Laboratory Manager Approval: Kristy E. Hrehor / 08/19/2021

QA Manager Approval: Jeffrey Moore / 08/19/2021

EPA 365.1 – Ortho Phosphorus in Water

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1. Scope and Application

1.1. This method covers the determination of ortho phosphorus in drinking, ground, and surface waters, and domestic and industrial wastes. This method determines ortho phosphorus or if the sample is filtered through a 0.45 micron pore size filter, the result is termed dissolved ortho phosphorus. The method is based on reactions that are specific for the ortho phosphorus ion. The ortho phosphorus ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of ortho phosphorus in the samples. This method is modified for use with the Lachat Quickchem Flow Injection Analysis (FIA) System (Quickchem Method 10-115-01-1-A).

1.2. Restricted Procedure

1.2.1. This procedure is restricted to use by an analyst experienced in the operation of a Lachat Quickchem Flow Injection Analysis (FIA) System. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2. Definitions

2.1. Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.7) for Quality Control Definitions.

2.2. Primary Source (PS) – A standard that is used to make up the calibration

points of a curve.

2.3. Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4. Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5. Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6. Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), Method Detection Limit Blank (MDLB), or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7. MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8. LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3. Interferences

3.1. Silica forms a pale blue complex which also absorbs at 880 nm. This interference is generally insignificant, as a silicate concentration of approximately 30 mg SiO_2/L would be required to produce a 0.005 mg P/L positive error in ortho phosphorus.

3.2. Concentrations of ferric iron greater than 50 mg/L will cause a negative error due to precipitation of, and subsequent loss, of orthophosphorus. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates.

3.3. Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HCl and rinsed with reagent water. Commercial detergents should rarely be needed but, if they are used, use special phosphorus-free preparations for lab glassware.

3.4. Sample turbidity must be removed by filtration prior to analysis. The immediate filtration requirement in orthophosphate measurement is to assess the dissolved or bio-available form of orthophosphorus (i.e., that which

passes through a 0.45-micron filter), hence the requirement to filter the sample immediately upon collection (i.e., within 15 minutes of collection).

4. Safety

4.1. Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision. (See SOP Reference 13.8)

5. Apparatus and Equipment

5.1. Sample Container: Samples are collected in 250 ml Nalgene bottle

5.2. Analytical Balance –capable of accurately weighing to the nearest 0.0001g

5.3. Glassware – Class A volumetric flasks, graduated cylinders, pipettes

5.4. Lachat Quickchem Flow Injection Analysis (FIA) System - equipment designed to deliver and react sample and reagents in the required order and ratios

5.4.1. Lachat XYZ Auto-sampler

5.4.2. Auto-sampler racks (90 position)

5.4.3. Reagent pump

5.4.4. Reaction unit or manifold

5.4.5. Colorimetric detector with 880 nm interference filter

5.4.6. Computer with Microsoft Windows operating system with Lachat Omnion software or equivalent.

5.5. Sonicator

5.6. 8.0 ml plastic culture tubes, 13mm OD x 100 mm, Fisher Scientific Part # 14-956-8E or equivalent or glass culture tubes 12 mm x 75 mm VWR part # 60825-502 or equivalent for loading samples on auto-sampler.

5.7. 50 ml centrifuge tubes with screw caps, VWR Part #21008-240 or equivalent for loading standards on auto-sampler

5.8. Rubber tubing, serological pipet and rubber stopper to assemble de-gassing wand

5.9. Vacuum source (for de-gassing reagents)

5.10. Disposable 1 mL pipette tips

5.10.1. Fisherbrand™ Standard Disposable Transfer Pipettes PN# 02-707-507 or equivalent

5.11. Disposable transfer pipettes:

5.11.1. Plastic - VWR® Disposable Transfer Pipets PN# 16001-190 or Fisherbrand™ Standard Disposable Transfer Pipettes PN# 13-711-7M or equivalent.

5.12. Air displacement pipettes of various volumes, auto-pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.

5.12.1. Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.

5.12.1.1. Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1g. Mechanical pipettes must be verified to be within ± 2.5 percent of the nominal volume.

5.12.1.2. Mechanical pipettes must be professionally calibrated every 6 months.

5.13. HDPE bottles, various sizes, for storage of standards

5.14. pH test strips

6. Reagents

6.1. Reagent Water

6.1.1. Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest (Deionized, HPLC, Milli-Q water, or equivalent. Milli-Q water has a resistivity of 18.2[MΩ.cm] @ 25oC and a TOC of 50 ug/L or less).

6.2. Stock Ammonium Molybdate Solution

6.2.1. In a 1L volumetric flask, dissolve 40.0 g of ACS grade ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in approximately 800 ml DI water. Dilute to volume and stir for four hours. Store in plastic bottle and refrigerate. Prepare fresh every two months.

6.2.2. Ammonium Molybdate Tetrahydrate is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner.

6.3. Stock Antimony Potassium Tartrate Solution

6.3.1. In a 500 ml volumetric flask, dissolve 1.5 g of ACS grade Antimony potassium tartrate (Potassium antimony tartrate hemihydrate $K(SbO)C_4H_4O_6\bullet ½H_2O$) or dissolve 1.61 g of ACS grade Antimony potassium tartrate (Potassium antimony tartrate trihydrate $C_8H_4O_{12}K_2Sb_2\ 3H_2O$) in approximately 400 ml of reagent water. Dilute to the mark and invert to mix. Store in a dark glass bottle and refrigerate. Prepare fresh every two months.

6.3.2. Antimony potassium tartrate (Potassium antimony tartrate hemihydrate $K(SbO)C_4H_4O_6\bullet ½H_2O$) and Antimony potassium tartrate (Potassium antimony tartrate trihydrate $C_8H_4O_{12}K_2Sb_2\ 3H_2O$) are stable until expiration date on bottle or within 2 years of opening date, whichever is sooner.

6.4. Molybdate Color Reagent

6.4.1. To a 500 ml volumetric flask add about 200 ml reagent water, followed by 17.5 ml concentrated sulfuric acid (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add 36 ml Stock

Antimony Potassium Tartrate Solution. Swirl to mix. Add 106.5 ml Stock Ammonium Molybdate Solution. Dilute to the mark, cap, and invert to mix. Prepare fresh weekly. Degas prior to running analysis.

6.5. Sulfuric Acid

6.5.1. This ACS grade purchased chemical is stable until expiration date on bottle or within 2 years from opening date, whichever is sooner. Store at room temperature.

6.6. Carrier Solution

6.6.1. Reagent water. Degas before each use.

6.7. Ascorbic Acid reducing Solution

6.7.1. In a 500 ml volumetric flask, dissolve 30.0 g of ACS grade ascorbic acid in about 350 ml of reagent water. Dilute to the mark and invert to mix. Pour solution into a 1 liter amber bottle, then add 0.5 g of ACS grade sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$). Invert to mix. Prepare fresh weekly. If there is excessive buildup of blue deposits in instrument lines, the mass of sodium dodecyl sulfate added to the solution may be doubled. Discard if solution becomes yellow. Degas prior to running analysis.

6.7.2. This purchased chemical is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.

6.8. NaOH-EDTA Solution

6.8.1. Add 65.0 g of ACS grade NaOH and 6 g of ACS grade tetrasodium EDTA to approximately 700 ml of reagent water in a 1000 ml beaker. (CAUTION: Solution becomes very hot!). Stir well. Once solution has cooled enough for safe handling, transfer to a 1L volumetric flask. Dilute to volume with reagent water. Prepare fresh every three months.

6.8.2. This purchased chemical is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.

6.9. 1:1 Hydrochloric Acid Solution

6.9.1. Add 250 ml of reagent water to a clean beaker. Then add 250 ml of of ACS grade Hydrochloric Acid. Stir well and allow the solution to cool. Transfer to appropriate wash bottle. This solution is used for cleaning glassware.

6.9.2. Solution is stable for one year.

6.9.3. This purchased chemical is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.

6.10. Primary Source (PS) Phosphorus Stock Standard A (1000 mg P/L)

6.10.1. Dissolve 4.3962 g of ACS grade anhydrous potassium phosphate monobasic (KH_2PO_4) that has been dried for one hour at 105°C in a 1L volumetric flask in approximately 800 ml of reagent water. Dilute to mark with reagent water and invert to mix. Prepare standard fresh every 6 months.

6.10.2. Anhydrous Potassium Phosphate Monobasic (KH_2PO_4), - is stable until

expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.

6.11. PS Phosphorus Intermediate Stock Standard Solution B (10 mg P/L)

6.11.1. In a 1L volumetric flask, add 10 ml of Stock Standard A (1000 mg P/L). Dilute to the mark with reagent water. Invert to mix. Prepare standard fresh every 3 months.

6.12. Phosphorus Spiking Solution (100 mg/L)

6.12.1. In a 100 ml volumetric flask, add 10 ml of Primary Source (PS) Phosphorus Stock Standard A (1000 mg P/L) and dilute to volume with reagent water. Invert to mix. Prepare standard fresh every three months.

6.13. Calibration standards

6.13.1. Prepare working standards from PS Phosphorus Intermediate Stock Standard Solution B as shown in chart. The calibration standards range from 0.00 mg P/L – 2.0 mg P/L. Prepare fresh daily.

Table 6.13.1.1.- Working Standards

Stock Standard (ml)	Stock Standard Solution	Final volume in ml	Concentration (mg P/L)
0.4	B	100	0.04
1.0	B	100	0.10
4.0	B	100	0.40
10	B	100	1.00
20	B	100	2.00

6.14. CB/ICB/MBLK/CCB/MDLB

6.14.1. Reagent water

6.15. Method Detection Limit Spike/Low level Standard (MDLS) 0.04 mg P/L Standard:

6.15.1. To prepare the MDLS, pipette 4 ml of PS Phosphorus Intermediate Stock Standard Solution B (10 mg P/L) and dilute to volume with reagent water. Invert to mix. Prepare standard fresh daily.

6.16. Volumes and amounts of reagents, chemicals, and standards may be altered as long as final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

6.17. ICV Phosphorus Stock Solution or Second Source (SS)

6.17.1. ICV Phosphorus Stock Solution (1000 mg P/L)

6.17.2. The ICV stock standard is typically a standard intended as a “QC Sample” but used as a second source standard instead.

6.17.3. This stock standard must be from a different source than the stock standard used to make the calibration standards.

6.17.4. This standard is purchased from a commercially available source. The purchased standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.

6.18. Intermediate ICV Stock Solution or Second Source (SS) 10 mg P/L

6.18.1. In a 1L volumetric flask, add 10 ml of ICV Phosphorus Stock Solution (1000 mg P/L). Dilute to the mark with reagent water. Invert to mix. Prepare standard fresh every 3 months.

6.19. ICV Phosphorus Solution(1.00 mg P/L)

6.19.1. A 10 ml aliquot of the Intermediate ICV Phosphorus Stock Solution (10 mg/L) is pipetted into a 100 ml volumetric flask and diluted to volume with reagent water.

6.19.2. The ICV solution must be prepared fresh daily.

6.20. Phenolphthalein Indicator

6.20.1. This purchased chemical is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner. Store at room temperature.

6.21. 11N Sulfuric Acid

6.21.1. Add 250 ml of reagent water to a clean 1L beaker. Then add 310 ml of concentrated H_2SO_4 and dilute to volume. Stir well and allow the solution to cool.

6.21.2. Solution is stable for 1 year.

6.22. 1N NaOH

6.22.1. Add 250 ml of reagent water to a clean 1L beaker. Then add 40 g of NaOH and dilute to volume. Stir well and allow solution to cool.

6.22.2. Solution is stable for 1 year.

7. Sample Collection

7.1. Samples submitted for ortho phosphorus analysis are collected in a 250 ml plastic bottle.

7.2. Samples are not chemically preserved.

7.3. Samples are filtered in the field, within 15 minutes of collection.

7.4. Samples should be cooled to 0-6° C (not frozen) as soon as possible after collection.

7.5. Sample holding time is 48 hours.

7.6. Samples are stored at 0-6° C (not frozen).

8. Calibration

8.1. Calibration Standards

8.1.1. The calibration curve consists of the calibration standards at the levels shown in concentration column of Table 6.13.1.1.

8.2. Calibration Curve

8.2.1. The Lachat Quickchem is calibrated daily with the standards shown in the concentration column of Table 6.13.1.1. Minimum acceptable correlation is 0.995 using a linear regression.

8.3. Calibration Verification

8.3.1. Initial Calibration Verification standard (ICV), a Continuing Calibration Check (CCC) and an Initial Calibration Blank (ICB) must be analyzed immediately after the calibration standards

8.3.1.1 The %Drift (see calculation 11.1.) of the ICV from the true value must be within ±10%. Repeat once if it fails. If it fails the second attempt, determine the source of the problem, correct and recalibrate.

8.3.1.2 The ICB, CCB and MBLK values must be less than the method RL or the run will have to be repeated.

8.3.1.3 A CCC and a Continuing Calibration Blank (CCB) must be analyzed every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB respectively.

8.3.1.3.1 The CCC may be from the same source as the calibration standards.

8.3.1.4 If the CCC or CCB do not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.

8.4. A MDLB (MDL blank) must be analyzed once per analytical batch to perform an ongoing MDL study. The MDLB may be combined with the MBLK. All batch QC must be valid to report this result.

8.5. A MDLS (low level mdl spike) at the concentration of 0.04 mg P/L must be analyzed with each batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

9. Quality Control

9.1. Refer to Table 14. 1 for Reporting Limits (RL's), Refer to Table A.1 for QC Control Limits, Appendix A for Quality Assurance Criteria, and Table 14. 2 for Quality Control Procedures associated with this method.

9.2. A method detection limit study must be performed twice per year. See reference 13.6.

9.3. For Initial Demonstrations of Capability (IDC) Method 365.1 requires a recovery range of 90% -110% (see calculation 11.2)

9.4. The EPD Laboratory uses the most current accuracy and precision control ranges in use for samples for Continuing Demonstrations of Capability (CDC). If 4 replicates are performed (as opposed to two LCS/LCSD pairs) a 20% RSD is required (see calculation 11.5)

9.5. Default control limits for recovery for LCS/LCSD pairs are based on Section 9.3.2 of EPA Method 365.1 (see reference 13.1) as noted in Table

9.4.1. below. By default, the EPD laboratory sets LCS/LCSD precision control limits to 0-15% RPD. Default control limits for recovery for MS/MSD pairs are based on Section 9.4.2 of EPA 365.1. MS/MSD precision limits are set by the EPD lab as 0-15% RPD. In-house limits based on control charts may never exceed the default limits. The default control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

9.6. MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.7. The actual MDL varies depending on instrument and matrix.

9.8. The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.9. The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.10. The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial “pairs” are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blank.

9.11. A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.12. The results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_OPHOS. The MDLSpike result will be entered using the MLOPHOS. The MDL Spiked Amount will be entered into the test code MAOPHOS. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-OPHOS.

9.13. MDL study must be performed every six months and before the MDL for the instrument expires.

9.14. See Reference 13.4. for control charting procedures.

9.15. See Reference 13.3 for training procedures.

Table 9.5.1. - Default QC Limits for Method EPA 365.1

QC Type	Analyte	Accuracy (%R) LCL	UCL	Precision (%RPD
LCS/LCSD	Ortho Phosphorus	90 -	110	15
MS/MSD	Ortho Phosphorus	90 -	110	15

10. Procedure

10.1. Sample Preparation

10.1.1. Remove sample bottles, standards and reagents from cold storage and allow to equilibrate to room temperature prior to sample preparation and/or analysis.

10.1.2. Pull a backlog of pending OPHOS samples. Batch field samples in groups of up to 20 field samples. Select QC samples for MS/MSD. MS/MSD pairs are to be analyzed at a frequency of 10% of samples over time.

10.1.2.1. For batches of 1 – 10 field samples, 1 MS/MSD pair is required. For batches of 11 – 20 samples, 2 MS/MSD pairs are required.

10.1.2.2. When 2 MS/MSD pairs are required, the QC samples should be selected as one sample from the first 10 samples in the batch and the second QC sample from the samples in the second part of the batch. QC samples with consecutive numbers should not be selected. If possible, the QC samples should come from different collection events (different locations).

10.1.3. Check pH of samples and record pH on batch sheet.

10.1.3.1. If samples of high (pH>8) are suspected add 1 drop of phenolphthalein indicator to a 50 ml aliquot of sample. If a red color develops, add 11 N sulfuric acid (310 ml concentrated H_2SO_4/L) dropwise to just discharge the color.

10.1.3.2. Acid samples (pH<4) must be neutralized with 1 N NaOH (40 g NaOH/L). Add 1 drop of phenolphthalein indicator to a 50 ml aliquot of sample. Slowly adjust pH up until color just disappears with 1 N NaOH. See Section 6.22.

10.1.3.3. Record final pH of sample on batch sheet after adjustment.

10.1.4. Check pump tubes for wear. Replace if necessary. Snap pump tube cartridges down into cartridge holders and adjust tension levers to tensioned position. Place instrument waste lines in waste container.

10.1.5. Place lines in reagent water and turn pump on. Set pump speed to 35 and press Manual Run. Pump reagent water through all reagent lines and check for leaks and smooth flow.

10.1.6. If lines need cleaning, place the color reagent and ascorbic acid lines into the NaOH-EDTA solution and the other lines in reagent water for 5 minutes and then place all lines in reagent water for 5 minutes.

10.1.7. Stop and power off pump. Turn auto-sampler power to "ON." Turn reagent pump power to "ON." Make sure speed is set to 35 and press Manual Run. Turn Lachat Quickchem power to ON. Switch lines from reagent water to degassed reagents and allow system to equilibrate.

10.1.8. The ICB/CCB/MBLK/MDLB must be poured into a 250 ml sample collection bottle before it is pipetted into the appropriate tubes. Record the lot # of bottle used.

10.1.9. The MDLS/0.04 mg P/L standard must be poured into a 250 ml sample collection bottle before it is pipetted into the appropriate tube. Record the lot # of bottle used.

10.1.10. Prepare the LCS and LCSD at the 1.00 mg/l level by pipetting 0.25 ml of spiking solution into a 25 ml volumetric flask. Dilute to volume with the blank that was stored in a 250 ml sample collection bottle. (see section 6.14.). Volume of LCS and LCSD may be altered as long as final concentrations remain the same. Record the lot # of bottle used. Make sure that auto-pipettor volume has been verified and recorded prior to use in the Pipette Calibration Log book.

10.1.11. Prepare the MS and MSD at the 1.00 mg/l level by pipetting 0.25 ml of spiking solution into a 25 ml volumetric flask. Dilute to volume with the QC sample. Volume of MS and MSD may be altered as long as final concentrations remain the same. Make sure that auto-pipettor volume has been verified and recorded prior to use in the Pipette Calibration Log book.

10.1.12. Load samples/standards in auto-sampler. Standards are loaded in order from high to low.

10.2. Instrument/Computer Procedure

10.2.1. On the windows desktop, click the Omnion 3.0 icon to launch the Omnion software.

10.2.2. Click the open button to open the folder containing all methods. Open the methods folder. Select the Ortho Phosphorus folder and click on it.

10.2.3. Open the OPHOS Template. If prompted to change the heater set point, select "Yes." Input sample batch information into the template, and save the file under the ortho phosphorus folder as the batch number.

10.2.4. Use the Preview button to monitor the baseline for air spikes, flow problems, instability, etc.

10.2.5. After allowing the system to equilibrate, verify heater temperature is 37° C. Click the start button located above the run worksheet to start the run.

10.3. Printing custom Reports and Exporting Worksheets

10.3.1. Select the tools pull down menu and click on custom report. Click on the custom report format and select layout. Once the report is created, the auto-fields should contain the name of the individual that is logged in, the current date and the page numbers of the report. Change the value in the author field to the analyst's initials. Use N=15 for number of samples per line.

10.3.2. Click Apply once, when all layout modifications have been made. If there are no layout modifications, click ok. Exit the custom report menu.

10.3.3. Click on the printer button to print the report. The report should contain the calibration curve.

10.3.3.1. From the main menu, select the run button and click on export worksheet to print the run log. Print two copies of the run log.

10.3.3.2. Following review of the sample run, reanalyze all samples (at a dilution) for which the responses are greater than 2.0 mg/L.

10.4. Dilutions

10.4.1. To prepare dilutions, use the blank to dilute the samples.

10.5. Volumes and amounts of reagents, chemicals, and standards may be altered as long as final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

10.6. Shutdown Procedure

10.6.1. After the run, place the color reagent and ascorbic acid lines into the NaOH-EDTA solution and the other lines in reagent water for 5 minutes and then place all lines in reagent water for 5 minutes.

10.6.2. After reagent water rinse, allow all lines to pump dry. Remove waste lines from waste container and seal waste container. Release tension on lines by releasing the tensioners and then disconnecting cartridge from the pump rollers.

10.6.3. To shut down the system, exit the Omnion program and shut down the computer, instrument, auto-sampler and reagent pump.

11. Calculations

11.1. Response Factor, RF, for a peak

$$RF = \frac{\text{Area}_{\text{Analyte}}}{\text{Concentration}_{\text{Analyte}}}$$

11.1.1 Where:

RF = Response Factor

Area $_{\text{Analyte}}$ = Area of the peak of the analyte of interest

Concentration $_{\text{Analyte}}$ = Concentration of the analyte of interest in mg/L

11.2. Quality Control Calculations

$$\text{LCS/LCSD/ICV \% Recovery} = \frac{R_{spike}}{\text{Expected Result}} X\,100$$

$$\text{\% RPD(precision)} = \frac{\left|R_{sample} - R_{duplicate}\right|}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} X\,100$$

11.2.1. Where:

R_{spike} =% recovery of spiked sample
R_{sample} =% recovery of sample
$R_{duplicate}$ =% recovery of duplicate sample

11.3. Percent Drift, %Drift

$$\%\text{Drift} = \frac{\left(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}}\right)}{\text{Concentration}_{\text{Expected}}} * 100$$

11.3.1. Where:
Concentration $_{Calculated}$ = Concentration calculated from result
Concentration $_{Expected}$ = Theoretical concentration of the standard

11.4. Calculation of Dilution Factors

$$C \times D = F$$

11.4.1 Where:
C = concentration from instrument in mg N/L
D = dilution factor, if any
F = final concentration in mg N/L

11.5.1 Percent Relative Standard Deviation (%RSD):

$$\%\text{RSD} = \frac{\sigma_{n-1}}{\overline{X}} * 100$$

11.5.1 Where:
σ_{n-1} = Sample Standard Deviation
$\overline{X}$ = Mean of the values

12. Waste Management

12.1. See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating Procedures (see reference 13.5).

13. References

13.1. Environmental Monitoring Systems Laboratory, Office of Research and Development. U.S.Environmental Protection Agency, Cincinnati, Ohio. Revision 2.0, August 1993, Method 365.1.

13.2. Lachat Instruments, Quickchem Method 10-115-01-1-A. Revision 29 November 2007.

13.3. GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.4. GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.5. GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.6. GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.7. EPD Laboratory Quality Assurance Plan, online revision.

13.8. GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14. Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14. 1 - Reporting Limits for EPA 365.1

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
EPA 365.1	Ortho Phosphorus	0.04	mg/L

Table 14. 2 - **Summary of Calibration and QC Procedures for Method EPA 365.1**

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 365.1	Ortho Phosphorus	Initial calibration for all analytes	Initial calibration prior to sample analysis	Correlation coefficient ≥ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration verification (ICV)	Once per initial calibration or quarterly, whichever is sooner	Ortho phosphorus concentration within 10% of expected value	Correct problem then repeat initial calibration	
		Initial calibration blank (ICB)	Once per initial calibration	Ortho phosphorus value must below reporting limit	Correct problem and repeat initial calibration.	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table, SOP 3-045 Appendix A and Initial Demonstration SOP(Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table, SOP 3-045 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Method Blank (MBLK)	One per analytical batch	Ortho phosphorus value must be below reporting limit	Correct problem then analyze method blank and all samples processed with the contaminated blank	If unable to reanalyze, flag with a “B”
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table, SOP 3-045 Appendix A	Correct problem then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to reanalyze, flag with a “J”
		Matrix Spike (MS/MSD)	MS/MSD at 10% of all samples over time	QC Acceptance Criteria Table, SOP 3-045 Appendix A	Evaluate out of control event, reanalyze or flag data	

Table 14. 2 - **Summary of Calibration and QC Procedures for Method EPA 365.1**

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 365.1	Ortho Phosphorus	Continuing Calibration Check (CCC)	Prior to analysis, after every 10 samples, and at the end of the sample run.	Ortho Phosphorus concentration within 10% of expected value	Correct problem then reanalyze CCC and all samples in affected batch	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run.	Ortho Phosphorus concentration must be < RL	Correct problem then reanalyze CCB and all samples in affected batch	
		MDL Low level Spike (MDLS) 0.04 mg/L	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB) *may be combined with the MBLK	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL study	Every six months or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	None
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	None

Appendix A – Quality Assurance Criteria for Method EPA 365.1

Table A.1 Quality Assurance Criteria for Method EPA 365.1

QC Type	Analyte	Accuracy(%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	Ortho phosphorus	90	-	110	15
MS/MSD	Ortho phosphorus	90	-	110	15
Control charts are generated twice annually for informational purposes only Control Chart data generated from 01/01/2019 – 01/01/2021					

Updates to Previous Version:
Appendix A added.
Section 2
Section 4
Section 9
Section 13
Table A.1
Table 14.2