



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 GET FROM HERE



TO HERE



Demand (PT-DEM-DMRQA) Lot #: 8527-07

Analyte	Method Code	Units	True Value	Result	Acceptance Limits	Evaluation
BOD	SM 5210B	mg/L	181	210	61.2-199	Not Acceptable
CBOD	SM 5210B	mg/L	181	201	48.0-199	Not Acceptable

Solids (PT-SOL-DMRQA) Lot #: 8527-09

Analyte	Method Code	Units	True Value	Result	Acceptance Limits	Evaluation
TSS	SM 2540D	mg/L	92.3	70.0	76.1-102	Not Acceptable

Demand (PT-DEM-DMRQA) Lot #: 8527-07

Analyte	Method Code	Units	True Value	Result	Acceptance Limits	Evaluation
BOD	SM 5210B	mg/L	181	189	61.2-199	Acceptable
CBOD	SM 5210B	mg/L	181	175	48.0-199	Acceptable

Solids (PT-SOL-DMRQA) Lot #: 8527-09

Analyte	Method Code	Units	True Value	Result	Acceptance Limits	Evaluation
TSS	SM 2540D	mg/L	92.3	90.8	76.1-102	Acceptable

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

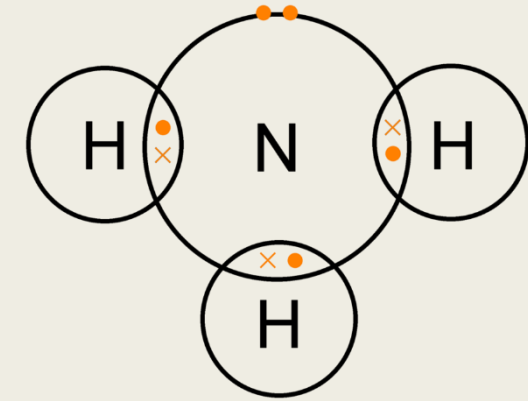


Ammonia (NH₃-N) Analysis

- Follow PT Provider instructions
- General Guidance
 - Warm the NH₃-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 NH₃-N free reagent water to prepare dilutions
 - MIX THE SOLUTION VIGOROUSLY 3-5 TIMES (INVERT AND SHAKE)
 - **IMMEDIATELY ANALYZE DILUTED STANDARD**



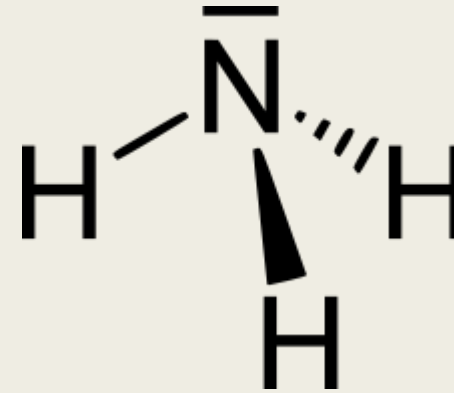
Ammonia (NH₃-N) Analysis



- Calibrate NH₃-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 – $R \geq 0.995$ (correlation coefficient)*
- Use a 2nd source NH₃-N standard to verify calibration standards
 - *Must fall within laboratory limits*
 - *Generally 90-110% Recovery*
 - $\%R = \frac{\text{Obtained value mg/L}}{\text{True Value mg/L}} \times 100$

Ammonia (NH₃-N) Analysis

- Perform method blank
 - *100 mLs of NH₃-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 (NH₃-N) Analysis

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

- Generally 90-110%R

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

- Relative Percent Difference 30% or less

- $$RPD = \frac{|(\text{Result 1} - \text{Result 2})|}{\text{Average of Result 1, Result 2}} \times 100$$

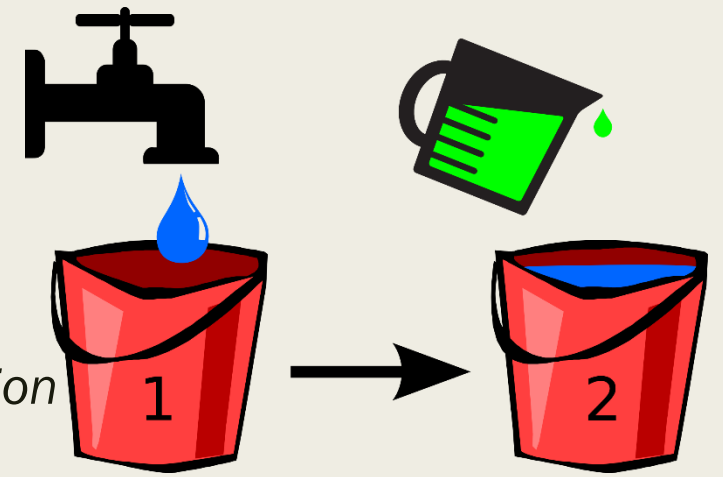


Ammonia (NH₃-N) Analysis



- 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 NH₃-N mg/L = obtained value mg/L × $\frac{\text{Final volume mLs}}{\text{Initial Volume mLs}}$*

Ammonia (NH₃-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:
 - $\text{DMR-QA NH}_3\text{-N mg/L} = \text{obtained value mg/L} \times \frac{\text{Final volume mLs}}{\text{Initial Volume mLs}}$
 - $\text{DMR-QA NH}_3\text{-N mg/L} = \text{obtained value mg/L} \times \frac{100 \text{ mLs}}{25 \text{ mLs}}$

Ammonia (NH₃-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)



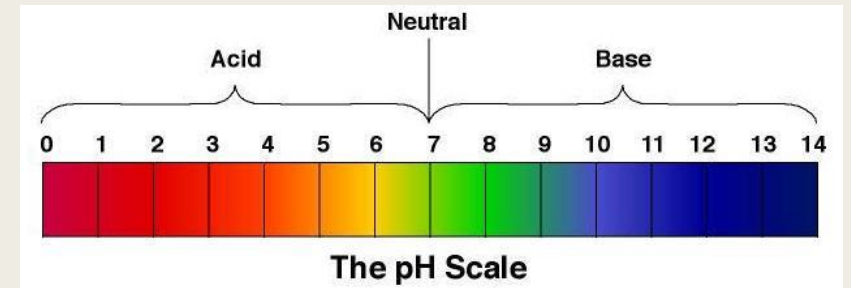
BOD/CBOD Analysis

- 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**



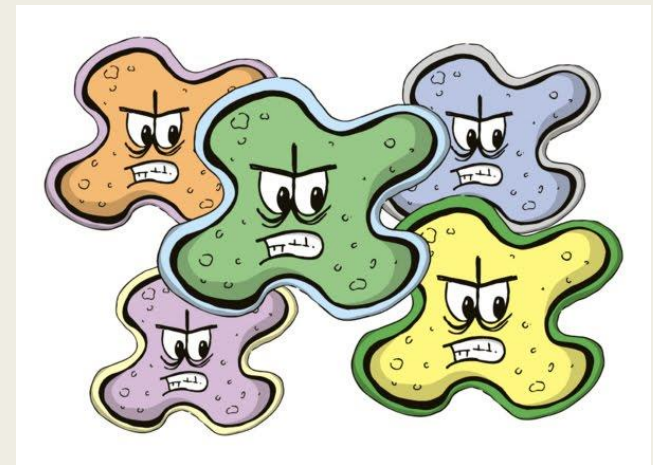
BOD/CBOD Analysis

- 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 H₂SO₄ to lower the pH*
 - Perform slowly
 - Do not dilute DMR-QA more than 0.5%
- Check DMR-QA for residual chlorine



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 $20 \pm 1^\circ\text{C}$
- 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 $20 \pm 1^\circ\text{C}$
- Calibrate D.O. meter
- Measure Final D.O.

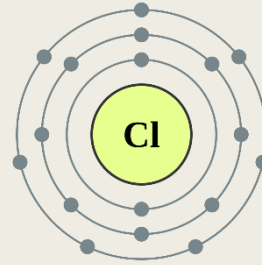
Add Additional Nutrient Pillow for bottles containing 200 mLs or more of sample.

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 $\leq 30\%$
- 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

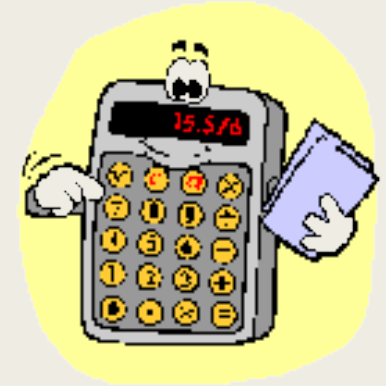


Residual Chlorine

- Perform method blank
 - *Use chlorine free reagent water*
- Analyze routine plant samples
- Analyze a plant sample in duplicate
 - *Verify RPD is $\leq 30\%$*
- Analyze the DMR-QA standard
 - *Result must be below the highest calibration standard concentration*
 - *If result is greater than highest calibration standard the DMR-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



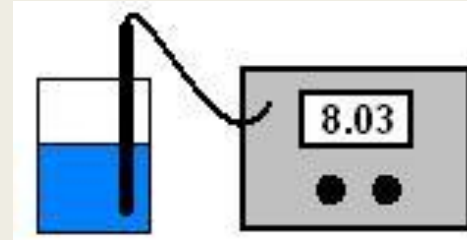
- Result must be below the highest calibration standard concentration
 - *If result is greater than highest calibration standard the DMQ-QA standard must be diluted.*
 - Use Class A glassware to prepare dilution
 - Prepare dilution to obtain result that falls mid-range of calibration standards
- Calculate the final Residual Chlorine result
 - *DMR-QA Residual Chlorine mg/L = obtained value mg/L x $\frac{\text{Final volume mLs}}{\text{Initial Volume mLs}}$*
- 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** (**A**utomatic **T**emperature **C**ompensation 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

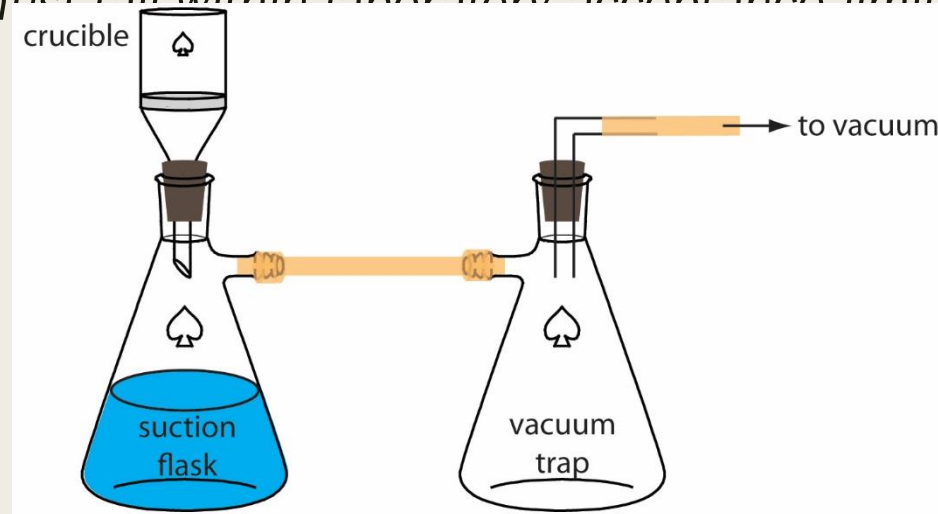
General Guidance

- 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**

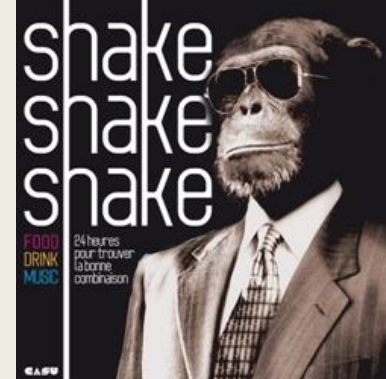


Total Suspended Solids (TSS) Analysis

- 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
 - $RPD \leq 30\%$



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.

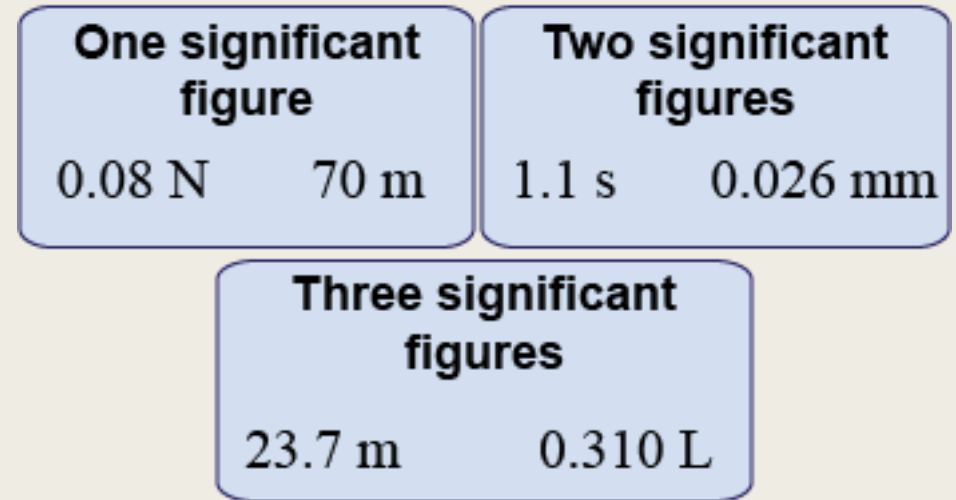
Total Suspended Solids (TSS) Analysis

- 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 - NH₃-N

- Report results to 3 significant figures
 - *NH₃-N example:*
 - 0.105
 - 1.05
 - 10.5
 - 105.



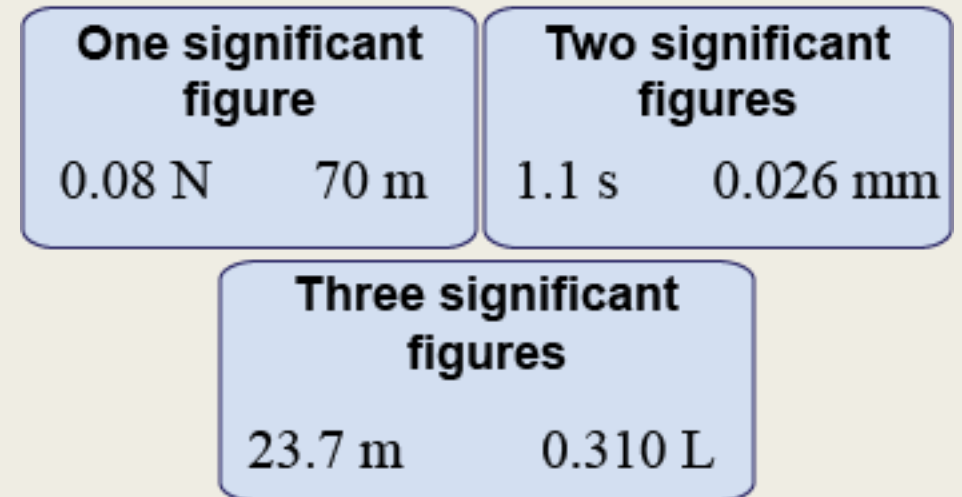
- Report result down to the Proficiency Testing Reporting Level (PTRL)
- PT Provider includes PTRL for each analyte with DMR-QA standards

DMR-QA Reporting - NH₃-N

- PTRL example:
 - *NH₃-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 NH₃-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.

One significant figure

0.08 N 70 m

Two significant figures

1.1 s 0.026 mm

Three significant figures

23.7 m 0.310 L

- 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

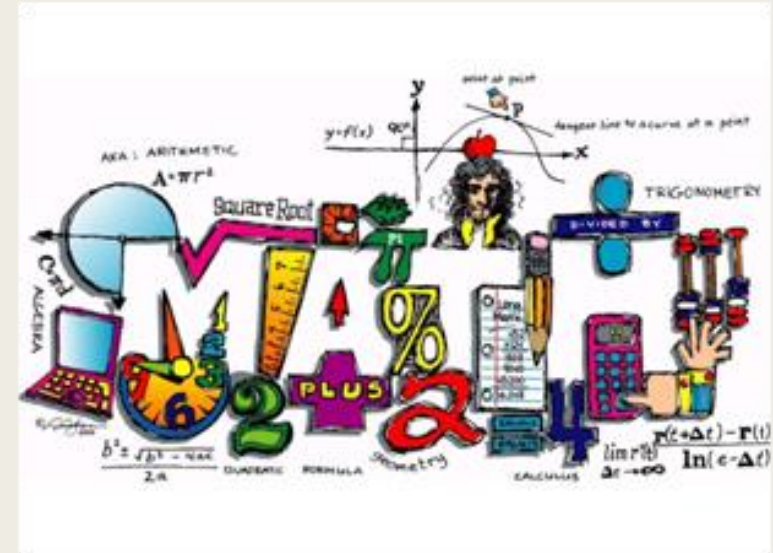
DMR-QA Reporting – pH

- Report results to two decimal places

– *pH example:*

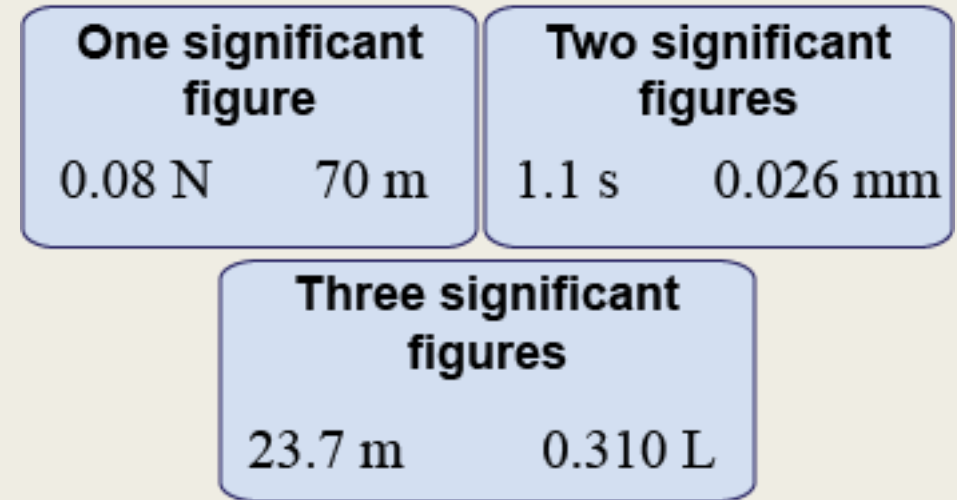
- 4.10
- 7.00
- 8.85
- 9.00

- 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

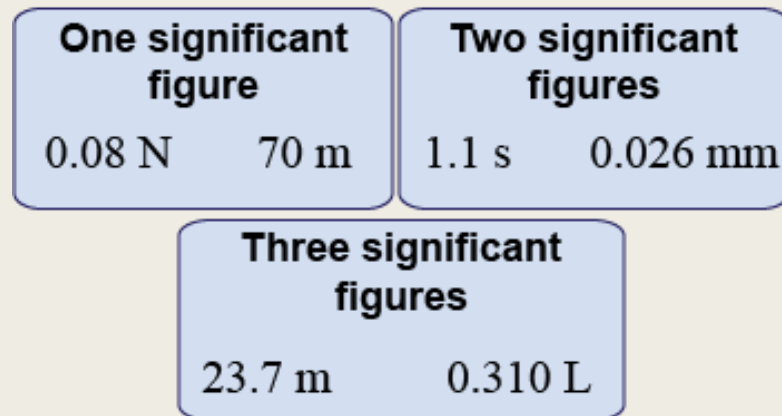
PTRL IMPORTANCE

- 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*



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TO HERE



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