

Total Phosphorus, SM 4500-P B (Sample Prep) and E, 22nd edition (1999) – Ascorbic Acid Method

Minimum Detectable Concentration – 4500-P E.1.c. – approximately 10 µg/L (0.010 mg/L)

Initial Demonstration of Capability (DOC)

- 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.
- 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**
 - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
 - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level ($5 \times 0.010 \text{ mg/L} = 0.050 \text{ mg/L}$).
 - Ideally, 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.
 - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values $\leq 20\%$.
- 4020 B.1.b. – Verify MDL at least **annually**.
 - Ideally use pooled data from several analysts rather than data from one analyst.
- **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**
- **Run this once a year**

Initial Calibration Verification (ICV) – 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 $\pm 10\%$.

- **Real people language – prepare a set of Phosphorus standards (4-5 standards) to verify the factory pre-set calibration curve **monthly** or more frequently if reagent lot # changes.**

Method Blank – goes through digestion

- 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 blank 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 less than reporting limit.**
 - **Reporting limit will be equal to your Method Detection Limit (MDL)**
 - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Blank (LFB) – 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 (see Control Charts below)
- **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) – goes through digestion

- 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 to a randomly selected routine sample
 - Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations (see Control Charts below)

- **Real people language – add a known amount of phosphorus to a sample and expect that amount to increase your sample concentration**
 - **Run on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent), see batch size for more information**
 - **Calculate RPD between spiked sample and spiked duplicate, target value should be close to the first value and have a small RPD (less than 20%).**
 - **Spike volume should be less than 1% of the volume.**
 - **Example: spike with 0.1 mL of 100 mg/L into 10 mL sample will equal a 1 mg/L increase in phosphorus concentration.**

Continuing Calibration Verification (CCV) – 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
- **Real people language – analyze mid-range Phosphorus standard daily (day of).**

Control Charts – 1020 B.13.

- **Real people language**
 - **Create and maintain control charts if you have 20-30 data points within 90 days.**
 - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

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

QC Acceptance Criteria

- Blanks < MDL
- LFB \pm 15%
- ICV/CCV \pm 10%
- LFM/LFMD \pm 20%
- RPD < 20%
- Reporting Limit = MDL

Batch Size –

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) 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
 - = $\frac{\text{LFM concentration} - \text{Sample concentration}}{\text{Concentration of spike}} \times 100\%$