Top Tips for Conducting DMR-QA Analyses

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Technical Manager
ERA – A Waters Company

ERA
A Waters Company

- Founded in 1977
- Golden, Colorado
- More than 7,000 laboratories
- More than 80 countries

- Waste water
- Drinking water
- Soils
- Air & emissions

- Microbiology
- Radiochemistry
- Custom standards

ISO/IEC 17043:2010
PROFICIENCY TESTING PROVIDER
CERTIFICATE NO. 1539.01

ISO/IEC GUIDE 34:2009
REFERENCE MATERIAL PRODUCER
CERTIFICATE NO. 1539.03

ISO/IEC 17025:2005
CHEMICAL TESTING LABORATORY
CERTIFICATE NO. 1539.02

ISO 9001:2008
CERTIFICATE NO. 10551

What is DMRQA

- DMRQA is an acronym which stands for Discharge Monitoring Report Quality Assurance
- It is a Proficiency Testing (PT) program required for facilities containing permits to discharge treated waters back into waterways.
- It is a once per year program designed to compliment the DMRs which treatment facilities submit to the states.
- Prior to discharging your effluent, the pollutants contained on your NPDES permit must be tested to ensure that these pollutants are below the maximum contaminant levels (MCLs) listed on your permit.
- Do I need to participate in this program and why?

What is DMRQA

- The EPA needs to ensure that the data being reported on the DMRs is accurate. There are two main ways of determining this information.
- Lab Audits or PTs.
- DMRQA is a series of PT samples which contain the pollutants of interest listed on your permit.
- What analytes do I need to run?
- The values of the contaminants are unknown to the testing laboratories. The PT samples must be tested by the same labs who perform the tests for the DMRs using the same methods and procedures used for the effluents. The labs then report back their findings. The test results are evaluated against a pre determined set of acceptance criteria.

The DMRQA Process

- Receive the 308A letter from EPA.
- Return your address verification form.
- Order your samples from an accredited provider.
- Analyze the samples for the pollutants on your permit.
- Report data back to the PT provider by the close of the respective study. Report results to 3 sig figs.
- Receive your report back from the PT provider.
- Compile PT reports and send to your DMRQA Coordinator – Steve Roberts
- Perform corrective action if necessary.

DMR-QA 37 Dates & Deadlines

- Opened Friday, March 24
- Closes Midnight, Friday, July 7
- PT providers send graded reports by August 4
- Contract labs forward PT provider graded reports to permittee by August 18
- Permittees send final report to DMR-QA coordinator by September 1
- Corrective Action reports due by October 27

DMR-QA 37 Dates & Deadlines

- If running WP, report results by close of WP study.
  - WP study results are returned within 2 business days of the close of the study. (ERA is the only provider to have results in 2 days; due to the enormous size of the DMR-QA study, DMR-QA results will be available in less than 21 days)
- If you choose to use a WP study for DMR-QA, the study must close between January 1 and July 7.

	Opens	Closes	Results
WP 264	Jan 16	Mar 2	Mar 6
WP 265	Feb 13	Mar 30	Apr 3
WP 266	Mar 13	Apr 27	May 1
WP 267	Apr 17	Jun 1	Jun 5
WP 268	May 15	Jun 29	Jul 3
DMR-QA	Mar 24	Jul 7	Aug 4

DMR-QA 37 Acceptance Limits

- Based upon EPA regression equations
- Find regression equations on the TNI website at www.nelac-institute.org
- 3 standard deviations/99% CI around an expected recovery
- Concentration dependent
- Expected recovery = assigned value * a + b
- Expected standard deviation = assigned value * c + d

DMR-QA 37 Acceptance Limits

			Demands [10b]	mg/L				mg/L
NPW	0038	1530	5-day BOD [10c]	18 to 230	0.6237	0.7022	0.0928	0.6636	4.9
NPW	0102	1555	Carbonaceous BOD [10c]	18 to 230	0.5648	0.6665	0.0965	0.8253	3.1
NPW	0036	1565	COD [10d]	30 to 250	0.9843	0.3171	0.0432	3.0191	16
NPW	0037	2040	TOC [10e]	6.0 to 100	0.9926	0.1680	0.0473	0.3536	4.2

EPA Regression Equation for BOD

a - 0.6237; b - 0.7022; c - 0.0928; d – 0.6636

at 18 mg/L limits = 27.4 – 105%

at 230 mg/L limits = 34.0 – 91.0%

DMR-QA 37 Acceptance Limits

Example Calculation MINIMUM BOD Value

Made at 18 mg/L

Expected Recovery = Value * a + b

18 * 0.6237 + 0.7022 = 11.93

1 Expected Standard Deviation (SD) = Value * c + d

18 * 0.0928 + 0.6636 = 2.334

3SD = 3 * 2.234 = 7.00

Limits = Expected Recovery ± 3SD = 11.93 – 7.00 = 4.93

DMR-QA 37 Acceptance Limits

Example Calculation MAXIMUM BOD Value

Made at 230 mg/L

Expected Recovery = Value * a + b

230 * 0.6237 + 0.7022 = 144.15

1 Expected Standard Deviation (SD) = Value * c + d

230 * 0.0928 + 0.6636 = 22.01

3SD = 3 * 22.01 = 66.03

Limits = Expected Recovery ± 3SD = 144.15 + 66.03 = 210

DMR-QA 37 Acceptance Limits

Working Concentration Ranges

BOD = 4.93 – 210 mg/L

CBOD = 3.15 – 200 mg/L

Total Residual Chlorine = 0.381 – 3.48 mg/L

Low Level Total Residual Chlorine = 5.00 – 310 µg/L

DMR-QA 37 Acceptance Limits

Working Concentration Ranges

pH = 4.80 – 10.2 s.u.

NH3-N = 0.599 – 23.7 mg/L

TSS = 12.3 – 110 mg/L

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 ration 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 you 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 form 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.

Residual Chlorine – Tips and Tricks

- 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.
- TRC has an affinity to adhere to the small pores which are contained in plastics. Therefore, no plastics should be used when diluting the sample.
- Use chlorine free cleansers (i.e. Bon-Ami) when cleaning.
- 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.

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 TRC.

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 – Low Level Concerns

- Low level analysis poses extra problems, most notably detection limits.
- Make sure your procedure will allow you to see down to 50 µg/L.
- Use flow through cell, if possible.
- Remember that Low Level Chlorine is reported in µg/L (ppb) and not mg/L (ppm).

Oil and Grease – Tips and Tricks – Sep Funnel Extractions

- Wear gloves, hands contain oils.
- Use lightweight pans, dry and cool pans before beginning test.
- Use a 4 or 5 place balance.
- Rinse sample bottle and cap with hexane
- Do three extraction cycles with hexane.
- Remember to remove and water from pan. It contains TDS
- Evaporate at 70^{o}C or lower, dry to constant weight.
- When reporting assume 1L of sample.

Oil and Grease – Tips and Tricks – Solid Phase Extraction - SPE

- Clean the disk with hexane first??? If so make sure all hexane is removed from the disk.
- Activate the filter disk first.
- Place bottle on extractor. Place cap to the side. Do not rinse cap with hexane and place in bottle.
- SPE Program will keep collection vessel valve closed to send water to waste. Then collect hexane rinses.
- Use a 4 or 5 place balance.
- Rinse sample bottle cap with hexane and combine in collection vessel after extraction.
- Evaporate at 70^{o}C or lower, dry to constant weight.
- When reporting assume 1L of sample.

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 27

Steve Roberts – Ohio DMRQA Coordinator

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QUESTIONS

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