Total Residual Chlorine, SM 4500-Cl G, 22nd edition (2000) – DPD Colorimetric Method

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

Initial Demonstration of Capability (DOC)

- 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 a chlorine or potassium permanganate ($KMnO_4$) standard at a concentration of 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.**
  - **Only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC.**
    - **DOCs demonstrate you are proficient with that one instrument.**

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 x 0.010 mg/L = 0.050 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 ≤ 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 chlorine or Potassium Permanganate ($KMnO_4$) standards 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)

- 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.

- **Real people language – prepare a set of chlorine or potassium permanganate ($KMnO_4$) standards in accordance with Guidance for Secondary Standards Use in Calibration 1-15-2016 monthly.**

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 adding a DPD powder pillow and waiting the 3-6 minutes 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)

- 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 chlorine or potassium permanganate standard at a concentration of 0.5 mg/L**
    - **Run on a 5% basis (see batch size for more information).**

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

- NONE

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (see batch size for more information) analyze 2 samples for chlorine, after reading one, pour out sample and start with a fresh sample**
    - **For reporting purposes, average sample and duplicate.**
    - **Target value should be close to the first value and have a small RPD (less than 20%)**

Continuing Calibration Verification (CCV)

- 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**
    - **Read Secondary Standards (gel standards) in accordance with Guidance for Secondary Standards Use in Calibration 1-15-2016 daily (day of).**
    - **OR run a chlorine or potassium permanganate standard daily.**

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 < Method Detection Limit (MDL)
- LFB ± 15%
- ICV/CCV ± 10%
- 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 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 allow 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!!
    - If sampling only once a month, need to run QC once a month (when samples are analyzed).

Calculations

- % Recovery for LFB
    - = $\frac{\text{LFB concentration}}{\text{Expected concentration}}$ X 100%

- RPD – relative percent differences for duplicates
    - = Difference between sample and duplicate X 100%
      Average of the sample and duplicate