

Calibration 101

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Environmental Laboratory Certification Program (ELCP)

- Qualifications for Personnel
 - Each Laboratory must have a Category Supervisor
 - Each supervisor: 3 months of testing experience for Analyze Immediately (AI) parameters, 1-5 years for other parameters
 - Each supervisor can train and manage a group of technicians under their supervision
 - Personnel are approved by the Department but it is the laboratory facility that is certified

Personnel Qualifications

- Quality Assurance Officer
 - Must meet the same requirements as the Category Supervisor
 - Must have some experience with quality control and have a working understanding of the regulations and how they relate to the operating permit requirements or project plan testing
 - Can be the same person as the Category Supervisor
 - Is responsible for the quality control procedures that have to be performed in the laboratory
 - Oversees training and quality assurance (commitment to quality work in the laboratory)

Personnel Qualifications

- Laboratory Manager
 - Defined as the person who has direct responsible charge of the laboratory
 - Can serve as the Category Supervisor and Quality Assurance Officer if they meet the same experience requirements
 - Responsible for providing written notification to the Department within 15 days of any changes to the facility's location, ownership or key personnel

Equipment and Reports

- The equipment used for testing must meet accuracy and precision requirements.
- Equipment must go the site. Samples with short holding times (i.e. 15 minutes from sample collection) cannot be brought back to the laboratory.
- Reported data must include all of the required information at N.J.A.C. 7:18-8.5(e) and must be signed by the Laboratory Manager (or designee) or in the format required by the project plan
- Designee name must be on file at OQA

Records Required

- Raw data analysis records:
 - Facility Name, Sampler and Analyst identification (signature log of all approved signatures retained on file)
 - Date and time of sample analysis (even if it's the same time as the sample is collected to verify compliance with holding times.
 - The method number used for the analysis (i.e. SM 4500-H B) and the type of testing being done (pH).
 - The results of the data generated including all environmental and quality control samples.

Proficiency Testing (PT)

- Need a PT performed with the instrument used and the technician that routinely performs the regulatory or project plan testing. Must pass to receive certification.
- Must be handled, managed and reported in the same fashion as routine samples
- No extra QC samples can be run with the PT unless a QC sample is run with every routine sample
- Maintain a passing PT each year thereafter (usually in March)

Laboratory Certification

- Required for all regulatory data reported to the Department
- Encouraged for data integrity where no regulatory requirements exist
- Effective July 1st - June 30th of each fiscal year
- Must be renewed every year

“It’s just pH testing.”

- pH is a parameter with complex chemistry which is simplified for our use by the invention of meters that allow for ease of testing samples
- pH is defined as “the symbol for the logarithm of the reciprocal of hydrogen ion concentration in gram atoms per liter, used to express the acidity or alkalinity of a solution on a scale of 0 to 14, where less than 7 represents acidity, 7 neutrality, and more than 7 alkalinity”.

pH Testing

- All pH samples must be tested within 15 minutes of sample collection
- USEPA sets holding times
- Outlined in Title 40 of the Code of Federal Regulations (40CFR)
- Supported by Laboratory Certification Regulations (N.J.A.C. 7:18) and the NJDEP's Field Sampling Procedures Manual
- Mandated by the conditions of the operating permit (Program requirements) or the project plan

pH Testing

- All samples for pH testing are grab samples
- Grab samples are defined as individual samples of at least 100mls volume and tested within 15 minutes of sample collection
- Must be representative of the permitted discharge and must meet the mandates of the permit and the program that will use the data
- Programs can have requirements that are in addition to the laboratory certification regulations and these requirements are defined by the Program and not the OQA.

pH Meter

- Valid results depend on a properly calibrated meter and the use of a reliable electrode
- All pH measurements must be temperature compensated
- pH values are dependent upon and influenced by changes in the temperature of the solution (standard buffer or sample) being tested.
- The temperature of the buffers must be recorded in the raw data records

pH Meter

- Must be allowed to warm up as per manufacturer's instructions (usually 15-30 minutes before calibration)
- Must be operated in accordance with the manufacturer's instructions and adherence to the laboratory certification regulations
- Must have a reliable power source. Maintain a supply of extra batteries on hand for emergencies.
- Keep a record of all maintenance performed on meter and electrode.

pH Electrode

- Sensing unit for the test, signals are converted and sent to the meter for display
- Must be prepared and stored in accordance with the manufacturer's instructions
- Stabilized before use during warm up period.
- Samples and buffer solutions must be stirred during measurements to allow for the interface of the hydrogen ions across the sensing portion of the electrode.
- Meter and electrode must be properly calibrated before use.

pH Calibration

- pH units are Standard Units (su)
- Requires a two point calibration
- Buffers used for calibration must bracket the expected range of the sample being tested.
- Accuracy required is ± 0.05 units of the true value in order for the calibration to be acceptable.
- Buffers to use for calibration are 4.01 and 10.01.

pH Calibration

- Immediately following the calibration, check the calibration with a mid-range 3rd buffer with the meter in the “measure” mode.
- Use a 7.00 buffer for the calibration check. Accuracy required is ± 0.10 units of the true value in order for the calibration to be acceptable.
- If meter is calibrated and left on for more than 3 hours before used for testing, a 3 hour check with the buffer used for the calibration check (7.0) must be checked. The accuracy required for continued operation is ± 0.20 units.

pH Calibration

- Calibration is required each day of use with fresh aliquots of standard buffer solutions.
- Turn on the meter and condition the electrode by immersing in tap water or electrode storage solution for about 15-30 minutes prior to calibration. (Follow the manufacturer's instructions for meter warm up)
- *Do not use distilled water as there are no ions in the distilled water to condition the electrode.
- Remove the electrodes from the conditioning solution and rinse with distilled water before beginning the calibration.

pH Calibration

- Record of the time of calibration in your records.
- Immerse the electrode about 1 inch into the first calibration buffer solution (4.01).
- With the meter in the “calibration” mode, begin the calibration
- Stir gently and allow for the meter to stabilize
- Follow the manufacturer’s instructions for the use of the meter. I.e. some meters at this point would have the user push the HOLD/ENTER or CALIBRATE button on the meter...
- Record reading for the first buffer (3.96-4.06 for acceptance) Record “as found” and “set” buffer values

pH Calibration

- Remove the electrode from the first buffer.
- Rinse the electrode with distilled water.
- Immerse electrode into the second calibration buffer (10.01) and stir gently.
- Allow the reading to stabilize.
- Follow the manufacturer's instructions for the use of the meter. I.e. some meters at this point would have the user push the HOLD/ENTER or CALIBRATE button on the meter...
- Record reading for the second buffer (9.96-10.06 for acceptance). ("As found" and "set" values)
- Record the slope if the meter displays this value.
- Exit the calibration and begin the measurement mode.

pH Calibration Check

- In the measurement mode, immerse the electrode into the third mid-range buffer (7.00), stir gently and allow for the reading to stabilize.
- Let the reading stabilize and record the result. If the 7.00 buffer is outside the range of 6.90-7.10, the meter must be recalibrated before testing any samples.
- Rinse the electrode with distilled water or the first sample to be tested and begin routine analysis.

pH Sample Testing

- Immerse the electrode into the sample to be tested and stir gently.
- Allow the reading to stabilize.
- Record the pH value and the temperature noted on the display. Record the time the sample is tested in the raw data records. Remove the electrode and rinse with distilled water.
- Perform a sample duplicate and record the results of the duplicate analysis. (Periodic QC at a frequency of once every 20 samples tested).

pH Sample Testing

- **Important Note!**
- **You cannot use the User Reset function of the meters. You cannot revert to the factory defaults. You must calibrate the instrument each day of use as required.**

Rounding Rules for Chemistry Data

- Rounding rules for chemical analysis are different than those you learned in school.
- If the final digit is 5, then instead of rounding up, they round to the nearest even number.
- Examples for values for 0.25 and 0.35

0.2 Value from meter= 0.25 0.3

0.3 Value from meter= 0.35 0.4

Quality Control for pH and Temperature

- Duplicates:
 - A separate duplicate aliquot shall be measured and the average of the two numbers reported. This must occur once every 20 samples tested.
- Calibration Check: each day of use for pH
 - Procedure described in the calibration section of this handout for the use of a 7.00 buffer solution

pH and Temperature (cont'd)

- Thermometer calibration: Once a year for glass and on a quarterly basis for all other types of thermometers
- Thermometers calibrated against a NIST certified thermometer and all applicable correction factors applied to all measurement made with the calibrated thermometer

Quality Control for Conductivity

(also known as Specific Conductance)

- Initially a 5 point calibration curve is required. This step verifies the instrument in all of the ranges of use.
- Each day of use the meter must be calibrated and checked with a standard. Most labs use either a 100 mS/cm or 1413 mS/cm standard.
- The check must be accurate to within 1% of the true value for the calibration to be considered acceptable.
- Duplicate testing is also required in the same fashion as pH and temperature testing.

Quality Control for Dissolved Oxygen

- All probes must be calibrated each day of use.
- Calibration must be performed with either air saturated water or water saturated air.
- Zero standards can be used for a calibration but each meter must be checked on a weekly basis against a Winkler titration. The accuracy required for DO testing is +/- 0.3ppm between the Winkler and the meter calibration or the meter must be recalibrated and rechecked with another Winkler test.

DO Probes

- Duplicate testing at a frequency of every 20 samples tested is required for DO testing.
- Note: Although not approved for use for regulatory compliance reporting until approximately in January 2012, the luminescence and optical type DO probes must also be checked weekly against a Winkler and must be calibrated in accordance with the manufacturer's procedures. **The use of these types of meters must be approved by the Department before analysis can begin. Once EPA Approval is established the use of the LDO for DO and BOD/CBOD and optical probes for DO will be approved for both NPDES reporting and NJ ambient water testing.**

General Quality Control

- The date first received and the date first opened must be marked on the containers of all reagents and standards, including the certified pH buffers used for calibration.
- Note: For single use pH buffer packets, retain a record of the lot number on the single use packets used for calibration in the raw data records.
- The expiration date must be on the containers. If it is not, contact the manufacturer for the expiration date or only purchase buffers that include the expiration date on the container.

General Quality Control

- Fresh aliquots must be used. Do not reuse buffer, reagent or standard aliquots.
- Any buffer, standard, or solution that is expired shall not be used and must be discarded.
- Distilled water must be used to rinse the electrodes initially before beginning calibration, after the calibration is completed, and in between samples.
- The electrodes can be rinsed with the sample to be tested once the calibration is complete and the calibration check is run and is acceptable.

Required Records

- Results of the calibration and check
- Temperature of the buffer solutions and samples
- Time of sample collection and sample analysis
- Name of technician (or initials) performing the sample collection
- Name of technician (or initials) performing the testing (even if they are the same person)
- Results of the analysis including all applicable units

Records Retention

- All data and associated records must be retained for at least 5 years. Data must be retained on the premises for one year after it is generated for availability for review on onsite audits. After the one year period has ended, the data may then be stored offsite if necessary due to space constraints but must be readily available for retrieval.

Raw Data Records

- Raw data is the data that is first recorded and this is the data that must be retained. If data is handwritten on a piece of paper and then that data is transferred to a data management system (i.e. a computer program), the hand written information must be retained.
- If data is input directly into a computer database, then the database records must be retained.
- A plan to protect the electronic data must be in place. (i.e. write protected and backed up routinely to prevent the loss of data)

Summary

- Quality Control as a standard practice
- True and precise records
- Accountability for analysis
- Reliable and consistent data