Health and Environmental Application Laboratory

Standard Operating Procedure
For
The Determination of pH

(based on Standard Methods 4500-H+)

SOP Number: AN.HEAL.EL.PH

Revision 19.2, effective 8 October 2024

Illinois State Water Survey
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NOTE THE HEALTH & SAFETY WARNINGS IN SECTION 4.0

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

Name (printed)	Signature	Date
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Yael Bartov	Yael Bartov	01/06/2025

Revision History

Starting revision number	Ending revision number	Revision Date	Revisions Made
	16.0	3/16/20	Updated, added some formatting and signature sheet. Updated SOP # to new convention, inserted information in section 9.2 about using a pH 10 buffer for calibration
16.0	17.0	8/3/21	Changed order of buffer measurement during calibration. Corrected the pH meter setup details and quality control/troubleshooting procedure. Reduced volume threshold for pouring 2 vials. Removed section 12.4 regarding weekly reanalysis. Acceptable slope value changed. Removed section 16.1 regarding pH sample values.
17.0	18.0		Changed order of SOP to match workflow, changed slope criteria, fixed wording and removed items no longer needed.
18.0	18.1	9/15/23	Changed QC scheme, edited SOP to follow lab workflow.
18.1	19.0	2/23/24	Changed FM/CCV to 7 buffer, inserted QC table
19.0	19.1	7/27/24	Changed QC scheme, changed FL to buffer 4 and limits to match RFP and Standard Methods. Removed blanks.
19.1	19.2	10/8/24	Updated electrode information in section 8. Also updated section 15.

Contents

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1.0 Scope & Applicability

This method is applicable for measuring the pH of drinking, surface, ground, and wet deposition water samples.

2.0 Summary of Method

2.1 About 4mL of sample is poured into a sample cup and measured using a calibrated pH meter. HEAL prepared solutions and externally purchased solutions are analyzed for quality assurance purposes.

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

3.0 Definitions

ACS American Chemical Society

CCV Continuing Calibration Verification. HEAL uses Buffer 4 as a CCV- a QC solution targeting the low end of the calibration curve for wet deposition analysis:

DI Deionized (water) at 18.0 Mohms-cm or higher

ICV Initial Calibration Verification. HEAL uses a simulated rain sample as an ICV:

FR50- a solution with target analyte concentrations at the 50th percentile of the NTN network results.

MDL Method Detection Limit

HDPE High Density Polyethylene

LIMS Laboratory Information Management System

QA Quality Assurance

QC Quality Control

R^2 Coefficient of Determination reflecting the deviation of the measured data points from the calibration curve

SDS Safety Data Sheet

SOP Standard Operating Procedure

4.0 Health & Safety Warnings

4.1 Always wear eye protection in the laboratory.

4.2.1 Food, drinks, and smoking are not allowed in the laboratory.

4.3 Safety Data Sheets (SDS) applicable to this SOP can be found online by using the University of Illinois Division of Research Safety (DRS) website: https://www.drs.illinois.edu/Programs/SafetyDataSheets.

4.4 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 https://go.illinois.edu/ISWS-Chemical-Hygiene-Plan.

4.5 The University of Illinois DRS has a laboratory safety guide available at https://www.drs.illinois.edu/site-documents/LaboratorySafetyGuide.pdf. The ISWS has their own laboratory safety manual, available at https://go.illinois.edu/ISWS-Laboratory-Safety-Manual.

4.6 The HEAL practices pollution prevention, which encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased should be based on the expected usage during its shelf life and disposal cost of unused material.

4.7 Laboratory waste management practices must be consistent with all applicable rules and regulations. Excess reagents and samples and method process wastes should be characterized and disposed of by DRS. It is the responsibility of the user of this method to comply with relevant disposal and waste regulations.

4.8 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 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. When a handling error occurs by laboratory personnel, it should be noted in the comment section of LIMs.

5.2 HEAL Electrode Cautions

5.2.1 The electrode must be stored in a 3 M KCl storage solution.

5.2.2 The fill hole (if the electrode has one) should be open during measurements and closed during storage.

6.0 Interferences

None

7.0 Personnel Qualifications

Analysts in training must complete at least five days of training with an experienced analyst or a manufacturer's training course, and a satisfactory demonstration of capability before analyzing routine samples.

8.0 Apparatus & Materials

8.1 Equipment

8.1.1 pH electrode, semi-micro, such as Mettler Toledo InLab Semi-Micro (Mettler Toledo #51343165).

8.1.2 Mettler SevenMulti Meter or approved equivalent.

8.1.3 PVC vial support blocks and plexiglass covers.

8.1.4 Temperature probe (not needed if pH electrode has a built-in temperature sensor).

8.2 Chemicals and Solutions

8.2.1 0.1 M HCl pH electrode cleaning solution - Add 8.3 mL concentrated HCl to approximately 900 mL DI water in a 1L volumetric flask. Dilute to 1L with DI water and mix thoroughly. The preparation must be performed in a fume hood.

8.2.2 0.1 M NaOH pH electrode cleaning solution - Dissolve 4.0 g NaOH in 1 L of DI water in a 1L volumetric flask.

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

8.2.4 pH 4.00 buffer for calibration (Fisher Cat # SB101-500 or equivalent).

8.2.5 pH 7.00 buffer for calibration (Fisher Cat # SB107-500 or equivalent).

8.2.6 pH 10.00 buffer for calibration (Fisher Cat # SB116-500 or equivalent).

8.2.7 FR50 – Lab-prepared pH 4.92 solution.

8.2.8 CCV - pH 4.00 buffer (can be same as calibration buffer)

8.2.9 KCl filling/storage solution (Mettler Toledo #30111142, or equivalent).

8.3 Supplies

8.3.1 Conical Polystyrene Sample Cups, 4 mL. Alternative vials or test tubes may be substituted.

8.3.2 Nalgene LDPE 500 mL Wash Bottle

8.3.3 Safety Glasses

8.3.4 Parafilm

8.3.5 pH Records Notebook

9.0 Sample Collection

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

10.0 Handling & Preservation

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

10.2 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.

10.3 When pouring samples into the sample cup, avoid splashing or spillage of sample into an adjacent cup.

11.0 Instrument or Method Calibration

11.1 HEAL pH Meter Information

11.1.1 The Mettler Seven MultiMeter is used in the laboratory for all precipitation and Water Chemistry sample analyses. For more detailed instructions on how to work with the Mettler meter, see the manual “Operating Instructions SevenMulti.”

11.1.2 The electrode must be calibrated at the start of analysis and every 30 samples thereafter. A CCV is analyzed every 10 samples.

11.1.3 If a QC is out of range, a new QC needs to be analyzed again. If it still does not pass, the meter must be recalibrated and all samples analyzed since the last passing QC must be reanalyzed.

11.2 Calibration Procedure

The SevenMulti meter has an automatic endpoint. The measurement 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.

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

11.2.2 Using a wash bottle, rinse the tip of the electrode thoroughly with DI water. Lightly flick excess water from the electrode tip. (Do not touch or wipe the electrode. This may cause a static charge and alter the readings.)

11.2.3 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>

11.2.4 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.

11.2.5 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.

11.2.6 Repeat the process from 11.2.1 through 11.2.5, using the 4 buffer.

11.2.7 Repeat the process from 11.2.1 through 11.2.5, using the 10 buffer.

11.2.8 End calibration with **End** button after reading the last calibration buffer. A table with the calibration results appears in the display. Slope must be between 95 to 105% and the offset must be ±15.

11.2.9 Press **Save** to accept.

11.2.10 If the slope is between 95% and 105%, then sample analysis may begin. If it is not, recalibrate the meter. If the slope is still out of range, clean the electrode.

12.0 Sample Sequence And Sample Preparation

12.1 QA/QC Samples

12.1.1 Every analytical batch begins with analyzing FR50 and CCV (Buffer 4).

12.1.2 After every 10 samples, at the beginning and at the end of the analytical sequence, a CCV solution is analyzed.

12.1.3 A duplicate of one sample every 10 samples must be analyzed as well.

12.2 Pouring the Sample Sequence

12.2.1 Each sample or QC is analyzed twice. The first analysis is a “conditioning” analysis and the second is to obtain the analytical result. Therefore, each sample gets poured into two vials on the sampling rack.

12.2.2 Pour each sample or QC solution into two vials and place in the sampling rack in the order they are to be analyzed. A minimum volume of ~1mL is required for analysis.

12.2.3 If the sample volume is less than 25ml, pour only one vial.

12.2.4 Label each sample in the rack so you can match the correct sample with the entry in the LIMS.

12.2.5 After three blocks of 10 samples (30 total samples + relevant QC solutions) the meter must be recalibrated. Therefore, a sample sequence should end after the third block of 10.

13.0 Sample Analysis

13.1 Setup of LIMS for pH Analysis

13.1.1 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.

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

13.1.3 Under the *Collect* heading, select *pH/conductivity*. The pH /conductivity collection screen is split into two channels.

13.1.4 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.

13.1.5 Select **Sample Range** button.

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

13.1.7 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.

13.2 Measuring pH of QC samples using the LIMS:

13.2.1 As QC samples do not appear in the sample list, this process is used when a QC sample is to be measured.

13.2.2 The bottle for each QC solution will be labelled with a barcode. Scan the barcode for the selected QC sample being measured. This will appear in the Current Sample text box.

13.2.3 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.

13.2.4 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.

13.3 Measuring pH of samples using the LIMS

13.3.1 If the pH of the previous buffer or sample was greater than 6.0, rinse the electrode with CCV to prevent carry-over.

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

13.3.3 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.

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

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

13.3.7 When finished analyzing samples, cover the fill hole of the electrode (if it has one) with parafilm and store the bulb in a storage solution.

14.0 Evaluating Quality Control Samples

Table 14-1. QC summary.

QC Name	QC Type	Frequency	Target Value	Acceptable Deviation
FR50	ICV	Every Batch	4.92	+/-0 .2
CCV	CCV	Every 10 Samples	4.00	+/- 0.1
Duplicate	DUP	Every 10 samples	--	+/-0 .2

14.1 CCV

14.1.1 The CCV value must read 4.00 ± 0.1 pH units.

14.1.2 If the CCV fails, reanalyze CCV solution. If it still does not pass, repeat the calibration procedure and analyze another CCV solution. All samples analyzed since the last passing QC must be reanalyzed.

14.2 ICV

14.2.1 The tolerance range for the ICV (FR50) is 4.92 ± 0.2, which is programmed into the LIMS and will indicate if the result is outside the range.

14.2.2 If the ICV (FR50) fails, reanalyze ICV solution.

14.2.3 If the FR50 still fails, repeat the calibration procedure, analyze another FR50 solution. If it passes, continue the analysis. If it fails, prepare a new batch of FR50 solution.

14.4 Duplicates

As you are pouring the samples, select a sample that is at least 50 mL for your duplicate.

These samples may be analyzed back-to-back or at different points in the sequence.

The original sample will be in the sample list with the original sample number.

The duplicate samples will be entered with “-Q” added to the end of the sample number.

The RPD of the samples must be within ±0.2.

15.0 Troubleshooting

15.1 First, visually inspect the electrode to ensure there are no broken parts. If KCl salt crystal deposits are observed on or inside the electrode, use the following cleaning procedure. Note that some electrodes do not have access to the internal filling solution- in that case, refer to electrode manual for care instructions.

Dissolve KCl buildups 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 deionized water.

If crystals are built up inside the barrel of the electrode, then rejuvenate the electrode by rinsing the barrel out with DI water three times. If there are excessive crystals built up inside, soak it in warm DI water until they dissolve. After the build-up is cleared, fill the electrode up with filling solution (usually 3 M KCl but verify with electrode manufacturer) three times to ensure all DI water is expelled. Let the electrode sit overnight before checking it to verify performance.

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)

15.2 Slope Value

Follow these steps when the slope value of the pH meter is not between 95% to 105% after calibration:

15.2.1 Re-calibrate the pH electrode.

15.2.2 Clean the electrode and calibrate the pH meter.

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

15.2.3 Replace the questionable electrode with a new electrode.

15.4 QC Check Solution

Follow these steps when the QC Check Solutions, ICV and CCV, do not measure within tolerance limits:

15.4.1 Replace the vials of QC Check Solution measured with new vials of the same QC Check Solution bottle.

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

16.0 Data Acquisition, Calculations & Data Reduction

This is automatically done by the LIMS.

17.0 Data Management & Records Management

17.1 Information on new pH electrodes and replacement/repair information on pH meters is the room 209 records notebook.

17.2 Each new pH probe should be labelled with the date it was put into use. Use lab tape to make a tag on the cord.

18.0 Quality Control and Quality Assurance

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

18.1.1 In the Benchchem program, select ***LIMS, Query, New Tables,*** from the toolbar.

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

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

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

19.0 References

19.1 Rea, E. 2023. Health and Environmental Applications Laboratory Quality Assurance Plan. Illinois State Water Survey. Champaign, IL.

19.2 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, p.4-92, (2012).

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Final Audit Report 2025-01-06

Created:	2024-12-17 (Central Standard Time)
By:	Evan Rea (erea@illinois.edu)
Status:	Signed
Transaction ID:	CBJCHBCAABAA1n3k8Rrb48vMcF0dp_TcM_mIiJ9xtjqZ
Number of Documents:	1
Document page count:	12
Number of supporting files:	0
Supporting files page count:	0

"AN.HEAL.EL.PH.19.2" History

Document created by Evan Rea (erea@illinois.edu)
2024-12-17 - 5:33:20 PM CST- IP address: 130.126.105.85

Document emailed to Margarita Bargon (rbargon@illinois.edu) for signature
2024-12-17 - 5:35:40 PM CST

Email viewed by Margarita Bargon (rbargon@illinois.edu)
2024-12-18 - 9:09:45 AM CST- IP address: 130.126.105.134

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2024-12-18 - 9:09:46 AM CST- IP address: 130.126.105.134

Margarita Bargon (rbargon@illinois.edu) authenticated with Adobe Acrobat Sign.
2024-12-18 - 9:11:37 AM CST

Document e-signed by Margarita Bargon (rbargon@illinois.edu)
Signature Date: 2024-12-18 - 9:11:37 AM CST - Time Source: server- IP address: 130.126.105.134

Document emailed to Evan Rea (erea@illinois.edu) for signature
2024-12-18 - 9:11:39 AM CST

Email viewed by Evan Rea (erea@illinois.edu)
2024-12-18 - 9:23:56 AM CST- IP address: 130.126.105.85

Agreement viewed by Evan Rea (erea@illinois.edu)
2024-12-18 - 9:37:16 AM CST- IP address: 130.126.105.85

Evan Rea (erea@illinois.edu) authenticated with Adobe Acrobat Sign.
2024-12-18 - 9:37:20 AM CST

Document e-signed by Evan Rea (erea@illinois.edu)
Signature Date: 2024-12-18 - 9:37:20 AM CST - Time Source: server- IP address: 130.126.105.85

Document emailed to Tatyana Grandt (tgrandt@illinois.edu) for signature
2024-12-18 - 9:37:21 AM CST

Reminder sent to Tatyana Grandt (tgrandt@illinois.edu)
2024-12-25 - 8:07:31 PM CST

Reminder sent to Tatyana Grandt (tgrandt@illinois.edu)
2025-01-01 - 10:06:08 AM CST

Email viewed by Tatyana Grandt (tgrandt@illinois.edu)
2025-01-02 - 9:12:37 AM CST- IP address: 130.126.105.117

Agreement viewed by Tatyana Grandt (tgrandt@illinois.edu)
2025-01-02 - 9:12:41 AM CST- IP address: 130.126.105.117

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2025-01-02 - 9:12:55 AM CST

Document e-signed by Tatyana Grandt (tgrandt@illinois.edu)
Signature Date: 2025-01-02 - 9:12:55 AM CST - Time Source: server- IP address: 130.126.105.117

Document emailed to Yael Bartov (ybartov@illinois.edu) for signature
2025-01-02 - 9:12:56 AM CST

Email viewed by Yael Bartov (ybartov@illinois.edu)
2025-01-06 - 9:28:57 AM CST- IP address: 130.126.105.172

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2025-01-06 - 9:28:58 AM CST- IP address: 130.126.105.172

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2025-01-06 - 9:35:37 AM CST

Document e-signed by Yael Bartov (ybartov@illinois.edu)
Signature Date: 2025-01-06 - 9:35:37 AM CST - Time Source: server- IP address: 130.126.105.172

Agreement completed.
2025-01-06 - 9:35:37 AM CST