To a 1 L flask containing approx. 600 mL of DI water, add 4.6 g of copper sulfate (4.1.8.). Bring to volume with DI water. Store in refrigerator. Holding time, 180 days.

4.2.7. Carrier (DI water) - The carrier container is filled with fresh DI water daily. DI water poured fresh every day is also used for all blanks (BLK, CCB) including the method blanks (MBLK).

4.2.8. HCl Cleaning Solution - Add 800 mL DI water to a 1 L volumetric flask. Add 100 mL concentrated HCL (4.1.10.) and bring to volume with DI water. Invert to mix.

4.2.9. 1 N NaOH Cleaning Solution - Add 800 mL DI water to a 1 L volumetric flask. Add 40 g NaOH pellets (4.1.11.) and bring to volume with DI water. Invert to mix.

4.3. Calibration Standards and Quality Control Standard:

4.3.1. TP/Orthophosphate 1000 mg P/L stock standard - To a 1 L flask containing approx. 400 mL DI water add 4.394 g anhydrous potassium dihydrogen phosphate (4.1.5.) which has been dried overnight at 105 ^{o}C. Dilute to the mark with DI water and invert 12 times. Store in refrigerator. Holding time, 180 days.

4.3.2. TP/orthophosphate 10 mg P/L working standard and spiking solution - Into a 100 mL flask containing approx. 50 mL DI water pipette 1.0 mL of the 1000 mg P/L stock standard (4.3.1.). Bring to volume with DI water. Store in refrigerator. Holding time, 30 days.

4.3.3. Orthophosphate working calibration standards - Prepare standards by pipetting the specified amounts of the concentrated stock standards into

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500 mL volumetric flasks and fill to volume with DI water. Store in refrigerator. Holding time, 30 days.

STD	(mg P/L)	Volume of 10 mg P/L (4.3.2.)	Final Volume
C1	0.005	0.25 mL	500 mL
C2	0.010	0.50 mL	500 mL (PQCK1)
C3	0.020	1.0 mL	500 mL
C4	0.050	2.5 mL	500 mL
C5	0.100	5.0 mL	500 mL (CHCK1)
C6	0.200	10.0 mL	500 mL
C7	0.300	15.0 mL	500 mL (DRIFT(1))

4.3.4 ALTQC standard:

4.3.4.1. The supplier for the standard reference material (currently Environmental Resource Associates) differs from the supplier of the calibration standards. This quality control standard (4.1.9.) is prepared from the ampule according to the manufacturer's instructions. Store ampule in refrigerator. For the concentration and expiration date of the ampule, see the manufacturer's certificate. Store in refrigerator. Holding time of the prepared stock standard, 180 days.

4.3.4.2. The stock ALTQC standard is diluted appropriately with the carrier (4.2.7.) so that the concentration falls within the calibration range. Store in the refrigerator. Holding time of the working solution, 30 days.

5. SAMPLE PREPARATION, PRESERVATION, AND STORAGE (SEE DEP SOP NU-033)

5.1. Upon receipt, samples are stored in the Nutrient refrigerators in the receiving room of the DEP laboratory at ≤ 6°C (not frozen). **Samples must be analyzed for orthophosphate within 48 hours of collection or results will be Q qualified.**

5.2. Remove the samples from the refrigerator following the proper protocols to preserve the samples' chain of custody. Allow samples to come to room temperature before pouring them into the sample cups for analysis.

5.3. Solid matrix samples first undergo an aqueous extraction procedure according to DEP SOP NU-044.

6. SAMPLE ANALYSIS/QUANTITATION

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6.1. Read the manufacturer's operation manual before proceeding. See DEP SOP NU-033.

6.2. Bran+Luebbe AA3 Detector and Pump Start-Up Procedure:

6.2.1. Turn on the autosampler, allow needle to return home. Turn on the AA3 pump. Finally turn on the AA3 Digital Colorimetric detector (heater will take approximately 15 min to come to temperature). Then secure platens for the tubing being used.

6.2.2. Double click the **AACE** icon on the desktop to start the main program. Click on **SYS.1 [AA3]** which minimizes it on screen.

6.2.3. Click **Charting** (make sure that the pump's two rocker switches are set to Run and Normal (speed) respectively) to display Channels 1 and 2 on screen.

6.2.4. Flush the reagent lines with the following reagents by placing the lines sequentially in containers containing the reagents listed below. Line flush reagents (in order):

a. DI water for 10 minutes

b. 2 g/L SDS solution for 10 minutes on fast

Note: Keep the sampler wash line in the DI water container.

6.2.5. Place all reagent tubes into reagent bottles and run for 10 minutes. Right-click and select **Auto Base** (normally 5 %), check the baseline is stable.

6.2.6. While proceeding with the wash procedure (6.2.4.), batch the samples using the following procedure:

6.2.6.1. Samples with conductivities greater than 5000 µmhos/cm are batched separately. If no conductivity value is given, batch according to the matrix identification in LIMS. Effluents are batched separately.

6.2.6.2. For each batch (maximum of 10 samples), prepare:

- One MBLK (4.2.7.)
- A matrix spike plus a duplicate of the QC sample or a duplicate matrix spike.

  The 0.10 mg P/L matrix spikes are prepared by adding 100 µL of the spiking solution (4.3.2.) into 10 mL portions of a selected sample. Spike code LO3.

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Select one sample per batch as the QC sample (to spike and/or analyze in duplicate) that is representative of the samples in the batch. If the selected sample has high PO_4^{3-} level (i.e., the combined sample and spike concentration is outside the calibration range), select another sample to spike from the same batch. Alternatively, if all samples are high, the entire batch may be diluted.

Samples may be screened for dilution by adding three drops of color reagent (4.2.2.) followed by two drops of ascorbic acid solution (4.2.3.) to approx. 4 mL of sample in a sample cup. If a blue hue develops the sample may be diluted prior to analysis. Start with a two-fold dilution. Dilute further only if necessary. Make sure the dilution factor is recorded on the bench sheet (see section 6.2.7.).

- One laboratory fortified blank (LFB) following the same procedure as above substituting carrier (4.2.7.) for the sample.

6.2.6.3. Additional samples may be added to the run as they become available during the day. Samples may also be added to predefined batches until they contain a maximum of 10 samples.

6.2.7. Once batching is done, start typing up the run - Click **Set Up → Analysis → Ortho with Color (new) → New Run → Tray Protocol**. Click "OK" to save the run, and print the tray protocol for a bench sheet (this printout will also contain the method parameters).

An example run sequence includes:

Primer (Copper sulfate reagent, 4.2.6.)
Drift (1), (0.300 mg/L standard C7, 4.3.3.)
Drift (2), (Copper sulfate reagent, 4.2.6.)
BLK (DI water, 4.2.7.)
Channel 1 Calibrants (STD C1-C7, 4.3.3.)
Channel 2 Calibrant (Copper sulfate reagent, 4.2.6.)
High (0.300 mg/L standard C7, 4.3.3.; this cup along with the next two blanks is used to calculate carryover)
Low (DI water, 4.2.7.)
Low (DI water, 4.2.7.)
BLK
PQCK1 (STD C2, 4.3.3.)
ERAQCPO4A (ALTQC, 4.3.4.)
CCB (DI water, 4.2.7.)
CHCK1 (STD C5, 4.3.3.)

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Batched samples, with an **MBLK**, **LFB**, and spikes for each batch (6.2.6.)
BLK
Baseline (DI water)
CCB
CHCK1
Drift (1)
Drift (2)
BLK
BLK
End

6.2.8. Place fresh standards in the standards rack on the autosampler. Standards may be kept in the rack covered with parafilm after a run in case the instrument has to be run more than once in one day. Standards must not be stored in the rack overnight.

6.2.9. While waiting for the baseline to stabilize (6.2.5.), pour up the run. Use the printed bench sheet to pour up QC and samples in order. Use clean 4 mL autosampler cups. Rinse each cup with a small amount of sample before filling the cup and placing it in the correct spot on the analysis tray. It is recommended to label each cup with a permanent (Sharpie) marker to avoid confusion.

6.2.10. After pouring up the samples, check the baseline for stability. Make sure it is stable since the baseline cannot be adjusted after starting the run. When ready to start, go to **Run → Start → Ortho with Color (new) →** select **run** (scroll down). Double click on "**Current Run**" and enter the analyst's initials next to the Operator field followed by Instrument A next to Instrument. Click "**Start**".

6.2.11. Monitor the run for bad peaks (peak shape, air spikes, etc.) and failing QC. Rerun any samples with poor peak shape at the end of the run. Rerun blanks (field blanks, equipment blanks) twice for confirmation if the result in the ongoing run indicates that they may be failing after the final integration is performed when the run is stopped. High samples requiring additional dilutions are also run at the end. Make note of the dilution factors on the bench sheet.

6.2.12. When ready to stop the run, go to **Setup → Analysis → Ortho with Color (new)**, and double click on **Run → Tray Protocol**. Add the label "End" at the cup number where the run should stop. Make sure that all samples are bracketed by passing CCVs and blanks (see section 8.2,). There should be a blank, CCB, CHCK1, Drift (1), Drift (2), and three blanks for the final Baseline reading (in that order) prior to the cup labeled "End". After the run is complete, flush the tubing with DI water for 10

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minutes before turning the pump off. Release the pump's platen cover to release the pressure on the pump's tubing.

6.3. Color Correction - The presence of organic matter and other colored material in the samples may result in positive interference for orthophosphate analysis. Color correction is carried out by running Acid Reagent (4.2.1.) in Channel 2 simultaneously with Color Reagent (4.2.2.) in Channel 1. Channel 2 is calibrated using Copper Sulfate (Color Correction Reagent, 4.2.6.) as a standard (called primer, Drift (2) and Cal. (2) on the run). Color correction is calculated by subtracting Channel 2 results greater than or equal to 0.0020 mg P/L from the Channel 1 sample results.

Note: The Copper Sulfate Reagent should be approximately the same height in Channel 1 as the highest standard (C7, 0.300 mg/L). This is evaluated periodically and the copper sulfate solution is adjusted accordingly.

6.4. Run files are automatically exported to the Nutrients drive (see section 7.4.). Convert the file in QC Manager, and save as raw data. Format, calculate, and save as review data. Select uploadable samples, and prepare folder for review by a supervisor.

6.5. Quantitation/Calculations:

6.5.1. After completion of the analysis, print a summarized report containing the peaks, calibration graph, and results. The instrument reports analysis results in mg P/L. Retrieve the raw data (called "digits") report and add to the analysis folder.

6.5.2. The QC Manager calculates recoveries for spikes and QC standards as well as relative percent differences (RPD) for duplicate samples and spikes. For general calculations including RPDs and spike recoveries see the FDEP Quality Manual (Section 5.9).

6.5.3. The individual calibration standards are prepared according to the section 4.3.3. The linear calibration curve is calculated by the instrument software and is a part of the analysis report. It includes the correlation coefficient to evaluate the fit and the percent errors of the calibration standards (see section 8.6.).

7. DATA ARCHIVAL

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labelled with the test (W-PO4 and/or W-PO4-F), initials of the analyst, and the file name(s). The file name follows the OPYYMMDDA format, where OP stands for ortho-phosphate, YY is the year, MM is the month, DD is the day of the

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month, and A indicates the instrument used. Postscripts 2, 3, etc. are used to denote the second, third, etc., runs of the day if necessary. For example, the first run on Feb 24, 2016 would be named OP160224A.

7.2. Each report folder should contain the following - report summary with calibration curve, bench sheet with method parameters, raw data report, reagent and standard logsheet, backlog report with batching documentation, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

7.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records center for long-term storage according to DEP SOP LB-006.

7.4. Bran+Luebbe instrument data excel transfer files (.txt) for upload to QC Manager are stored in electronic format in the current year's subfolder located on the Nutrients drive at:
\\FLDEP1\DEAR\LABS\Lab3\Chem_Data\Inorganic\Nutrients\SFA\BL\PO4\ .

7.5. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in
\\fldep1\dear\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations .

8. QUALITY CONTROL (SEE DEP SOPS NU-038 AND NU-043)

8.1. For method performance and acceptance criteria for QC measures and corrective action for handling out-of-control or unacceptable data refer to the following DEP SOPs: NU-038 and NU-043.

8.2. A continuing calibration verification, CHCK1 (4.3.3.), and a CCB (4.2.7.) are run as check standards every 10 samples and at the end of each run. Acceptance limits for the recovery of the CHCK1 are 90 - 110 %. Acceptance limits for the MBLK and CCB are < 0.004 and > -0.004 mg P/L.

8.3. One certified standard reference material, ALTQC (4.1.9.), is analyzed on every analytical run. Acceptance limits for the recovery of the ALTQC are 90 - 110 %.

8.4. One practical quantitation limit level standard, PQCK1 (4.3.3.), is analyzed on every analytical run. Acceptance limits for the recovery of the PQCK1 are 70 - 130 %. The PQCK1 is also used as a spike for the ongoing MDL and PQL verification.

8.5. An LFB (6.2.6.2), a matrix spike (6.2.6.2.), and a duplicate sample and/or duplicate matrix spike should be analyzed for every batch of 10 samples. Acceptance limits for the recoveries of the LFB and matrix spike are 90 - 110 %.

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The sample/matrix spike reproducibility should be less than 20 % RPD for results above the PQL.

8.6. Linear Calibration Range (LCR) - See Quality Manual, Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The correlation coefficient of the linear calibration must be equal to or larger than 0.995. Acceptance limits for the percent error of the PQL level standard are ±30%. Acceptance limits for the percent error of calibration standards above the PQL are ±10%.

8.7. Every day samples are analyzed a new calibration has to be performed at the beginning of the analysis and the LCR must be verified (See 8.6.). Consecutive runs on one day may use the same calibration.

8.8. The carryover percentage should be less than 2 %; high carryover indicates the need for instrument maintenance or troubleshooting.

9. MANIFOLD CLEANING, MAINTENANCE

9.1. Observe routine maintenance as recommended by instrument manufacturer, and enter the maintenance performed in the maintenance logbook.

9.2. Flush the reagent lines with the HCl Cleaning Zolution (4.2.8.) and 1 N NaOH (4.2.9.) for 10 minutes every 2 days, or more often if contamination occurs during analysis.

9.3. Clean the sample probe wash well with 1 % v/v hypochlorite solution (4.2.4.) at least once per month, or as needed if the carryover percentage exceeds 2 %.

10. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

10.1. Review the Laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

10.2. Safety glasses, gloves and lab coats should be worn at all times whilst handling samples and reagents.

10.3. Read the MSDS information for safe reagent and sample handling.

10.4. Sample waste, excess reagents, and waste exiting the flow cell may be poured down the sink while flushing with water.

11. REFERENCES

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For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

11.1. EPA method 365.1, Rev. 2.0 (1993).

11.2. Bran+Luebbe™ Analyzer Series AA3 System Operation Manual.

11.3. Bran+Luebbe method for orthophosphate analysis 696B-82W.

11.4. DEP SOP NU-033, Summary of Sample Analysis Procedures for the General Chemistry and Nutrients Workgroups.

11.5. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

11.6. DEP SOP NU-041, Reagent Preparation Procedure.

11.7. DEP SOP NU-042, Standard Preparation Procedure.

11.8. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

11.9. DEP SOP NU-044, Aqueous Extraction of Orthophosphate, Nitrate, Chloride and Sulfate from Soils and Sediments.

11.10. DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

11.11. Quality Manual, Bureau of Laboratories, FDEP.

11.12. Laboratory Health and Safety Plan.

11.13. DEP SOP NU-082, Analysis of Low Level Total Phosphorous Using the Bran+Luebbe Segmented Flow Analyzer.

Appendix of Significant Changes

02/21/2008 Updated SOP to comply with the latest revision of method:_365.1, *Revision 2.0*, August 1993.

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02/24/2010 Updated SOP to comply with the latest revision of the Bran_Luebbe method G-146-95, Revision 3.

03/14/2011 Section 8: Verification of the LCR was clarified.

03/30/2012 Starting 04/05/2012, sample with conductivities greater than 10,000 µmho/cm are analyzed undiluted. A section (6.2.6.) was added to describe the sample batching procedure. The manifold cleaning procedure (9.2.) was modified replacing the bleach wash with NaOH and HCl.

04/06/2015 The holding times of the Color Reagent, the Sulfuric Acid Reagent, and the Ascorbic Acid Reagent were changed from 7 days to 5 days. Data archival information was clarified in section 7. Cleaning procedure was amended in section 9.

04/05/2016 Reagent and Standard logsheet information was updated in Sections 4 and 7.2. The 100 mg P/L intermediate stock standard was removed from section 4.3. The holding time for the 10 mg P/L working standard and spiking solution was changed to 30 days. The preparation instructions for the 10 mg P/L working stock solution in section 4.3.2. and the working calibration standards in section 4.3.3. were updated. File paths were updated. The file naming convention in Section 7.1. was corrected.

12/10/2019 Section 4 entries for Copper Sulfate Reagent and acid cleaning solution were modified. In Section 6 the reference to MDL in the run sequence was removed and clarification for the color reagent added. Section 8 was modified to include the acceptance limits for the calibration standards recovery and use of thePQCK1 standard for the ongoing MDL and PQL verification.

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