Top Tips for Conducting DMR-QA Analyses

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ERA – A Waters Company

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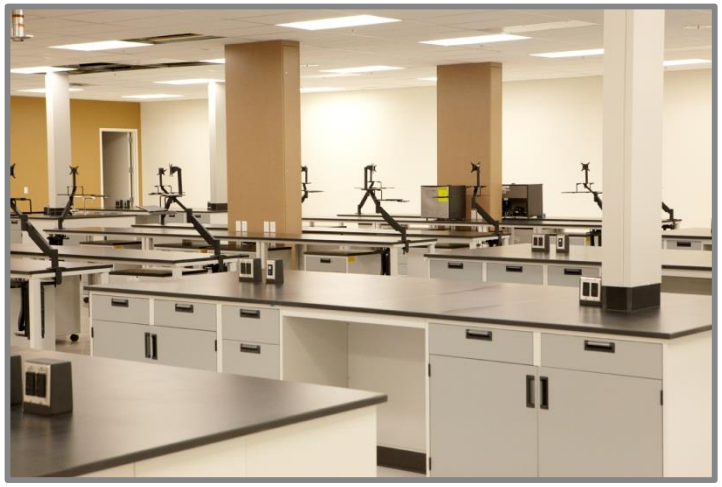

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Agenda

- Analysis Tips and Tricks
  - BOD
  - pH
  - Residual Chlorine
  - Total Suspended Solids (TSS)
  - Ammonia
  - Phosphorus

- Questions??

Today's Discussion

- From an analytical standpoint, running your tests for DMRQA is no different than running the tests for your DMRs.
- For your DMRs, you need to make sure your values are below your permit limits so you can discharge your effluent back into the environment.
- For the DMRQA, you will be given a sample with a known amount of analyte and must return a value within a defined set of acceptance limits.
- So, what may be good enough for your DMRs may not be good enough for the DMRQA.
- We won't discuss how to run the tests, because you already know that. We will focus on tips and tricks to hopefully help tighten up the processes.

BOD – Tips and Tricks

- There are many places for things to go wrong. The DMRQA acceptance limits reflect this. Taking care to ensure your process is in control can solidify your analysis and leave you within the acceptance range.

BOD - SM 5210 B – Overview of the Method

- Adjust sample pH according to your version
- Prepare and check your dilution water
- Perform necessary dilutions, seed, and fill bottles
- Include all necessary method QC
- Take initial DO readings
- Incubate for 5 days at 20°C
- Take final DO readings
- Perform calculations

BOD – Preparing for the test

- Dilute your sample properly. Adjust your pH. The diluted sample will have a pH of about 3.5-4. the test requires pH of 6.5-7.5. Use dilute NaOH solution to adjust (0.2 N is recommended). More concentrated solutions will cause the pH to shoot up past the upper range.
- pH out of the range will distress the microorganisms and cause low results.
- Residual chlorine will distress or kill your microorganisms. Ensure all your glassware, water, and reagents used for the test are free from chlorine.
- The BOD bottles are filled with nutrient (dilution) water. Nutrient water must be fresh to assure sufficient ammonia remains in the water. Nutrient water must be free of chlorine and organics.

BOD – Preparing for the test

- Ensure the chemicals you use for your nutrient water are fresh and of good quality.
- There are nutrient water packs available that make the process easier.
- Prepare your dilution water fresh and use within 24 hours.
- Test your dilution water to ensure the pH is at 7 and it free of organics.
- Perform proper dilutions of the sample. The dilutions performed on your sample are extremely important for proper testing. Do a series of dilutions to ensure that you have multiple samples meeting method requirements.
- The DMRQA BOD will be between 18 and 230 mg/L. Perform your dilutions to meet this range. Use your historical analyses to help determine the proper dilutions.

BOD – Preparing for the test

- The samples you receive from your provider will not contain seed and thus need to be seeded prior to the analysis. The seed must be strong and consistent. Most plant raw will satisfy this need. Poly seeds are commercially available. The poly seed is generally not as strong and will require additional volume than the raw seed.
- Seed each bottle with the same amount of seed. Do not seed your dilution water, as different volumes of dilution water are used and will vary the amount of seed in each sample.

BOD – Performing the test

- Once the dilutions are performed and seed is added, fill the bottle with nutrient water.
- Take an initial DO reading. If using the electrode method, make sure the electrode is maintained and calibrated. You can analyze a DO QC sample to check the calibration of the meter.
- The DO probe must be maintained. Clean the gold plate on the probe at least monthly and change the membrane at least weekly. Dirty membranes and gold plates will cause the probe to drift. Do a water check at the beginning and end of your run. This check should not show a DO difference of more than 0.15 mg/L. A drift greater than this will cause erroneous readings.

BOD – Performing the test

- The initial DO should ideally be between 7-9. DO can be added or removed from the sample if needed. Replace any displaced nutrient water before capping the sample.
- When filling the BOD bottles full, make sure there is a small amount of nutrient water above the cap to ensure there is a water barrier. The cap of the bottle should be covered to prevent moisture loss. This will prevent any air from being introduced into the sample during incubation. Introducing air into the sample will add DO to your sample.

BOD – Performing the test

- The samples need to be incubated in the dark at 20°C ± 1°C for 5 days ± 5 hours
- Improper incubation temperature will cause erroneous results. Your temperature needs to be 20 ± 1°C. Low temperatures will slow the microorganisms causing low results. High temperatures will speed up microorganisms causing high results.
- Incubating for longer than the prescribed time will cause excess oxygen depletion resulting in high values, or for shorter than the prescribed time will cause low oxygen depletion resulting in low values.
- When incubation is complete test the final DO.

BOD – Important Method QC

- Run a seed control sample. Seed contains BOD. Your seed control sample should return BOD values of 0.6-1.0 mg/L.
- Ensure that your seed control values are subtracted out from your samples before performing final calculations.
- Check the quality of the nutrient water to ensure there is no BOD. Perform this check by incubating a bottle with just Nutrient water. Your nutrient water should contain BOD at less than 0.2 mg/L.
- The incubation should result in a minimum DO depletion of 2.0 mg/L and a minimum residual DO of 1.0 mg/L. Use only samples that meet this requirement for performing calculations.

BOD – Important Method QC

- Your GGA standard should return a value of 198 ± 30.5 mg BOD/L.
- Your water checks during analysis should not show drift of more than 0.15 mg/L.

pH

- pH is certainly the easiest test in DMRQA. However, due to ecological importance it also has the tightest limits
  - ± 0.2 s.u.
- It is recommended to leave your calibration buffers and pH sample on the bench together to equilibrate to the same temperature.

pH - Tips and Tricks

- Calibrate the pH meter each time an analysis is performed.
- Bracket the concentration being analyzed with the appropriate buffers.
- If possible, use two buffers to narrow your dynamic range (i.e. 4-7 or 7-10).
- Use fresh buffer each time. Do not reuse buffers or pour used buffer back into the containers.
- Ensure that the buffers and samples to be run are at the same temperature.
- Use a temperature compensation probe (ATC). The ATC can compensate up to about 5^{o}C change in temperature.

pH - Tips and Tricks

- Air contains CO2. CO2 will adsorb into the sample and change the pH. Avoid exposing pH buffers and samples to air. The pH 10.0 buffer is extremely sensitive to CO2 adsorption. It is recommended not to use the pH 10 buffers for more than 3 months after opening the bottle. Air exposure is minimized if you are using cubitainers to hold your buffers.
- Monitor the performance of your probe to determine how well it is working. Here is an easy trick. Set your meter to read mV and not pH. Place the probe in the pH 7 buffer. The meter should read 0 mV. Acceptable ranges are -30 to +30. Place the probe in the pH 4 buffer. The meter should read 171 mV difference from the 7 to 4. If this difference is more than ±30 mV, your probe needs maintenance or replacement.

pH - Tips and Tricks

- If the probe mV readings are in acceptable ranges for the 7 to 4, place the probe in the 10 buffer. The difference between the 7 and 10 should also be ± 171 mV. If not the 10 buffer may be going bad. Replace the buffer.
- If using the refillable electrodes, Clean the inside of the probe monthly using DI water.
- The buffers used to calibrate will cause film buildup on the outside of the electrode. Clean this using about a 1M nitric acid solution for an hour and DI rinse.

pH - Tips and Tricks

- MOST IMPORTANTLY: The limits for pH are very tight. At ± 0.2 s.u., there is very little wiggle room. The tips and hints presented may allow your analysis to become more accurate by 0.02 s.u., but it may be the difference between passing and failing your PT.

Residual Chlorine – Facts

- Chlorine is very unstable. The samples should be run as quickly as possible after diluting. ERA research has shown that the samples will be stable for about 2 hours after dilution.
- Chlorine has an affinity to adhere to the small pores which are contained in plastics. Therefore, no plastics should be used when diluting the sample.
- Chlorine is easily oxidized, so minimize exposure to air to prevent degradation.
- Chlorine photo degrades, so if not running within 15 minutes try to protect from light.
- DMRQA offers both a mg/L (ppm) and µg/L (ppb) level sample.

Residual Chlorine – Preparing the Sample

- Your Residual Chlorine sample should come in an amber flame sealed ampule.
- The sample needs to be homogenized prior to aliquoting.
- Mix the sample by inverting the ampule at least 3 times. Make sure there is no sample left in the neck of the vial.
- The water used for sample dilution must be chlorine and organic free. Most sources of DI and distilled water are acceptable. If using distilled water it is essential to ensure that the still is not copper based. Copper is an interferent in TRC analysis.

Residual Chlorine – Preparing the Sample

- Chlorine has an affinity to adhere to the micro pores which are contained in plastics. Plastics also have a large chlorine demand. Therefore, no plastics should be used when diluting the sample.
- Glassware needs to be clean. The most effective way to clean glassware used is to soak in a weak bleach solution for at least an hour to remove chlorine demand. Ensure that you thoroughly rinse with DI or distilled water after.
- Fill a clean Class "A" volumetric flask with some DI water. The amount is not critical, just do not add to an empty flask. An amber flask will help delay the degradation of chlorine.
- Use a glass pipet or gas tight syringe to aliquot.

Residual Chlorine Analysis Tips
Automated Amperometric Titration

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- Automated amperometric titrators (Autocat 9000) can detect low levels of chlorine. Time of analysis is a concern.
- Ensure that reagents and titrants are fresh so chemical reactions take place quickly.
- This technique back titrates iodine. Add acetate buffer first as the reaction needs to take place at pH of 4.
- Chloramines oxidize iodide to iodine allowing analysis of combined as well as free chlorine. PAO is used to titrate.
- If using a cathode, make sure the cathode is scrubbed well to remove any oxidation.

Residual Chlorine – Tips and Tricks - DPD

- Allow ample time for chemical reaction. Chemicals weather
- Run 1 more minute.
- Make sure your meter is on the correct setting (low or high range).
- If calibrating your meter with KMnO4, make sure standards are made fresh.
- Avoid excess mixing of standards. KMnO4 tends to stick to the glassware.

Residual Chlorine – Tips and Tricks - DPD

- Most analysis is performed on HACH meters. HACH meters are internally calibrated. These meters work great, but the internal calibration will drift over time. It is recommended to have these meters recalibrated every year.
- Zero the meter prior to running the PT samples by placing an aliquot of the sample in the cell and do not add reagent to the sample.
- HACH powder pillows are designed for two different sample sizes. Choose the correct sample size.
- Remember to add KI if running for Total Chlorine.

Residual Chlorine - Low Level Specific Tips

- Low level analysis poses extra problems, most notably detection limits.
- Make sure your procedure will allow you to see down to 50 µg/L for PT analysis or lower if permits have lower limits.
- Hach has specs that can see this low. Cleanliness at these levels is ultra important.
- The best option is to use a flow through cell. This allows a greater amount of sample loading and thus lower detection limits.

Residual Chlorine - Low Level Specific Tips

- Ensure the flow though cell is clean. Check for film on the cell. Use a soft cloth or optical tissue to clean the cell windows as paper towels or other paper products may scratch the cell.
- Check the cell for scratches. Scratches on the cell will cause erroneous results.
- Flush the cell thoroughly between analyses with DI water.
- Make sure you are using the DPD indicator for ultra low level chlorine.
- If buildup of colored reaction products occurs, clean the flow through cell with dilute sulfuric acid.

Total Suspended Solids (TSS) – Tips and Tricks

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- When using gravimetric tests, ensure that you can accurately and appropriately read the amount of residue left in the pan.
- For TSS, mix the sample extremely well as the TSS is heavier than water and will sink to the bottom of the sample container.
- TSS powder sticks to everything. Make sure you rinse all glassware that comes into contact with TSS thoroughly with DI water, at least three times to ensure no TSS has stuck to glassware (graduated cylinders, vacuum apparatus).
- Ensure that the sample is completely dry. Dry the sample using your normal procedure. Once the dry weight is measured, place the sample back into the oven for at least 30 minutes and reweigh your sample until a constant weight is achieved (< 0.5mg or 4%).
- Use a desiccator to ensure that you are not introducing moisture when cooling.

Total Suspended Solids (TSS) – Environmental Controls

- Always wear gloves when handling filters and pans. Your hands contain oils that will add to the weight of the filter. This will cause falsely high readings.
- Use an analytical balance that measures to at least 4 decimal places. Any fewer places will not provide sufficient resolution for accurate measurements.
- Ensure your balance is level. Each balance has a level indicator.
- Check the calibration of your balance each day you make measurements for accuracy. Use weights that will bracket the masses you are measuring.
- Tare the balance prior to each reading. The balance will drift over time.

Total Suspended Solids (TSS) – Environmental Controls

- The balance has an associated uncertainty. This uncertainty cannot be avoided so its effect needs to be minimized.
- When measuring mass on a balance you notice that the last decimal place in the balance rarely remains constant. It routinely changes. This is called the uncertainty because you are uncertain which number to record.
- The uncertainty can be minimized by at much as 3.5% by increasing the mass on the balance.

Total Suspended Solids (TSS) – Balance Uncertainty

- TSS made at 23 mg/L
- Using 100 mL of sample will place 2.3 mg of residue on the balance.

0.0022

0.0023

- You have to record one value. The difference between these two values in 4.5%.

Total Suspended Solids (TSS) – Balance Uncertainty

- TSS made at 23 mg/L
- Using 500 mL of sample will place 11.5 mg of residue on the balance

0.0115

0.0116

- You have to record one value. The difference between these two values in 1%.

- So by increasing the amount of sample used for your test, you have minimized the potential error caused by the uncertainty of the balance by 3.5%

Total Suspended Solids (TSS) – Controlling Moisture

- Moisture is an enemy of TSS analysis. All labs have moisture issues to address.
- Always cool your pans and filter paper in a desiccator that contains a drying agent which will pull moisture out of the chamber.
- Minimize the number of times the chamber is opened and closed during the test as moisture can be introduced.
- Minimize the length of time the pans and filter paper are left in the desiccator prior to being used for TSS. Long times can result in moisture gain prior to measuring the filter tare. This will cause falsely low readings as this moisture is driven off during the drying process.

Total Suspended Solids (TSS) – Controlling Moisture

- To help monitor the effects of moisture in the analysis run a filter blank.
- Prepare a filter similar to those used for the sample. Filter only DI water through the filter. DI water contains no TSS, so in a perfect world this filter blank should record a TSS value of 0.
- In a real world analysis this filter blank rarely shows a value of 0. The difference will be minimal.
- It is not uncommon to see filter blank differences of 0.0002 mg on the balance.
- It is a good assumption that if you are seeing moisture gain/loss on the filter blank you are also seeing it in your sample.
- Blank subtraction is not allowed, so moisture effects must be minimized.

Total Suspended Solids (TSS) – Controlling Moisture

- TSS made at 23 mg/L
- Using 100 mL of sample will place 2.3 mg of residue on the balance.

Sample should read 0.0023

Filter blank of 0.0002

Moisture affected reading 0.0025

- In this instance the moisture gain in the lab has affected the value by 9%.

Total Suspended Solids (TSS) – Controlling Moisture

- TSS made at 23 mg/L
- Using 500 mL of sample will place 11.5 mg of residue on the balance.

Sample should read 0.0115

Filter blank of 0.0002

Moisture affected reading 0.0117

- In this instance the moisture gain in the lab has affected the value by 1%.
- So by increasing the amount of sample used for your test, you have minimized the potential error caused by the potential moisture gain by 8%.

Reporting TSS Results

- Make sure to report your results as mg/L. If you use a sample volume less than 1L, adjust your results for the volume used.
- Report your results to 3 significant figures. Reporting too few/too many significant figures can cause failures.
- For example if the upper acceptance limit is 100 mg/L and you report 100.2 mg/L, you will receive a “not acceptable” evaluation.
- Do not blank subtract. It is not allowed in most states for reporting.

Ammonia as N – Tips and Tricks

- It is extremely important to remember that the Ammonia is reported as N and not NH_3. Ensure that your calibration stock is certified as N. Otherwise a conversion of the value is necessary. If your calibrating as NH_3, you must convert your values to N by multiplying the value by 0.8224. This is the ratio of N/NH_3.
- Distillation of the DMRQA Ammonia sample is not necessary as the ammonia is already free in the water. However, you must follow your method as you normally run it. Therefore, if you normally distill your samples, you must distill the DMRQA sample as well.
- Ammonia electrode measurements are based on partial pressure. The readings are based on differential pressure on the membrane from the solution inside the probe and the sample.

Ammonia as N – Tips and Tricks

- Proper electrode operation is critical for acceptable analysis. The membrane of the electrode should be changed at least weekly as film buildup will affect the partial pressure readings.
- Check the slope of the electrode each day you run. Spike a 100 mL beaker of DI with a 10 fold change of ammonia (i.e. 1 mg/L and 10 mg/L). The difference in mV reading should be 54-60 mV. If outside this range, perform maintenance of the electrode.
- Calibrate your electrode for each analysis. Samples should be quantitated within your calibration range. The most accurate part of your curve is the middle two thirds. Your curve will be less accurate as you approach the extremes of the calibration range.

Ammonia as N – Tips and Tricks

- When calibrating your electrode, the tighter the dynamic range of your curve the more accurate your measurements will be.
- The DMRQA sample will be between 1-20 mg/L. Calibration should be as close to this range as possible. It is much more difficult to quantitate a sample at 5 mg/L if you are calibrating to 100 mg/L instead of 20 mg/L.
- Run a calibration check prior to analyzing samples. Use a secondary source, different from your calibration source to ensure your calibration source is accurate and your electrode is calibrating properly.
- Run QC checks during your run to ensure your electrode is not drifting. This source can be either your calibration source or a secondary source.

Ammonia as N – Tips and Tricks

- Temperature changes will affect your electrode. Ensure that there is no heat transfer from your stir plate to the sample. This can be accomplished with thin cork or packing material. A 1^{o} change in temperature can affect your readings by as much as 5%.
- Ammonia will be released at a ph > 11. Make sure your sample is pH adjusted. Using blue ISA solution is easy as this solution is designed to stay blue at pH > 11. Otherwise, if you just use NaOH, you need to check the pH of the sample.

Phosphorus – Tips and Tricks

- The DMRQA Phosphorus sample is an organically bound phosphorus.
- A digestion is not required if analyzing by a total phosphorus method (i.e ICP), but should be digested if you digest DMR samples.
- If analysis is performed by spectrophotometry, a digestion is required to convert all forms of phosphorus to ortho phosphate.
- There are three digestion techniques available. It is recommended to use either the sulfuric/nitric acid or sulfuric acid/ammonium persulfate digestion techniques. The third uses perchloric acid and is not recommended.

Phosphorus – Tips and Tricks

- The sulfuric acid-nitric acid digestion technique requires the use of a heating block such as those used for TKN digestions.
- The simplest method is the Persulfate digestion method.
- Add 1mL of sulfuric acid and 0.4 g ammonium persulfate or .5 g potassium persulfate to 50 mL of sample. You must add the persulfate or the organic phosphorus bond will not be broken.
- It is important to digest the calibration standards as well. Use an organically bound phosphorus as the calibration material to accurately determine the effectiveness of the digestion procedure.
- Make sure the pH of the samples post digestion is equal.
- pH play a big role in color development. A sample at pH 7 will develop color different from a sample at pH 8.

Phosphorus – Tips and Tricks

- The two most common methods for analysis are the Vanado Molybo phosphoric acid method (yellow color) or the Ascorbic acid method (blue color).
- The reagent for the Ascorbic acid must be used within 4 hours of making it. Allow 10 minutes for color development but color will start to fade after about 30 minutes.
- The reagents for the Vanadomolybo method last a lot longer. Color development also takes about 10 minutes but will last for a day.

Avoid Surprises

- Run analyses as soon as possible
- Allow time for things to go wrong
- Establish a routine quality control process with the use of Certified Reference Materials

Ohio Corrective Action

- Required for all "Not Acceptable" Results
- Do a Root Cause to try to determine what went wrong
  - Man, Machine, Materials, Method
- Fix the problem
- Run WP or Quick Turn sample
- Write a Corrective Action Report
- Send Report with Acceptable PT report to Steve Roberts by October 26

Steve Roberts – Ohio DMRQA Coordinator

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QUESTIONS

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