Health and Environmental Application Laboratory

Standard Operating Procedure
For
The Determination of pH

SOP Number: AN.HEAL.EL.PH.17.0 (AN-0023)

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Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820-7495

NOTE THE HEALTH & SAFETY WARNINGS IN SECTION 4.0

Prepared by: _____ Date: 08/05/2021
Kristina Freeman, Physical Science Technical Assistant

Reviewed by: Nina Gartman _____ Date: 08/05/2021
Nina Gartman, Laboratory Supervisor, HEAL Co-Interim Director

Approved by: _____ Date: 08/05/2021
Evan Rea, QA Specialist, HEAL Co-Interim Director

The following individuals (in addition to those listed on the cover) have reviewed this SOP.

Name (printed)	Signature	Date
Stacey Coffman	Stacey Coffman	08/05/2021

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1.0 Scope & Applicability

Samples are measured for pH using unfiltered aliquots.

2.0 Summary of Method

2.1 pH meters are standardized and calibrated with both externally purchased solutions and HEAL prepared solutions every 12 samples for quality assurance purposes. Control charts are generated.

2.2 A Laboratory Information Management System (LIMS) is used to record and track analysis for pH.

3.0 Definitions

DI	Deionized (water) at 18.0 Mohms-cm or higher
FBYY####	DI Blank
FHYY####	An external prepared quality control standard. This is a low ionic strength 6.97 pH buffer.
FLYY####	An in-house prepared quality control sample (pH = 4.3).
FR50YY##	An in-house prepared quality control synthetic sample targeting the 50th percentile concentration of all samples analyzed for the NADP/NTN.
HDPE	High-Density Polyethylene
LABNO	Laboratory identification number
LDPE	Low-Density Polyethylene
LIMS	Laboratory Information Management System
QA	Quality Assurance

4.0 Health & Safety Warnings

4.1 Safety eyewear is required to be worn in the lab beyond the partition when filtration is in progress.

4.2 Safety Data Sheets (SDS) applicable to this SOP are available through the **Division of Research Safety,** and can be found online at http://www.drs.illinois.edu.

4.3 The Illinois State Water Survey Chemical Hygiene Plan covers the ISWS laboratory safety program, including, but not limited to, personal protective equipment used, control equipment inventory and operations (such as vented hoods), employee training programs, medical programs, and safety. The ISWS Chemical Hygiene Plan is available at http://isws.illinois.edu/staffonly/resources/manuals.asp. Procedural notes are included in test methods used (e.g. ASTM International, United States Environmental Protection Agency (USEPA), or Standard Methods for the Examination of Water and Wastewater).

4.4 The University of Illinois **Division of Research Safety** requirements for chemical safety can be found at http://www.drs.illinois.edu/trainingapp/Quizzer/qdbQuizMain.aspx?hfo=10.

4.5 The HEAL has listed known health and safety warnings for this SOP, but this list should not be assumed to comprise all health and safety issues.

5.0 Cautions

5.1 Personnel Cautions

5.1.1 Personnel need to be organized and detailed in all aspects of pH measurement. Detailed quality assurance data logs are kept and carefully monitored for potential problems.

5.1.2 Personnel need to be extremely careful not to contaminate the bottle, sample, or aliquots removed for pH analysis. ANY accidental touching/handling errors may invalidate the sample data. Should a handling error occur by laboratory personnel, it should be noted in the “Bottle Comments” text box in the LIMS.

5.1.3 There will be no food or eating allowed in the laboratory area beyond the designated area. Hands should be clean, free of grease, salts, and dirt, and kept as dry as possible while working.

5.2 HEAL Electrode Cautions

5.2.1 The electrodes in use at the HEAL are the Broadley-James combination pH electrode. For more information on this electrode, see SOP SS.HEAL.EL.evaluation (SS-2026, pH *Electrode Evaluation)*.

5.2.2 Because of the response characteristics of this electrode, it is best to use it with a meter which has Auto Read Function capability.

5.2.3 This electrode must be stored in the Broadley-James 3.8 M KCl Filling Solution only.

5.2.4 The fill hole should be open during measurements, closed during storage. Use parafilm to cover the fill hole during storage and prevent evaporation of the filling solution.

5.2.5 Electrodes may be agitated slightly in sample vials to more rapidly reach equilibrium, but the solution must be quiescent when the pH measurement is being taken. For example, carefully agitate the electrode in the sample vial for a few seconds until the pH is no longer changing in large increments. Let the electrode sit quietly in the sample until a stable measurement is obtained.

5.2.6 Never wipe down the electrode! A static charge can develop which will affect analyses. Lightly flick excess water from the electrode tip. Do not touch the glass bulb inside the plastic cover!

6.0 Interferences

None

7.0 Personnel Qualifications

Several days training with qualified staff.

8.0 Apparatus & Materials

8.1 Equipment

8.1.1 Broadley James Combination Electrodes.

8.1.2 Mettler SevenMulti Meter.

8.1.3 PVC vial support blocks and plexiglass covers.

8.1.4 LIMS Preplab Module.

8.2 Chemicals and Solutions

8.2.1 An in-house prepared 0.1 M HCl solution - stored on laboratory counter in room 209. To prepare the solution – add 8.3 mL concentrated HCl (Fisher Scientific Cat # A508SK-212) to approximately 900 mL DI water; dilute to 1L; mix thoroughly. The preparation must be performed in the working hood in room 306.

8.2.2 An in house prepared 0.1 M NaOH solution - stored on laboratory counter in room 209. To prepare the solution, dissolve 4.0 g NAOH (Fisher Scientific Cat # S318-500) in 1 L of DI water.

8.2.3 Deionized water, with a resistivity of 18.0 Mohms or better.

8.2.4 Fisher pH Buffers: 10 pH (Cat # SB116-500), 7 pH (Cat # SB107-500), and 4 pH (Cat # SB101-500) - stored on laboratory benches and cabinet in room 209.

8.2.5 Orion pH Buffer 6.97 (ThermoFisher Scientific Cat # 700702) - stored on laboratory benches and cabinet in room 209.

8.2.6 Quality Control Solution (FR50) - stored on the laboratory benches in room 209 and in the cooler # 214.

8.2.7 Quality Control Solution 4.3 pH - found on laboratory benches in room 209 and in cooler # 218.

8.2.8 Broadley-James 3.8 M KCl fill solution (Broadley-James Corporation Cat # AS-3120-C20-0500) - stored on laboratory benches and cabinet in room 209.

8.3 Supplies

8.3.1 Broadley-James Combination Electrodes

8.3.2 Conical Polystyrene Sample Cups, 4 mL (stored in room 209 in cabinet labeled “vials”)

8.3.3 Nalgene LDPE 500 mL Wash Bottle

8.3.4 Safety Glasses

8.3.5 Parafilm

8.3.6 ULINE Wipers

8.3.7 Reanalysis Notebook (stored on the bookshelf in room 209)

8.3.8 Room 209 Records Notebook (stored on the laboratory benches in room 209)

9.0 Instrument or Method Calibration

9.1 HEAL pH Meter Information

9.1.1 The Mettler Seven MultiMeter is used in the laboratory for all precipitation sample analyses. For more detailed instructions on how to work with the Mettler meter, see the manual “Operating Instructions SevenMulti” located on the bookshelf in Room 209.

9.1.2 The meter and electrode must be standardized and calibrated at the start of analysis and every 36 samples thereafter. Alternate with a high and low QC solution every 12 samples - continue if in range.

9.2 Standardization and Calibration of Mettler SevenMulti Meter

The SevenMulti meter has an automatic endpoint. The measurements will endpoint once the measurement signal changes less than 0.5 mV in 10 seconds. With the automatic endpoint, the selected stability criterion determines the end of an individual reading depending on the behaviour of the sensor used. This ensures an easy, quick, & precise measurement.

9.2.1 Pour two vials of pH 7 buffer and place in support block. The first vial is used as a “conditioning rinse” of the electrode. The second vial is the solution measured.

9.2.2 Using a wash bottle, rinse the tip of the electrode thoroughly with DI water. Lightly flick excess water from the electrode tip.

9.2.3 Place the electrode in the first conditioning vial of pH 7 buffer solution and momentarily stir with electrode to ensure proper contact. Wait approximately 30 seconds. Do not press any buttons during this time. <u>If any buttons on the meter are pressed during this time, it will invalidate the calibration procedure.</u>

9.2.4 Remove the electrode from the conditioning vial and flick to expel excess solution from the electrode tip. Without rinsing, place the electrode in the second vial of pH 7.

9.2.5 Press the **cal** button to begin calibration of the meter. “Cal 1” on the sensor indicates that the first calibration point is being measured. The value is displayed when the measured value is stable.

9.2.6 Repeat the process from 9.2.1 through 9.2.5, using the 4 buffer.

9.2.7 Repeat the process from 9.2.1 through 9.2.5, using the 10 buffer.

9.2.8 End calibration with **End** after reading the last calibration buffer. A table with the calibration results appears in the display. Press **Save** to accept.

9.2.9 If the meter and electrode are standardized and calibrated correctly, proceed to pH 7 buffer recheck (section 9.3). If it is not, recalibrate the meter.

9.3 pH 7 Buffer Recheck

9.3.1 After the meter and electrode system have been standardized and calibrated, the pH 7 buffer must be measured again to re-check the value.

9.3.2 Measure pH of the pH 7 buffer, using two new vials of pH 7 buffer. Use the first vial as a “conditioning rinse,” and the second vial for the measurement.

9.3.3 Value must read 7.00 ± 0.01 pH units to proceed to section 9.4. If it does not, repeat 9.3.2. After the buffer recheck, a DI reading needs to be taken before proceeding to the QA solutions.

9.4 Initial pH measurement of Quality Assurance/Quality Control Check Samples

9.4.1 After the pH 7 buffer recheck, three additional QA solutions must be analyzed before precipitation sample analysis can occur. The LIMS is used to record these values; see section 12.3 for detailed use of the LIMS.

9.4.2 Using two vials for sample measurement (the first for conditioning, the second for measurement), measure the pH of 6.97 – FHYY####. The value should read within the control limits as defined on the Daily Control Chart to proceed to section 12.3 “Measuring pH using the LIMS”. If it does not read within tolerance, try recalibrating and restandardizing, then remeasure the 6.97. If it fails a second time, see troubleshooting section 13.0.

9.4.3 Using two vials for sample measurement, measure the pH of FR50 as above. The value should read within the control limits of that solution to proceed to section 12.3 “Measuring pH using the LIMS”. If it does not read within tolerance, try recalibrating and restandardizing, then remeasure the 6.97 (see 9.4.2) and FR50. If it fails a second time, see troubleshooting section 13.0.

9.4.4 Using two vials for sample measurement, measure the pH of QC Sample 4.3 - FLYY#### as above. The value should read within the control limits of that solution to proceed to section 12.3 “Measuring pH using the LIMS”. If it does not read within tolerance, try recalibrating and restandardizing, then remeasure the 6.97, FR50 and FLYY####. If it fails a second time, see troubleshooting section 13.0.

10.0 Sample Collection

Samples to be analyzed are stored at 4˚C ± 2˚C in the walk-in cooler, room 301.

11.0 Handling & Preservation

11.1 All samples are to be handled with care, avoiding any direct hand/body contact with the sample or interior of the bottle and lid.

11.2 Keep sample bottles tightly sealed when not being poured. Keep samples and standards covered as much as possible prior to analysis to reduce airborne contamination.

11.3 When pouring samples into the sample tubes, avoid splashing or spillage of sample into an adjoining sample tube.

12.0 Sample Preparation and Analysis

12.1 Setup of LIMS for pH Analysis

12.1.1 Turn on computer and click on ***Shortcut to BenchChem*** icon, or you can find BenchChem on the network at \\pri-fs1\HEAL\HEAL- IT\Program Install Files\Lims\BenchChem).

12.1.2 Select ***Chemistry, pH, Load Sample List, Create List.***

12.1.3 Under the *Collect* heading, select *pH/conductivity*. The pH /conductivity collection screen is split into two channels. Channel 4 is connected to pH meter 1 and channel 5 is connected to pH meter 2.

12.1.4 Select **Sample Range** button.

12.1.5 Enter the sample range for analysis in the **First and Last Sample ID** textboxes. Select **Add to List** button, then **Save** button.

12.1.6 The sample list will appear. Click on first sample on the list. The current sample for analysis will be highlighted and appear in the **Current Sample** text box. You will need to select the serial port for each meter before sending any values to LIMS (this is located at the bottom of the screen in the **Serial Port** text box). Each meter has a number located on the upper left corner of the meter.

12.2 Measuring pH of QC samples using the LIMS:

12.2.1 Standardize and calibrate meter and electrode as described in section 9.

12.2.2 After initial calibration and after every twelve samples, the QC solutions are measured. After 36 samples, recalibrate with 7, 4 and 10 buffers along with your QC solutions.

12.2.3 Scan the selected QC sample. This will appear in the **Current Sample** text box.

12.2.4 Place electrode in first vial of selected QC solution and press **Read** on the meter. A few seconds after the meter stabilizes the value will appear on the screen in the **Initial** text box.

12.2.5 Place electrode in the second vial and press **Read** on the meter. The second value will appear in the **Final** text box. Click the **Save Result** button.

12.3 Measuring pH of samples using the LIMS

12.3.1 Begin measuring samples after the meter and electrode have been calibrated and QC samples have been measured. If there are any pH readings over 6.0, the electrode needs to be rinsed with 4.3 check solution so there is no carry-over into the next sample.

12.3.2 Check to make sure the sample ID appearing in the text box matches the correct sample vials.

12.3.3 Samples with volumes of 30 mL or more will have 2 sample vials. Samples with less than 25 mL will have 1 vial. Place electrode in the first vial of sample and press **Read**. After the meter stabilizes the value will appear on the screen in the **Initial** text box.

12.3.4 Place electrode in the second vial and press **Read**. The second value will appear in the **Final** text box. Click the **Save Result** button.

12.3.5 After the sample is written, the computer will automatically go on to the next sample on the list.

12.3.6 For samples with only 1 vial, take both readings from that vial.

12.3.7 When finished analyzing samples, cover the fill hole of the electrode with parafilm and store the bulb in fill solution.

13.0 Troubleshooting

13.1 Make sure electrode is functioning properly.

- Visually inspect electrode to make sure there are not broken parts.
- If KCl crystal build-up occurs in electrode barrel, clean the electrode.
    - Dissolve the deposit by immersing the electrode in 0.1 M HCl for 5 minutes followed by immersion in 0.1 M NaOH for five minutes.
    - Thoroughly rinse with distilled water.
- Rejuvenate the electrode (see SOP #SS-2026, *Electrode Evaluation and Shipment*.)
- Perform an electrode test. This will allow you to check the drift, slope, offset, and response time of your pH electrode (see Mettler-Toledo, *Operating Instructions, Mettler SevenMulti pH Meter*, p. 32. under Electrode Test)

13.2 Slope Value

Follow these steps when the slope value of the pH meter is not between 90% - 105% after calibration:

13.2.1 Attempt to re-standardize and re-calibrate the pH meter and electrode.

13.2.2 Attach the questionable electrode to the other pH meter known to be working and standardize and calibrate with the new meter.

13.2.3 Replace the questionable electrode with a new electrode.

13.2.4 Stop all analyses and inform the laboratory supervisor and Quality Assurance chemist.

13.3 7 Buffer Recheck

Follow these steps when the 7 Buffer re-check value does not measure 7.00 + 0.01 pH units:

13.3.1 Replace the vial of 7 buffer solution measured with a new vial of the same 7 buffer solution bottle.

13.3.2 Replace the 7 buffer solution with a new bottle of 7 buffer solution.

13.3.3 Replace the questionable electrode with a new electrode.

13.3.4 Use the pH 610022 calibrator set to check meter calibration.

13.3.5 Stop all analyses and inform the Quality Assurance chemist.

13.4 QA Check Solution

Follow these steps when the QA Check Solutions, 6.97, FR50, and 4.3, do not measure within tolerance limits:

13.4.1 Replace the vials of QA Check Solution measured with new vials of the same QA Check Solution bottle.

13.4.2 If the QA Check Solution still does not pass, measure the same solution with a second working electrode.

13.4.3 Stop all analyses and inform the Quality Assurance chemist.

14.0 Data Acquisition, Calculations & Data Reduction

This is automatically done by the LIMS.

15.0 Computer Hardware & Software

LIMS software/hardware.

16.0 Data Management & Records Management

16.1 Information on new pH electrodes and replacement/repair information on pH meters is recorded in “Electrode Record” (Appendix A - New pH Electrodes) and The “Records Notebook” in room 209 on laboratory benches.

17.0 Quality Control and Quality Assurance Section

17.1 Control charts are generated in the LIMS by the QC data entered.

17.1.1 Select ***BenchChem, LIMS, Query, New Tables,*** from the toolbar (see section 12.1.1).

17.1.2 Select **QC Samples** button from the **Query** options. Select desired QC.

17.1.3 QC charts can be viewed by analyst or date range from one day to the entire year. Select if desired.

17.1.4 Use drop-down menus to select desired Sample ID, Analyte, and Date Range. The control charts will appear on the screen.

17.1.5 As a quality control check once a month, use the pH calibration checker (model # 610022) to check meter calibration per manufacturer’s specifications. If it is out of range, contact Quality Assurance chemist.

17.2 Quality Assurance Replicates

- Three replicates for any random sample are measured within a run. As you are pouring your samples, select a sample that is at least 50 mL for your replicates.
- After pouring the original sample, pour the sample three additional times and set them aside.
- Two of these samples will be analyzed back-to-back.
- The original sample will be in the sample list labeled #SW.
- The three additional samples will be entered as #SW-Q.
- The replicate samples may serve as a QC sample.

18.0 References

18.1 Standard Operating Procedure for Electrode Evaluation and Shipment. SOP # SS.HEAL.EL.evaluation (SS-0026).

18.2 Standard Operating Procedure for 4.3 Quality Control Check Sample Preparation. SOP # PR.HEAL.0.4-3QCSprep (PR-0000).

Appendix A New pH Electrodes

Electrode #	Date of testing	Calibration			pH 7	DI 1	DI 2	QCS						Sent to site/ Date	Returned	Recycled	
								pH4.3			pH 6.97						
		pH 7	mV	pH 4				auto	1 min	2 min	auto	1 min	2 min				
E100 1BJ13	1-16-13	7	0.9	4.01	7	5.55	5.56	4.34	4.33	4.34	6.91	6.94	6.95	in use			TG
E100 4BJ13	4-19-13	7	.01	4.01	7	5.47	5.51	4.33	4.33	4.32	6.95	6.95	6.95	in use			TG
E100 5BJ13	5-8-13	7		4.01	7	5.42	5.42	4.34	4.32	4.28	6.94	6.95	6.95	in use → Given to Trent			TG
E100 6BJ13	6-5-13	7	2.6	4.01	7	5.44	5.51	4.30	4.28	4.34	6.94	6.94	6.95	in use			TG
E100 7BJ13	9-3-13	7	2.2	4.01	7	5.79	5.78	4.40	4.34	4.33	6.94	6.94	6.95	TN00 9/3			KB
E100 8BJ13	9-19-13	7	9.9	4.01	6.99	5.76	5.74	4.35	4.33	4.33	6.94	6.94	6.94	WV99 10/18	E100 4BJ11		KB
E100 9BJ13	9-19-13	7	17.6	4.01	6.99	5.74	5.72	4.34	4.33	4.33	6.94	6.94	6.94	Lab use			KB
E1010 BJ13	10-25-13	7	6.5	4.01	7	5.67	5.63	4.30	4.33	4.33	6.94	6.94	6.94	Lab use			AW
E1011 BJ11	11-12-13	7	9.1	4.01	6.99	5.64	5.63	4.33	4.33	4.33	6.96	6.96	6.97	Lab use			KB
E100 4BJ11	11-18-13	7	8.4	4.01	7.01	5.71	5.69	4.35	4.33	4.33	6.98	6.99	6.97				KB
E1012 BJ09	11-18-13	~~7~~	~~24.7~~	~~4.01~~	~~7.02~~	~~5.78~~	~~6.73~~	~~4.34~~	~~4.33~~	~~4.33~~	~~6.96~~	~~6.97~~	~~6.88~~	→		Discard	KB

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