STEPS TO DMR-QA SUCCESS

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Presentation Overview

■ Purpose of DMR-QA

■ Preparation

■ DMR-QA Ethics

■ Analysis

    – *Ammonia*

    – *BOD*

    – *Residual Chlorine*

    – *pH*

    – *TSS*

■ Quality Control

■ Reporting

What is DMR-QA?

- **Discharge Monitoring Report - Quality Assurance**
  - *A study program for NPDES Permittees and laboratories performing testing for NPDES Permittees.*
  - *Designed to evaluate a lab's ability to analyze and report results within defined acceptance limits.*
  - *Designed to evaluate a Permittee's ability to report laboratory results to state DMR-QA coordinator for each lab performing analyses to meet NPDES compliance requirements.*
  - *All major NPDES Permittees are required to participate*
  - *A select few minor NPDES Permittees are required to participate*
  - *How do I know if I need to participate?*
    - Facilities receive a mailed packet with instructions, deadlines and analyte check lists

How to Prepare for a DMR-QA Study?

- *Follow the instructions included in the packet.*
  - Complete acknowledgement of receipt
  - Notification of Lab(s)
    - *Complete checklist(s) for each lab testing NPDES analytes*
      - The Study includes chemistry, microbiology and WET (Whole Effluent Toxicity)
    - *Check the tests the lab routinely performs*
      - Note: Not all tests listed in a NPDES permit are included in the study
- *If your facility laboratory performs testing for the NPDES permit order standards for the tests your laboratory analyzes.*
  - Be sure to order from an approved Provider.
  - Approved Providers are included in the packet

What to Order?

- Obtain Quotes from Approved Providers and select a Provider
- Evaluate the types of standards supplied by each Provider
  - *Whole volume samples*
    - Does the provider sell samples already prepared?
    - Reduces the risk of preparing the standards incorrectly
    - Simulates real world samples
  - *Standard Concentrates (Vials/Ampules)*
    - Laboratory needs to prepare standards based on instructions received by Provider
    - Increases time to prepare the sample and then analyze
    - Increases risk of contamination from:
      - *Volumetric pipets, volumetric flasks*

Receipt of PT Standards

- Follow instructions received from the Proficiency Testing (PT) Provider
    - *Immediately Upon Receipt - Store According to PT Provider recommendations until analysis is performed*
        - Refrigeration may be required
- Inform laboratory staff
- Review instructions for each test to be analyzed
- Evaluate laboratory supplies
    - *Class A glassware*
    - *Laboratory Water*
    - *Supplies for each test*

DMR-QA Ethics

- DMR-QA standards are to be analyzed and reported following the same procedures used for NPDES plant samples.

  - *DMR-QA standards must be reported from a single determination*

    - An average of several determinations must not be reported

- The primary analyst for each test should analyze the DMR-QA standard

- Consulting with other labs who used same PT provider to compare final results before the study is closed is not permitted.
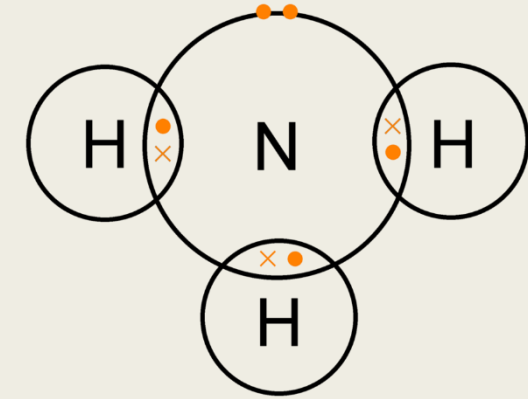
DMR-QA Requirements

- Analyze DMR-QA standards with a normal batch of plant samples
  - *This ensures all quality control requirements are performed for the DMR-QA standard*
    - Calibration
    - Method Blanks
    - Duplicates
    - Matrix Spike/Matrix Spike Duplicate
    - Laboratory Control Standard (LCS) or (QC) Standard

Ammonia (NH$_3$-N) Analysis

■ Follow PT Provider instructions

■ General Guidance

   – *Warm the NH$_3$-N PT standard to room temperature*

   – *If the standard is a whole volume sample dilution is not required*

      ■ ANALYZE THE SAME DAY THE STANDARD IS OPENED.

   – *If the standard is a concentrate dilution is required*

      ■ Use clean Class A glassware to prepare dilutions

      ■ Use NH$_3$-N free reagent water to prepare dilutions

      ■ MIX THE SOLUTION VIGOROUSLY 3-5 TIMES (INVERT AND SHAKE)

   ■ IMMEDIATELY ANALYZE DILUTED STANDARD

Ammonia (NH$_3$-N) Analysis

■ Calibrate NH$_3$-N meter following SOP

   – *Verify calibration standards are within expiration date*

■ Verify calibration meets requirements

   – *Point to Point Calibration (i.e. 1 mg/L and 10 mg/L standards) – slope must be between -54 to -60*

   – *5 Point linear curve – R ≥ 0.995 (correlation coefficient)*

■ Use a 2nd source NH$_3$-N standard to verify calibration standards

   – *Must fall within laboratory limits*

   – *Generally 90-110% Recovery*

   – $\%R = \dfrac{Obtained\ value\ mg/L}{True\ Value\ mg/L} \times 100$

Ammonia (NH$_3$-N) Analysis

- Perform method blank
  - *100 mLs of NH$_3$-N free reagent water*

- Analyze routine plant samples

- Perform Matrix Spike/Matrix Spike Duplicate on one of the plant samples
  - *The results of the Matrix Spike and Matrix Spike Duplicate must fall within laboratory acceptance limits*
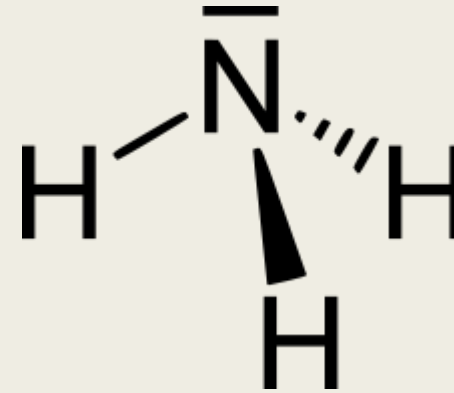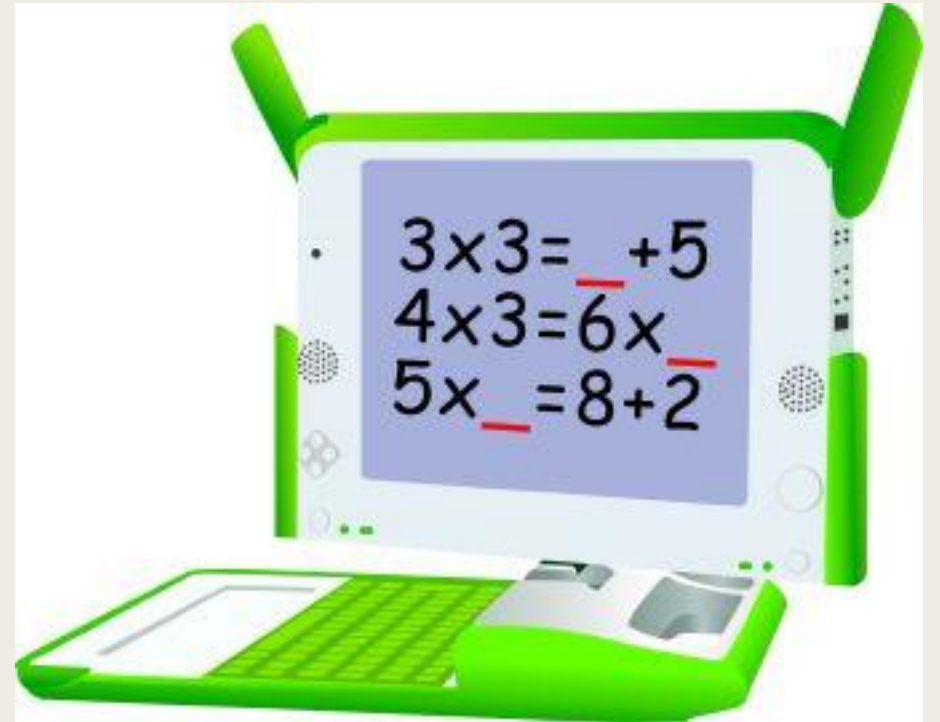
Ammonia (NH$_3$-N) Analysis

– *The results of the Matrix Spike and Matrix Spike Duplicate must fall within laboratory acceptance limits*

- ■ Generally 90-110%R

- ■ $\%R = \dfrac{(Spiked\ result\frac{mg}{L} - Unspiked\ result\frac{mg}{L})}{True\ Value\ of\ Spike}$ x 100

- ■ Relative Percent Difference 30% or less

- ■ $RPD = \dfrac{|(Result\ 1 - Result\ 2)|}{Average\ of\ Result\ 1, Result\ 2}$ x 100

Ammonia (NH$_3$-N) Analysis

- Analyze the DMR-QA standard
  - *The result must be bracketed by the calibration standards*
  - *If result is greater than highest calibration standard the DMQ-QA standard must be diluted.*
    - Use Class A glassware to prepare dilution
    - Prepare dilution to obtain result that falls mid-range of calibration standards
    - Example: 1 mg/L and 10 mg/L calibration standards were used
      - *DMR-QA result on the prepared sample read 20 mg/L*
      - *Take 25 mLs of prepared DMR-QA standard and dilute volumetrically to a final volume of 100 mLs.*
      - *This is equivalent to a 1:4 dilution and should yield a result around 5 mg/L*
      - *The obtained result must be multiplied by the dilution factor*
      - *Use the following equation when the prepared sample is diluted:*
      - *DMR-QA NH$_3$−N mg/L = obtained value mg/L x $\dfrac{Final\ volume\ mLs}{Initial\ Volume\ mLs}$*

Ammonia (NH$_3$-N) Analysis
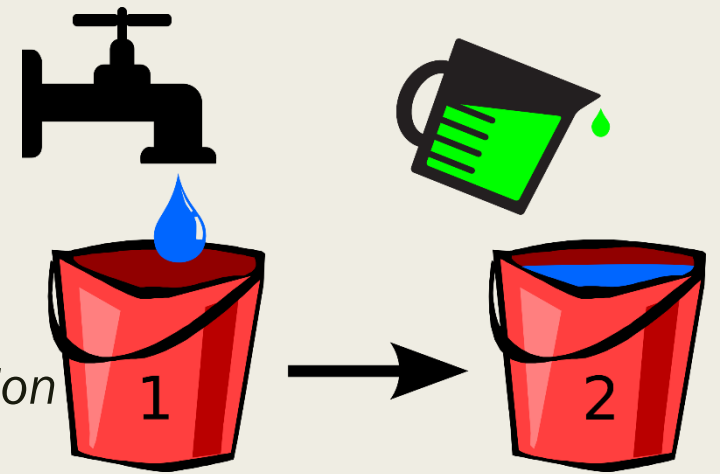
– *Example:*

– *1 mg/L and 10 mg/L calibration standards were used for calibration*

- DMR-QA result on the prepared sample read 20 mg/L

- Take 25 mLs of prepared DMR-QA standard and dilute volumetrically to a final volume of 100 mLs.

- This is equivalent to a 1:4 dilution and should yield a result around 5 mg/L

- The obtained result must be multiplied by the dilution factor

- Use the following equation when the prepared sample is diluted:

- DMR-QA NH$_3$−N mg/L = obtained value mg/L x $\dfrac{Final\ volume\ mLs}{Initial\ Volume\ mLs}$

- DMR-QA NH$_3$−N mg/L = obtained value mg/L x $\dfrac{100\ mLs}{25 mLs}$

Ammonia (NH$_3$-N) Analysis

- After every 10th sample analyzed read the 2nd source standard to verify calibration is still holding

- After the last sample analyzed read the 2nd source standard to ensure calibration is still holding.

- All samples must be bracketed by acceptable 2nd source standard results.

- Verify that the final reported result for the DMR-QA standard falls within the concentration range specified by the PT Provider.

- Report results down to the Proficiency Testing Reporting Level (PTRL)

BOD/CBOD Analysis

- BOD/CBOD concentrates are typically preserved with acid by the PT Provider.

- Follow PT Provider instructions

- General Guidance
  - *Warm the BOD/CBOD PT standard to room temperature*
  - *If the standard is a whole volume sample:*
    - ANALYZE THE SAME DAY THE STANDARD IS OPENED.
  - *If the standard is a concentrate dilution is required*
    - Use clean Class A glassware to prepare dilutions
    - Use demand free reagent water to prepare dilutions
    - MIX THE SOLUTION BY INVERTING 3-5 TIMES AND SWIRLING
   - IMMEDIATELY ANALYZE DILUTED STANDARD PER SOP

BOD/CBOD Analysis

- Temperature of DMR-QA prepared sample or whole volume sample must be 17-23˚C

- Check pH of the DMR-QA prepared sample or whole volume sample
  - *pH must be 6.0 – 8.0*
  - *If not, adjust to 7.0 – 7.2*
  - *Use a dilute solution of NaOH to raise the pH*
  - *Use a dilute solution of H_2SO_4 to lower the pH*
    - Perform slowly
    - Do not dilute DMR-QA more than 0.5%

- Check DMR-QA for residual chlorine

The pH Scale

Acid   Neutral   Base

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
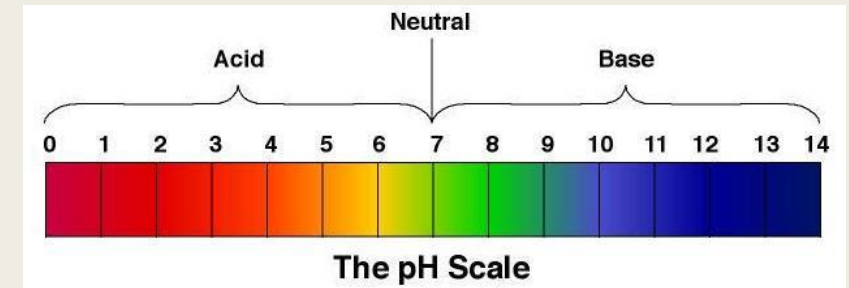
BOD/CBOD Analysis

- **The DMR-QA for BOD and/or CBOD must be seeded**

- Perform a series of dilutions to obtain at least one bottle that depletes at least 2 mg/L and has a Final D.O. ≥ 1 mg/L.

- Review the paper work from the Provider

    - *Ranges will be provided for expected concentration of the DMR-QA*

    - *Prepare dilutions according to the range provided*
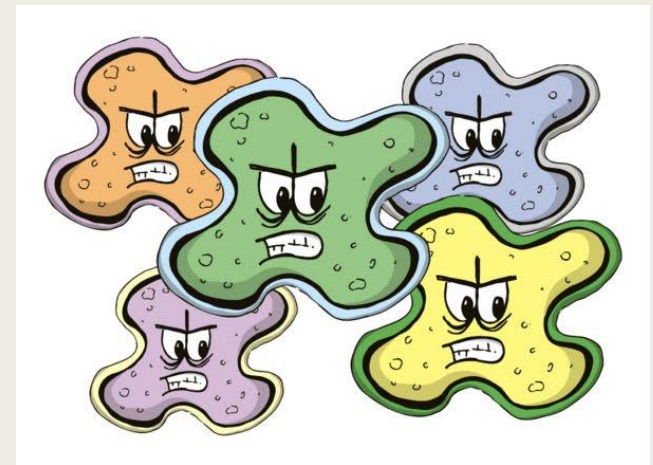
BOD/CBOD Analysis

- **What dilutions should I use?**
  - *Use dilutions that have overlapping useable ranges that fall within entire concentration range.*

- For example: BOD or CBOD expected concentration range is 18.0 – 230 mg/L

- Use dilutions of 100, 30, 10 & 3 mLs

Sample Volume mLs	Useable Range mg/L
300	2.0 - 7.0
200	3.0 – 10.5
100	6.0 – 21.0
60	10.0 – 35.0
50	12.0 – 42.0
40	15.0 – 52.5
30	20.0 – 70.0
25	24.0 – 84.0
20	30.0 – 105.
15	40.0 – 140.
10	60.0 – 210.
5	120. – 420.
4	150. – 525.
3	200. – 700.
2	300. – 1050.
1	600. – 2100.

BOD/CBOD Analysis

BOD

- Analyze the DMR-QA with regular batch of plant samples

- Follow SOP for preparation of BOD water, Seed and GGA standard

- Aliquot QC samples, plant samples and DMR-QA to BOD bottles

- **Blank** – contains only BOD dilution water

- **Seed Control** - 5, 10 & 15 mLs of seed + dilution water

- **GGA** – contains GGA + seed + dilution water

- Samples – sample + seed + dilution water

- Duplicate a plant sample

- Calibrate D.O. meter

- Measure Initial D.O.

- Incubate 5 days at 20 ± 1˚C

- Calibrate D.O. meter

- Measure Final D.O.

CBOD

- Analyze the DMR-QA with regular batch of plant samples

- Follow SOP for preparation of BOD water, Seed and GGA standard

- Aliquot QC samples, plant samples and DMR-QA to BOD bottles

- **Blank** – contains only BOD dilution water

- **Seed Control** - 5, 10 & 15 mLs of seed + nitrification inhibitor + dilution water

- **GGA** – contains GGA + seed + nitrification inhibitor + dilution water

- Samples – sample + seed + nitrification inhibitor + dilution water

- Duplicate a plant sample - sample + seed + nitrification inhibitor + dilution water

- Calibrate D.O. meter

- Measure Initial D.O.

- Incubate 5 days at 20 ± 1˚C

- Calibrate D.O. meter

- Measure Final D.O.

Add Additional Nutrient Pillow for bottles containing 200 mLs or more of sample.

BOD/CBOD Analysis

- Calculate the final result using all dilutions that meet the 2 mg/L depletion and have a final D.O. ≥ 1 mg/L.

- Verify GGA standard falls within acceptance limits
  - *BOD 198 ± 30.5 mg/L*
  - *CBOD 198 ± 30.5 mg/L or within laboratory calculated limits*

- Verify the Duplicate RPD ≤ 30%

- Verify that the final reported result for the DMR-QA standard falls within the concentration range specified by the PT Provider.

- Report results down to the Proficiency Testing Reporting Level (PTRL)

Residual Chlorine

- Follow PT Provider instructions

- General Guidance

  - *Warm the Residual Chlorine PT standard to room temperature*

  - *Generally the Residual Chlorine standard is a concentrate and dilution is required to prepare the sample for analysis.*

    - Use clean Class A glassware to prepare dilutions

    - Use chlorine free reagent water to prepare dilutions

    - **MIX THE SOLUTION, INVERT AND SWIRL 3-5 TIMES**

    - IMMEDIATELY ANALYZE PREPARED STANDARD

Residual Chlorine

- Calibrate chlorine meter or verify factory calibration following SOP
  - *Verify calibration standards are within expiration date*
- Verify calibration using 2nd source standards
  - *Gel standards are acceptable*
    - Follow instructions supplied by manufacturer
    - Verify result is within manufacturer limits stated on certificate

Residual Chlorine

- Perform method blank
  - *Use chlorine free reagent water*
- Analyze routine plant samples
- Analyze a plant sample in duplicate
  - *Verify RPD is ≤ 30%*
- Analyze the DMR-QA standard
  - *Result must be below the highest calibration standard concentration*
  - *If result is greater than highest calibration standard the DMQ-QA standard must be diluted.*
    - Use Class A glassware to prepare dilution
    - Prepare dilution to obtain result that falls mid-range of calibration standards

Residual Chlorine

- Result must be below the highest calibration standard concentration
  - *If result is greater than highest calibration standard the DMQ-QA standard must be diluted.*
    - Use Class A glassware to prepare dilution
    - Prepare dilution to obtain result that falls mid-range of calibration standards
- Calculate the final Residual Chlorine result
  - *DMR-QA Residual Chlorine mg/L = obtained value mg/L x $\dfrac{Final\ volume\ mLs}{Initial\ Volume\ mLs}$*
- Verify that the final reported result for the DMR-QA standard falls within the concentration range specified by the PT Provider.
- Report results down to the Proficiency Testing Reporting Level (PTRL)

pH Analysis

- Follow PT Provider instructions

- General Guidance

  – *Warm the pH PT standard to room temperature*

  – *Generally the pH standard is a whole volume sample ready for analysis*

  – *If it is a concentrate dilution is required to prepare the sample for analysis.*

    - Use clean Class A glassware to prepare dilutions

    - Use reagent water to prepare dilutions

    - **MIX THE SOLUTION, INVERT AND SWIRL 3-5 TIMES**

    - **IMMEDIATELY ANALYZE PREPARED STANDARD**

pH Analysis
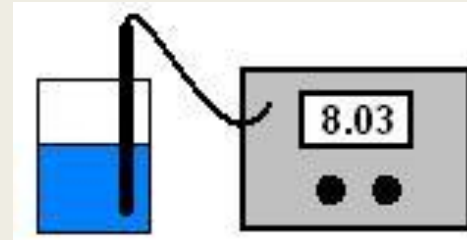
- Calibrate pH meter
  - *Use an ATC (Automatic Temperature Compensation meter and probe)*
  - *Slowly mix buffers and samples during measurement*
  - *Use 7, 4 and 10 pH buffers*
  - *Alternating use either 7 & 4 or 7 & 10 pH buffers*
  - *The pH of all samples including the DMR-QA standard must be bracketed by pH buffers used for calibration.*
  - *Performing a 3 point calibration eliminates the need to re-calibrate*
- Document slope
  - *Ensure slope falls within manufacturer's recommendations*
  - *Typically 95-105, but can vary*

pH Analysis

- Verify calibration using a 2nd source buffer
  - *If using 7.00, 4.00 & 10.00 buffers for calibration use a 2nd source pH 7.00 buffer*
  - *If using 7.00 & 4.00 buffers for calibration use a 2nd source pH 5.00 or pH 6.00 buffer*
  - *If using 7.00 & 10.00 buffers for calibration use a 2nd source pH 8.00 or pH 9.00 buffer*
  - *Limits ± 0.10 standard units (s.u.)*
  - *Record results to two decimal places*
- If slope and verification buffer meet limits proceed with analysis

pH Analysis

- Analyze routine plant samples
  - *Report to two decimal places*
  - *Results must be bracketed by pH calibration buffers*
- Analyze a plant sample in duplicate
  - *Duplicate results must be ± 0.10 s.u.*
  - *Report results to two decimal places*
- Analyze the DMR-QA standard
  - *Shake the bottle before removing a portion for analysis.*
  - *Result must be bracketed by pH calibration buffers or the meter will need to be recalibrated with buffers that bracket the sample*
  - *Report results to two decimal places*
- Verify that the final reported result for the DMR-QA standard falls within the concentration range specified by the PT Provider.

Total Suspended Solids (TSS) Analysis

Follow PT Provider instructions

General Guidance

- *Warm the Total Non-Filterable (TSS) PT standard to room temperature*

- *If the standard is a whole volume sample dilution is not required*

    - ANALYZE THE SAME DAY THE STANDARD IS OPENED.

- *If the standard is a concentrate dilution is required*

    - Use clean Class A glassware to prepare dilutions

    - Use reagent water to prepare dilutions

    - **MIX THE SOLUTION VIGOROUSLY 3-5 TIMES (INVERT AND SHAKE)**

    - IMMEDIATELY ANALYZE DILUTED STANDARD

Total Suspended Solids (TSS) Analysis

■ Perform method blank

– *500 mLs or 1000 mLs of reagent water*

■ Analyze routine plant samples

■ Perform Duplicate on one of the plant samples

– *The results of the Duplicate must fall within laboratory acceptance limits*

– *RPD ≤ 30%*
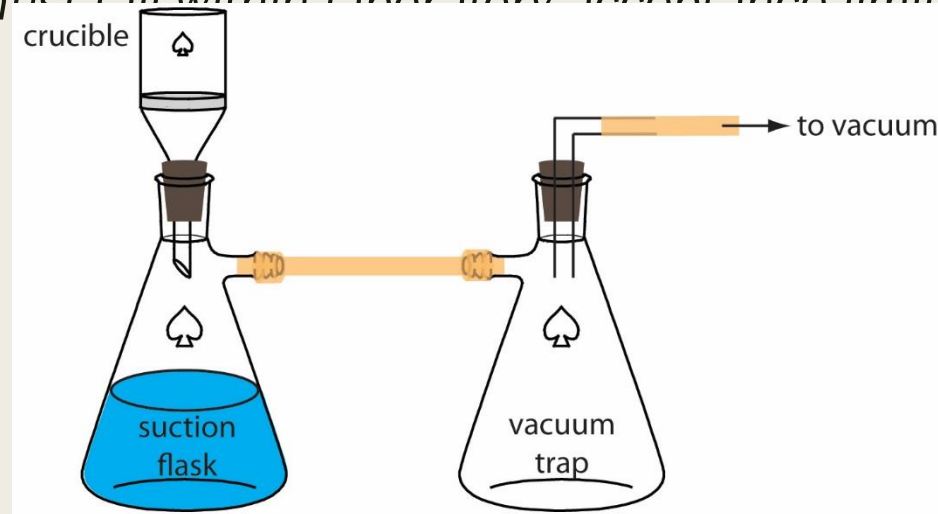
Total Suspended Solids (TSS) Analysis

- Analyze the DMR-QA standard
    - *Shake sample vigorously immediately prior to measuring sample volume for filtration and pour directly to a Class A graduated cylinder*
    - *Filter enough sample volume to yield at least 0.0100 grams – 0.2000 grams of dried residue*
    - Dried Residue = Final filter weight (g) − Initial filter weight (g)
    - *Suggest using 250 mLs to 500 mLs of DMR-QA standard depending on the expected range listed by the PT Provider*
        - Example: TSS range is 20 mg/L – 100 mg/L
        - Maximum residue on filter per liter of sample filtered is 100 mg
        - If Lab uses 500 mLs of DMR-QA the maximum residue filtered would be 50 mg and the minimum residue would be 10 mg.

Total Suspended Solids (TSS) Analysis

- Rinse the graduated cylinder 3 times with reagent water to ensure a complete transfer of solids to the filtration unit.

- Dry filters at 103-105˚C for at least one hour

- Remove, desiccate at least one hour and weigh

- Repeat the heating, desiccating and weighing process to achieve constant weight.

- Verify that the final reported result for the DMR-QA standard falls within the concentration range specified by the PT Provider.

- Report results down to the Proficiency Testing Reporting Level (PTRL)

DMR-QA Reporting - NH_3-N

- Report results to 3 significant figures
  - *NH_3-N example:*
    - 0.105
    - 1.05
    - 10.5
    - 105.

- Report result down to the Proficiency Testing Reporting Level (PTRL)
- PT Provider includes PTRL for each analyte with DMR-QA standards

DMR-QA Reporting - NH$_3$-N

- **PTRL example:**
  - *NH$_3$-N PTRL = 0.600 mg/L*
  - *Laboratory needs to report down to 0.600 mg/L*
    - Results below 0.600 should be reported as < 0.600 mg/L
  - *Laboratory needs to calibrate NH$_3$-N meter using a low calibration standard of at least 0.600 mg/L or lower.*

DMR-QA Reporting – BOD/CBOD

- Report results to 3 significant figures
  - *BOD/CBOD example:*
    - 2.00
    - 10.0
    - 100.
    - 1000.

- Report result down to the Proficiency Testing Reporting Level (PTRL)
- PT Provider includes PTRL for each analyte with DMR-QA standards

DMR-QA Reporting – BOD/CBOD

- PTRL example:
  - *BOD PTRL = 4.90 mg/L*
  - *Laboratory needs to report down to 4.90 mg/L*
    - Results below 4.90 should be reported as < 4.90 mg/L

DMR-QA Reporting – Residual Chlorine

- Report results to 3 significant figures
  - *Residual Chlorine example:*
    - 0.100
    - 1.00
    - 10.0
    - 100.

- Report result down to the Proficiency Testing Reporting Level (PTRL)

- PT Provider includes PTRL for each analyte with DMR-QA standards

DMR-QA Reporting – Residual Chlorine

- PTRL example:
  - *Residual Chlorine PTRL = 0.380 mg/L*
  - *Laboratory needs to report down to 0.380 mg/L*
    - Results below 0.380 should be reported as < 0.380 mg/L

DMR-QA Reporting – pH

- Report results to two decimal places
  - *pH example:*
    - 4.10
    - 7.00
    - 8.85
    - 9.00

- Report result down to the lowest pH buffer concentration used for calibration

- PTRL is not applicable for pH DMR-QA standards

DMR-QA Reporting – TSS

- Report results to 3 significant figures
  - *TSS example:*
    - 12.0
    - 100.
    - 1000.

- Report result down to the Proficiency Testing Reporting Level (PTRL)
- PT Provider includes PTRL for each analyte with DMR-QA standards

DMR-QA Reporting – TSS

- PTRL example:
  - *TSS PTRL = 12.0 mg/L*
  - *Laboratory needs to report down to 12.0 mg/L*
    - Results below 12.0 should be reported as < 12.0 mg/L

PTRL IMPORTANCE

■ If a laboratory results a less than result for a parameter at a concentration higher than the PTRL the laboratory will receive a Not Acceptable Score

■ Example

– *TSS PTRL = 12.0 mg/L*

– *Laboratory reported < 20.0 mg/L*

– *Laboratory needs to use sufficient volume of sample to achieve a reporting level of at least 12.0 mg/L.*

3 Significant Figures Importance

- Example:
  - *DMR-QA Residual Chlorine Acceptable Range was 0.994 – 1.250 mg/L*
  - *Laboratory reported 0.99 mg/L*
  - *The actual measurement from meter read 0.995 but lab rounded result.*
  - *The rounding and reporting of 0.99 mg/L yields a Not Acceptable score*
  - *If lab reported 0.995 mg/L an Acceptable Score is achieved*

THANK YOU