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Massachusetts Water Watch Partnership

Standard Operating Procedure Rivers-4

For pH and Alkalinity

Revision 0

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11-13-01
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Overview

This procedure describes how to collect a river grab sample for pH and alkalinity and how to measure pH and alkalinity in the laboratory using a pH-meter and a digital titrator.

1.0 Field Equipment List

___ High Density Polyethylene (HDPE) bottle, 500 ml

___ Field sheets and pencils

___ Cooler

___ Ice

___ Frozen koolits

___ Zip-log bag (1 gallon size)

___ Gloves (optional)

___ Boots

2.0 Sampling Protocol

2.1 Note: Sample bottles should be pre-labeled according to your program's protocols

2.2 Use a 500ml HDPE sample bottle.

2.3 Samples should be take from representative, flowing water. The water must be deeper than the sample bottles and free of surface scum and debris. If the water is not deep enough at your regular sampling site, look for another location nearby which is equally representative of the site but deeper. If there is none, do not collect a sample and indicate on your field sheet that water level is too low. Note that sampling from the streambank is discouraged, as it can result in non-representative samples.

2.4 Carefully wade into the stream, walking upstream and avoiding to stir up bottom sediment. Wait for pre-disturbance (from wading in) conditions to return before taking sample. If you are in a canoe, have your partner steady it.

2.5 Take sample in mid-stream, if possible. If not, get as far out from shore as is safe. Walk upstream and collect sample so that you are not standing or floating upstream of the bottle.

2.6 Uncap sample bottle and rinse three times with river water: fill bottle partially, cap, shake, and empty downstream.

2.7 To take sample, dip bottle completely under water, filling to overflowing.

2.8 Cap bottle while it is still underwater, in order to eliminate any air from the sample bottle.

2.9 Return to shore and place sample in cooler with ice.

2.10 Fill out river field sheet completely right away, writing “pH/ANC” in ‘Chemistry’ column.

3.0 Transporting the Sample

3.1 Place sample in cooler with ice.

3.2 If you cannot put ice directly in your cooler because you store other materials in there, use a gallon-size zip-loc bag filled with ice. Put your sample in that zip-loc bag, zip shut and place in cooler with frozen koolit.

3.3 Deliver to lab within 8 hours of collection. Holding time for alkalinity is 14 days.

4.0 Lab Equipment List[1]

___ SAFETY GOGGLES

___ Rubber gloves (optional)

___ Wash bottle

___ Graduated cylinder, 100 ml

___ Beaker, 150 ml

___ pH meter in good working order

___ Hach Digital Titrator, with clean delivery tube

___ Sulfuric acid cartridge, 0.16N

___ Distilled or deionized water to clean

___ Lab data sheets

Optional, but preferred:

___ Magnetic stirrer, with stir bar

___ Ring stand and clamp to hold titrator

___ Kim wipes

[1] Inclusion of the trade names does not constitute endorsement by the MA Water Watch Partnership, the University of Massachusetts, or the Commonwealth of Massachusetts nor does it imply a comprehensive list of providers.

5.0 pH Meter Care and Maintenance

5.1 General electrode care and handling procedures are very important in your lab because pH measurements will only be as good as the condition of your electrode(s). For greater accuracy in your measurements and longer electrode life, there are a few areas of electrode care with which you should be familiar.

5.2 Storage:

5.2.1 Glass combination or separate pH and reference electrodes should be kept wet. The reference electrode requires a free-flowing junction, so be sure to maintain the reference filling solution at a level significantly above the storage or sample solution level at all times. This will provide a positive head pressure, which forces the filling solution out through the junction rather than the storage solution into the probe.

5.2.1 Whenever reference electrodes are placed in or stored in buffer solution, the vent hole MUST be open to allow the free flow of filler solution out the bottom of the electrode. Failure to keep the vent hole open and the reference solution height above the level of the buffer will allow the buffer to contaminate the filler solution and the electrode will be ruined.

5.2.2 The filler solution should be topped up periodically if the electrode is stored in the buffer. Because the filler solution is continually bleeding out the end of the electrode, the filler solution height will decrease with time. When it falls below the level of the buffer, the electrode will be ruined. Maintaining the electrode properly will ensure a long life and proper functioning when needed. Electrodes can last ten years or more if they are well maintained.

5.2.3 For dry storage, the sleeve or plug should cover the filling hole to reduce the flow of filling solution. During the measurement or storage in pH 4 buffer, however, this sleeve or plug must be slid away or removed to allow flow of the reference solution into the sample.

5.2.4 To obtain a faster electrode response, the glass electrode should be stored in a slightly acidic solution. In the protective cap for the glass electrode, put a drop or two of pH 4 buffer and put the cap on the electrode, carefully. Distilled water extracts ions from the bulb causing a slower response; pH 7 buffer over a long time period ages the electrode slightly.

5.2.5 If using a separate reference electrode, the best solution would be to place the reference electrode in its own filling solution but this can be messy. Providing KCl to both sides of the junction keeps it flowing freer. To reduce the salt crust of saturated solution, an approximately 0.1 M KCl solution may be used, but for storage only. Experience indicates that simply covering the filling hole with the protective sleeve and storing dry suffices in most instances as long as the soaking procedure is followed.

5.2.6 For combination electrodes, store the electrode in a combined solution of approximately 0.1 M KCL and pH 4 buffer.

5.2.7 One day or more prior to analysis, soak both electrodes in pH 4 buffer and, during analysis, place the electrodes in the same buffer when not in use.

5.3 Reference Electrode Filling Solution

5.3.1 Read the instructions that came with your electrodes carefully. Saturated calomel reference electrodes such as those used by the Acid Rain Monitoring Project must not be filled with filling solutions containing silver chloride (AgCl). We use 4M KCl solutions only. However, the most common filling solution for combination electrodes is 4 M KCl saturated with AgCl. Be sure to ascertain which filling solution is correct for your electrode(s) and double check that your filling solution matches these requirements.

5.3.2 Permanently filled or Gel electrodes: Due to their unique micropore junction, it is recommended that they be stored hanging dry.

5.4 Preliminary Electrode Response Testing

5.4.1 If your electrode exhibits slow response, poor span between two buffer values or undue sensitivity to movement of the electrode, rejuvenation may be necessary to improve performance.

5.4.2 Response varies with the electrode and the solution it is in. Generally working electrodes reach 0.05 pH units of the final reading in buffer within 10 seconds. A stable reading (less than 0.01 pH units per minute change) should be reached in fresh water samples within a minute or two. If you have to wait too long (5 minutes or more) then the pH itself may change due to the contact of the water sample with air.

5.4.3 Electrodes may also require adjusting the slope to values significantly different from 100% for two point calibration. Perform the following test if in doubt:

- Set your meter to 100% slope and room temperature
- Standardize as usual with pH 7 buffer
- Without moving the slope dial, read a pH 4 buffer. It should read between 3.85 and 4.15
- Set the slope to read pH 4, the slope should be 95% to 105%.

If your electrode exhibits either of the above problems or is sensitive to movement, rejuvenation is in order.

5.5 Glass Electrode Rejuvenation

5.5.1 To treat the bulb of the reference electrode:
EAL can provide 2 bottles of acid and base (01.N). BE CAREFUL WHEN HANDLING THESE SOLUTIONS. IF YOU GET ANY ON YOU RINSE OFF WITH LOTS OF WATER.To treat, simply dip the bulb into the acid and immediately into the base. Repeat this several times. Then rinse the electrode

under tap water and let sit in pH 4 buffer for 2 hour. Rinse the electrodes and restandardize as you normally do with pH 7 and pH 4 buffers. You may need to do this several times a year.

5.5.2 To treat the reference electrode:
Replace the 4M KCl solution in the reference electrode and get rid of crystals that may have formed. If there are lots of crystals, then shake out the solution and put deionized pure water into the filling hole and soak the electrode tip in hot tap water for 15 minutes or so until the crystals have dissolved. Then shake all the liquid out of the filling hole in the reference electrode and refill with fresh 4 M KCl. Let the electrode sit at room temperature for 2 hour before use. Frequently add more 4M KCl solution to the reference electrode since it will continually leak out and evaporate. The solution in the electrode should be within 2 inches of the filling hole. The hole should be open when reading pH but close it when you are through for the day or else the solution will evaporate and new crystals will form. If you still have problems with slow response, try rubbing the tip on your blue jeans or on very fine (600 grit) sandpaper.

5.6 Final Test For Linearity

5.6.1 Standardize the meter as described below.

5.6.2 Rinse the electrodes and your sample cup with pure deionized water.

5.6.3 Then titrate 100.0 ml of deionized water with your 0.16N acid as follows:

5.6.4 Make sure your digital titrator is working and reset to zero.

5.6.5 Add 10 digits of acid, record digits and pH, increase acid to 20 digits, record pH.

5.6.6 Repeat in 10-digit increments until you have added 100 digits of acid and stop. Send the results to us and we will send you a report. If you want to see the results yourself, try plotting the hydrogen ion concentration ($H = 10^{(-pH)}$) vs. digits and see if the line is straight.

5.7 Movement Sensitivity: If your meter gives wild readings and is sensitive to your touch, it may not be properly grounded. Try using a three-prong power plug or attach a wire from the meter to a cold water pipe. Sometimes a problem of fluctuating readings or consistency wrong readings can be solved by disconnecting and reconnecting the electrode connectors several times. Apparently an oxide layer can sometimes cause these symptoms.

6.0 Calibration[2]

6.1 The pH meter should be standardized (calibrated) prior to sample analyses and after every 25 sample analyses. Buffers should be at room temperature (68^{o}F).

[2] Calibration steps may vary with pH-meters. Read and follow your meter's instructions.

6.2 Remove the electrodes from the pH 4 buffer solution where they have been soaking for at least one day.

6.3 Rinse with deionized water.

6.4 Insert the electrodes in pH 7.00 buffer and adjust the calibration dial until exactly pH 7.00 shows on the meter.

6.5 Remove the electrodes and rinse with deionized water.

6.6 Place the electrodes in pH 4.01 buffer and adjust the slope until the meter shows pH 4.01.

6.7 Rinse with deionized water.

6.8 A note on buffers. The accuracy of your pH measurement is in direct relation to the accuracy of the standard buffer solution used to calibrate your pH meter. In order to maintain a reasonable degree of accuracy when making a pH measurement, a number of precautions concerning the care and use of buffers should be observed. These include:

6.9 Do not use buffers after their expiration date. Mold growth, CO_2 absorption and contamination cause changes in the buffer pH.

6.10 Do not use buffers which have mold growth floating in the buffer.

6.11 Always cap the buffer container when storing to prevent contamination and reduce CO_2 pickup.

6.12 pH buffer values change with temperature. Be sure to measure the temperature of the buffer and look up its value at that temperature before standardizing the meter (see below).

6.13 Do not pour used buffer back into the bottle.

6.14 Buffer Values at Various Temperatures

Temperature		Buffers	
°C	°F	pH 4	pH 7
0	32	4.003	7.119
5	41	3.998	7.086
10	50	3.996	7.058
15	59	3.996	7.035
20	68	3.999	7.015
25	77	4.004	7.000
30	86	4.011	6.988

7.0 Quality Control Protocol using EAL[3] QC sample

7.1 Review section 5 on pH meter care and maintenance. Check your pH meter out thoroughly each month before you proceed with analysis. Accurate use of a pH meter requires calibration with known pH buffers before each use. These buffers have a limited shelf life. It is a good idea to warm up both the analyst and the pH electrode with a trial titration before you begin QC or field sample analysis.

7.2 Quality control for pH and alkalinity consists of normal pH measurement and titration of a QC sample provided by UMass-EAL and sent to you prior to field collection. The procedures for analyzing QC and field samples are exactly the same.

7.3 **Remember, the general QC program requires that you:** Always standardize your pH meter using the pH 4 and 7 buffers prior to any analysis of QC samples or field samples.

7.4 Prior to measuring alkalinity, it is a good idea to check your titrator before inserting the sulfuric acid cartridge to see if the counter works properly. Some have been known to skip a digit at the ten or hundred place.

7.5 Run a QC sample (see section 8) 2 - 5 days prior to testing your field samples. Record your results.

7.6 Call UMass-EAL (contact person and phone number located on instructions that came with the QC sample) with the results of this test. Resolve any problems encountered.

7.7 Run a QC sample immediately before and immediately after you analyze your field samples. Record your results on the pH & alkalinity lab data sheet.

8.0 pH Measurement

8.1 After calibrating your meter (see section 6), follow the same steps for analyzing both the field and QC samples:

8.2 Remove QC or field sample from refrigerator, bring to room temperature before testing (about an hour). **Keep bottle capped while it is warming up, to avoid sample coming into contact with air.**

8.3 Rinse a 100 ml graduated cylinder with sample water. Measure **100 ml** of the sample.

8.4 Rinse a 150 ml or larger beaker with distilled water and pour measured sample into it. Recap QC bottle.

[3] EAL: University of Massachusetts Environmental Analysis Lab. QC samples may also be purchased from commercial laboratories

8.5 Rinse your pH electrode in deionized or distilled water, then place the pH electrode in the beaker with sample. **pH should be analyzed within 5 minutes of uncapping the sample bottle.**

8.6 The sample should be stirred very gently, preferably with a magnetic stirrer. **Careful not to break the glass pH electrode!**

8.7 Watch for the meter reading to become stable. (This may take up to 3 minutes.)

8.8 When stable, but not in excess of 5 minutes, record the sample pH to the nearest 0.01 pH unit.

8.9 Record pH value on the lab data sheet. Keep the pH electrode immersed in the sample as you continue with the alkalinity procedure.

8.10 **IF** the pH of your sample is ABOVE 4.5, proceed directly to the lab procedure for alkalinity in section 9. **IF** the pH of your sample is at or BELOW 4.5, proceed to section 9.17 for additional steps required for the lab procedure for alkalinity.

9.0 Alkalinity Titration Protocol

9.1 Titrations go better if the delivery tip is positioned under the surface of the solution being titrated. For one or two samples, the titrator can be held in the hand. However, it is easier to mount the titrator on a ring stand using a clamp.

9.2 Try to keep the titrator in a vertical position (delivery tube down) throughout all titrations; putting the titrator horizontally on the bench between titrations may introduce bubbles in the tip.

9.3 **Put on your safety goggles!** Gloves are optional and at your discretion.

9.4 Attach a sulfuric acid cartridge to the Hach Digital Titrator. Attach a clean delivery tube to the cartridge.

9.5 Above a sink, advance the plunger manually or with the delivery knob until titrant is forced out of the delivery tip and the delivery tube is filled with solution. Do this as you would a hypodermic syringe, with the delivery tip nearly straight up to remove all bubbles.

9.6 Check for leaks where the tip connects to the cartridge.

9.7 Rinse the tip **gently** with distilled water; this is important because the titrant is concentrated and even a small amount left on the tube can affect your results. Do not flush titrant out of the tip.

9.8 Reset the digital titrator counter to zero and you are ready to titrate the 100ml sample.

9.9 Holding the titrator vertically, immerse the delivery tip into the sample, and begin adding titrant. Titrate until the pH is lowered to 4.5.

9.10 Record the number of digits of titrant it takes to get to pH 4.5.

9.11 Continue titrating, **without** resetting the counter, until you get to pH 4.2. Keep an eye on the digital counter to make sure it does not accidentally skip digits.

9.12 Record the number of digits shown on the counter.

9.13 After completing a titration and recording the digits of titrant used, rinse the delivery tip with distilled water. **This is easily forgotten when busy.**

9.14 RESET THE COUNTER before titrating the next sample.

9.15 Calculate alkalinity using the formulas provided in section 10.

9.16 If you make a mistake and overshoot the initial 4.5 pH mark:

9.16.1 Record the pH value you reached and the number of digits required to get there.

9.16.2 Continue titrating as above, until you reach a pH value 0.3 units below the value you reached above.

9.16.3 Record the second pH value and the number of digits. Calculate alkalinity using Method 1 in section 10.1.

9.17 If the initial pH of your sample is at or BELOW 4.5:

9.17.1 Make a note of the initial pH value on your data sheet.

9.17.2 Enter "0" in the 4.5 column of the data sheet.

9.17.3 Titrate as described in steps 1-12 above until the pH is 0.3 units below the initial pH value.

9.17.4 Enter the digits of titrant used in the 4.2 column of the data sheet.

9.17.5 Write down the pH reading where you stopped (as an accuracy check).

9.17.6 Calculate alkalinity using Method 2 in section 10.3.

10.0 pH and Alkalinity Calculation

Calculating alkalinity in mg/l CaCO3:

10.1 If initial pH was <u>above</u> 4.5, use **Method 1**:

Alkalinity = (2A - B) x 0.1.
where:
A = digits used to pH 4.5.
B = digits used to pH 4.2 (INCLUDING digits to get to 4.5).

Example: It took 100 digits to lower pH to 4.5, another 20 to lower to 4.2.
A = 100. B = 120.
Alkalinity = (2x100 - 120) x 0.1 = 8.0 mg/l CaCO3.

10.2 The volume of sample you analyze affects this calculation. You should always titrate 100 ml of sample. Should the need arise to titrate 50 ml, use equation (2A - B) x .02; if titrating 200 ml, use equation (2A - B) x 0.05.

10.3 If initial pH was at or below 4.5, use **Method 2**:

Alkalinity = (2A - B) x 0.1
where:
A = 0
B = the endpoint # of digits.

Example:
Initial pH is 4.3. The sample required 22 digits to lower the pH to 4.0.
A = 0. B = 22.
Alkalinity = (0 - 22) x 0.1 = - 2.2 mg/l.

Although the negative alkalinity value may not seem to make much sense, it is an extremely important measurement for assessment of acidification. Negative alkalinity values indicate that not only has all the buffering capacity of the water been exhausted, but the water now has an excess of strong acids present which further depress the pH.