Total Phosphorus, SM 4500-P B-5 -2011 (Sample Prep) and E - 2011, (SM 22nd edition) – Ascorbic Acid Method

SM 4500-P (B(5), E–H)–2011, phosphorus and ortho-phosphate, persulfate digestion, digestion, followed by any of the following: Manual or automated ascorbic acid reduction. The ‘‘B Part 5’’ method is the persulfate digestion procedure and is required prior to measurement of total phosphorus using SM 4500 P (E–H). The ‘‘E’’ through ‘‘G’’ methods are approved for both total phosphorus and orthophosphate. The ‘‘H’’ method is only approved for total phosphorous. *August 27, 2018 revision*

	EPA	Standard methods
Ascorbic acid reduction	365.1 Rev. 2.0 (1993)	4500–P (F-H)–2011

Minimum detectable concentration – 4500-P E.1.c. - 2011 – approximately 10 μg/L (0.010 mg/L)

Initial demonstration of capability

- 1020 B. 1 – As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
    - Upper Control Limit = Mean + 3(Standard deviation)
    - Lower Control Limit = Mean - 3(Standard deviation)
- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to analyze 4 samples of Phosphorus standard at a concentration of about 0.5 mg/L**
    - **Keep a folder for each analyst, keep a copy here**

Method Detection Limit

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, us an estimate of five times the estimated true detection level (5 x 0.010 mg/L = 0.050 mg/L).
    - Prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
- **Real people language – have several operators, who run this test, analyze a Phosphorus standard at a concentration of 0.05 mg/L over several days with a total of at least 7 samples**
    - **Joe analyzes 3 samples on Monday**
    - **Bob analyzes 3 samples on Tuesday**
    - **Mary analyzes 3 samples on Wednesday**

- Annual (every 13 months) verification required using data collected within the past 24 months. Include all data from the On-going Data Collections and the initial MDL determination where appropriate (<24 months old). A minimum of 7 data points are required for ***both spiked samples (MDL_s) and method blanks (MDL_b)***.
- Refer to the MDL Examples and EPA Guidance for complete requirements.
- Refer to document titled “Method Update Rule – Method Detection Limit Math 2019” on Fleming Training Center website for MDL Calculator.

Initial Calibration Verification – does not go through digestion

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020.B.2.a. – Calibrate initially with at least one blank and three calibration standards.
    - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
    - The back-calculated and true concentrations should agree within ± 10%.
- **Real people language – Analyze 2-3 different standards within the curve**
    - **Run on a 5% basis, see batch size for more information**

Method Blank

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank daily or with each batch of 20 or fewer samples, whichever is more frequent.
    - If any method blanks measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by going through all digestion and reagent addition before reading.**
    - **Target value is zero**

Laboratory Fortified Blank – goes through digestion

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits
- **Real people language – analyze Phosphorus standard at a concentration of 0.5 mg/L**
    - **Run on a 5% basis, see batch size for more information**

Duplicate –

- NONE

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- 1020 B.7.– A laboratory fortified matrix (LFM) is an additional portion of a sample to which a known amount of the analyte of interest is added before sample preparation
    - The LFM is used to evaluate analyte recover in a sample
    - Sample batch = 5% basis = 1 every 20 samples
    - Add a concentration that is at least 10 times the MRL (minimum reporting level), less than or equal to the midpoint of the calibration curve.
    - Preferably use the same concentration as the LFB
- 4020 B.2.g. – When appropriate for the analyte, include at least one LFM/LFMD daily or with each batch of 20 or fewer samples

- Add a known concentration of analyte (ideally from a second source) to a randomly selected routine sample without increasing its volume by more than 5%
- Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations

- **Real people language – add a known amount of phosphorus to a sample and expect that amount to increase your sample concentration**
  - **Hach's method uses 0.1 mL increments, therefore spiking volume is 1% of total sample volume**
  - **If you have a phosphorus standard solution that is 50 mg/L of PO_4, when you add 0.1 mL to a 10 mL sample, that should increase your sample concentration by 0.5 mg/L PO_4. Example from Hach's Phosphorus, Reactive (Orthophosphate) Method (Hach Method 8048):**

Standard additions method (sample spike)
Required for accuracy check:

- Phosphate 10-mL Ampule Standard, 50-mg/L PO_4^{3-}
- Ampule breaker
- TenSette Pipet

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select standard additions from the instrument menu:

Instrument	Navigate to:
DR 5000	**OPTIONS>MORE>STANDARD ADDITIONS**
DR 2800	**OPTIONS>MORE>STANDARD ADDITIONS**
DR 2700	**OPTIONS>MORE>STANDARD ADDITIONS**
DR/2500	**OPTIONS>STANDARD ADDITIONS**
DR/2400	**OPTIONS>STANDARD ADDITIONS**

3. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution ampule.
5. Prepare a 0.1-mL sample spike by adding 0.1 mL of standard to the unspiked sample. Press the timer icon. After the timer expires, read the result.
6. Prepare a 0.2-mL sample spike by adding 0.1 mL of standard to the 0.1-mL sample spike. Press the timer icon. After the timer expires, read the result.
7. Prepare a 0.3-mL sample spike by adding 0.1 mL of standard to the 0.2-mL sample spike. Press the timer icon. After the timer expires, read the result. Each addition should reflect approximately 100% recovery.

Continuing Calibration Verification – does not go through digestion

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
    - For the calibration verification to be valid, check standards must not exceed 10% of its true value, and calibration blank results must not be greater than one-half the reporting level
- **Real people language – analyze mid-range Phosphorus standard daily.**

Control Charts – 1020 B.13.

Corrective Action - 1020 B.5., B.8,. & B.15.

Batch Size –

- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would suggest twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations –

- % Recovery for LFB
    - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$
- RPD – relative percent differences for duplicates and LFM/LFMD
    - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$
- % Recovery for LFM – when using less than or equal to 1% spike volume compared to sample volume
    - $= \frac{\text{LFM concentration} - \text{Sample concentration}}{\text{Concentration of spike}} \times 100\%$