Analysis of pH

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As performed at the University of Massachusetts, Environmental Engineering Research Laboratory

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Standard Operating Procedures

Analysis of pH

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting analysis of pH in the UMass Environmental Engineering research laboratories. It aspires to outline our standard operating procedures, as they exist at the present time. It also emphasizes elements of quality control that are necessary to assure high quality data. Please help me keep this document current by alerting me to any errors or long-term changes in methodology or equipment. Special thanks to Guanghui Hua for his help with the first draft.

Dave Reckhow
Faculty QC officer for pH analysis

Scope

This method has been used in the UMass Environmental Engineering Laboratory for analysis of pH in clean water samples (i.e., drinking water, surface waters and uncontaminated groundwaters). It has been found to meet data quality criteria with all waters of these types for which it has been tested. This method should not be used for other media without further validation.

Method Overview

Reproduced below is a simple, step-by-step outline of our pH method for quick reference.

Table 1: Summary of Procedure for pH Measurement

1. Bring sample to room temperature
2. Connect electrode meter and turn on.
3. Calibrate with pH 7 standard
4. Adjust "slope" calibration with either pH 4 or pH 10 standard
5. Measure pH of samples
6. Turn off meter and store electrode in soaking solution

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with Standard Method 4500-H^+ B. Electrometric Method. Please refer to the latest version of this method (currently from the 20th edition, dated 1999; attached as Appendix 1) for all details. However, the analyst should keep in mind that we have occasionally made some specific modifications. Such modifications are itemized below in Table 2.

Table 2. UMass Protocol Specifics and Departures from Standard Method 4500-H^+ B

	Step or Apparatus	4500-H^+ B protocol	UMass protocol
1	pH calibration solutions	Preparing buffer solutions from solid salts	Using commercially available buffer solutions.

UMass Detailed Procedures

Sample Preservation and Pretreatment

1. **Place aqueous samples, headspace-free in a refrigerator until analysis.**
   - Samples should be analyzed as soon after collection as possible, but under no circumstances should more than 4 hours be allowed to elapse.

Selection of pH Meter and Electrode

In the environmental engineering laboratory, we have many research-quality pH meters as listed in Table below.

Otherwise, the selection of a meter is largely a matter of convenience and availability

Table 3: EVE Research pH Meters

Model	Use	Usual Location	Serial #
Orion 520A	General	Room 304	010388
Fisher 600			
Fisher 610A			
Fisher 630			
Orion 940	General		058531
Orion 940	General		058530
Orion 940	General	Room 308	1384
Orion 720A	General	Room 304	076174
Fisher AP61	General	Room 308	

Startup of pH Meter and Electrode

1. **Select meter and electrode to be used**
   - See prior section on available meters and capabilities
   - All bench-top meters are of "research grade"
2. **Prepare meter/electrode system**[1]
   a) Place function switch on standby
   b) Remove the electrode from its soaking solution, and carefully secure it in the adjustable electrode holder
   c) Connect electrical leads from electrode to meter
   d) Slip the rubber sleeve down the electrode so the fill hole is barely exposed.
   e) Carefully lower the electrode and holder assembly into a beaker until it is properly immersed in the solution (porous glass frit must be submerged), but still about 1/2 inch above the bottom. Position the small metal collar immediately below the holder and tighten. This serves as a safety stop to protect the electrode's fragile glass bulb.

Calibration of pH meter/electrode system

Modern 3-point method

a) Select "calibrate" function from the control board of the pH meter.
b) Enter "3" for the question of "Number of Buffers?".
c) Place the electrode in the first buffer solution (pH 4), Wait until it is ready and answer "Yes" for the question of "Calibrate as pH 4?".
d) Place the electrode in the second buffer solution (pH 7), Wait until it is ready and answer "Yes" for the question of "Calibrate as pH 7?".
e) Place the electrode in the second buffer solution (pH 10), Wait until it is ready and answer "Yes" for the question of "Calibrate as pH 10?".
f) After calibration, place the electrode again into pH 7 buffer. The pH reading should be within 0.05 units. Otherwise, recalibrate the pH meter.
g) If the slope cannot be adjusted to read the target buffer pH, this means that the electrode is in need of cleaning or replacement.

Note: always rinse probe off with distilled water between operations; also, in order to achieve maximum precision, moderate agitation of roughly the same magnitude (i.e., same rpm of the magnetic stirring bar) must be maintained for all standards and samples.

[1] Depending on the frequency of use, electrodes may be stored in holder and connected to their meters.

Older 2-point method

1. **pH 7 adjust (offset)**
   a) With the function switch on "standby" place electrode in the pH 7 buffer, and provide mild stirring. If necessary allow several minutes for temperature equilibration.
   b) Change function switch to "pH" and adjust "calibrate" knob so that the meter reads the correct pH to within 0.01 units.
   c) Return to "standby".
2. **pH slope calibration**
   a) Place the electrode in either the pH 4 or the pH 10 buffer depending on whether you're interested in having the greatest accuracy in the acid or base ranges.
   b) Switch function to "pH", and adjust the temperature knob until the meter reads the correct pH (do not re-adjust "calibrate"!).
   c) If the slope cannot be adjusted to read the target buffer pH, this means that the electrode is in need of cleaning or replacement.

Note: always rinse probe off with distilled water between operations; also, in order to achieve maximum precision, moderate agitation of roughly the same magnitude (i.e., same rpm of the magnetic stirring bar) must be maintained for all standards and samples.

Analysis of samples

1. **With the function switch on "standby" place the probe in solution to be measured.**
2. **Provide mild agitation, and if necessary, allow time for temperature equilibration.**
3. **Switch to "pH" and record the reading.**
4. **Return function switch to "standby" and remove probe from solution.**

It is important to avoid streaming potential effects in dilute solutions. Therefore, such samples should be allowed to stand quiescently for several minutes before measuring (McQuaker et al., 1983).

pH Meter/electrode standby and storage procedure

1. **Verify that function switch is on "standby".**
2. **Slide rubber sleeve over fill hole.**
3. **Remove probe from holder and place it in the specially sealed storage bottle (filled with electrode storage solution (Fisher)).**

Data Analysis & QC Reporting

According to the standard method, a precision of ± 0.02 pH unit and an accuracy of ±0.05 pH unit cab be achieved by careful use of a laboratory pH meter with good electrodes. However, ± 0.1 pH unit represents the limit of accuracy under normal conditions. The pH values are reported to the nearest 0.1 pH units.

Standard Solutions, Solvents and Supplies

Preparation/Acquisition of Calibration Standards

pH buffers are available commercially in a powdered form (to be added to distilled water) or as a prepared liquid. We generally use the prepared solutions that are color-coded. All of these solutions contain acids and bases whose equilibria are dependent on temperature. As a result the precise pH is also a function of temperature. For example the buffers available from VWR Scientific vary with temperature as shown in Table 3 below.

Table 3: Standard Buffers

	Actual pH		
Temp.(°C)	Phthalate	Phosphate	Borate
0	4.01	7.12	
10	4.00	7.06	10.15
20	4.00	7.02	10.06
25	**4.00**	**7.00**	**10.00**
30	4.01		9.96
40	4.03	6.97	9.87
50			9.80
60	4.09	6.98	9.73

Supplies

Table 4. Summary of Supplies for pH Analysis

Item	Catalog #	Approx. Price	Approx # used/run[2]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
pH 4 buffer	Fisher: SB101-500	1/$24.75	
pH 7 buffer	Fisher: SB107-500	1/$24.75	
pH 10 buffer	Fisher: SB115-500	1/$24.75	
Electrode storage solution	Fisher: SE40-1	1/$35.82	
DIUF Water	Fisher: W2-20	$32.29	Not normally used
H_2SO_4	UMass Stockroom		

[2] Assuming about 30 samples analyzed

Maintenance and Troubleshooting

Regular Maintenance Activities

Nearly all maintenance for pH measurement focuses on the pH electrode.

Electrode:

Daily Checks

a) Check level of internal filling solution daily; refill as needed from commercial solution
b) Check for crystallization of internal filling solution
c) Check for presence of solid residue in porous plug

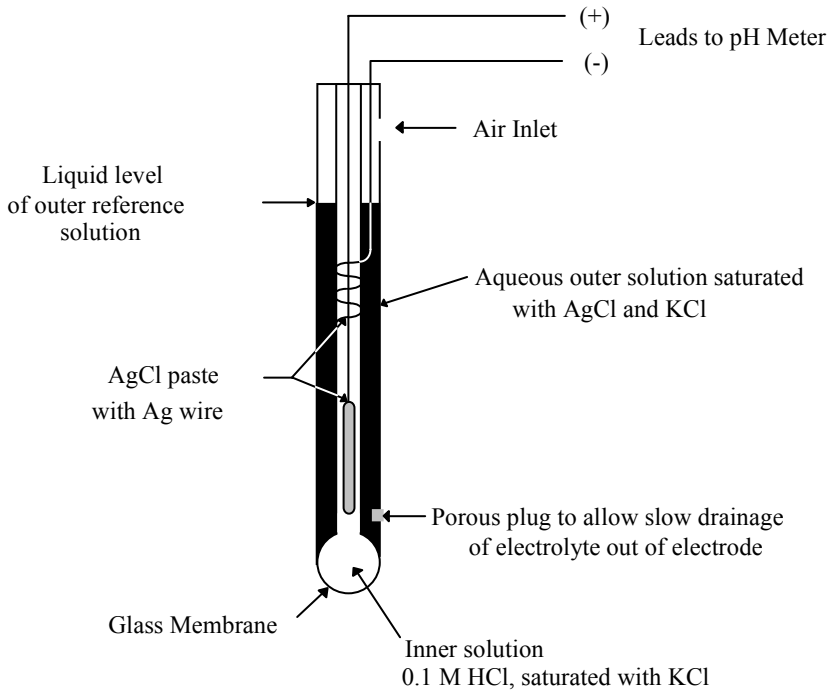

Figure 1: A Standard Glass Combination pH Electrode

Meter:

1. **Periodic Checks**
   a) Check zero

Troubleshooting

Past difficulties have resulted from:

- A clogged junction can cause increase in response time and drift in reading
  - A clogged junction can be cleared by applying suction to the tip or by boiling tip in distilled water

For further assistance:

- Consult electrode manuals
- Call Orion technicians (1-800-255-1480)

Quality Assurance/Quality Control

General Approach

Quality assurance is an essential and integral part of a research study. The purpose of any QA plan is to insure that valid and reliable procedures are used in collecting and processing research data. The procedures outlined are designed to eliminate or reduce errors in experiments, sample preparation and handling, and analytical methods. Emphasis must be given throughout one's lab work to incorporate the plan into the research project by all research personnel.

Any equipment and experimental procedures that are used to provide numerical data must be calibrated to the accuracy requirements for its use. Records are to be kept of all calibrations (pH calibrations are one of the few exceptions). Calibration schedules are generally established for all aspects of physical and chemical measurements and these must be strictly followed. Physical standards and measuring devices must have currently valid calibrations, traceable to national standards. Most chemical standards are acquired from commercial suppliers, and they should be of the highest purity available. When necessary, unavailable standards should be synthesized using the best methodology available.

As a general rule, experiments should be replicated to assure reproducibility. All data reported should include a statement of its uncertainty, and the means for the determination and assignment of such limits. Standard reference materials are used for this purpose where possible. Statistically established confidence limits and an analysis of sources of systematic error are to be used in the absence of experimental demonstration of limits of inaccuracy.

All data will be subject to review by the faculty QC officer before release. The analysts involved will certify reports as well as all who review them. All analysts and QC officers must attest that the data and associated information contained in the report are believed to be correct and that all quality assurance requirements have been fulfilled, unless exceptions are approved and noted. Careful and detailed laboratory records will be maintained by each analyst, including source of reagents, meticulously detailed procedures (referring to an SOP, and any departures or clarifications), instrument and conditions of analysis, failed experiments, etc. Data output will be archived.

Regular meetings will be held to review the results and project progress, and to plan further experiments. The results will be analyzed promptly and summarized by means of internal reports or formal reports for external review. The experimental and analytical procedures will be reviewed for their performances and changes will be made as necessary. The quality assurance program as described in this document must be strictly observed.

Quality Assurance Objectives

The precision, accuracy and method detection limits will be evaluated, and where there are existing methods, held within the control limits set forth in the accepted references (e.g., APHA et al., 1999; USEPA-EMSL, 1990; ASTM, 1994). In addition to the analysis of sample replicates, a minimum of 10 percent of the time is typically involved in analytical determinations that are devoted to quality control. The precision of each test is determined through analysis of sample replicates. These are commonly presented in the form of control charts (e.g. Section 1020B of APHA et al., 1999).

The accuracy of each analysis will be determined by measuring spike recoveries in the matrix of interest (again, pH is one of the few measurement for which this cannot be done). The relative errors will be calculated and will be considered acceptable if they fall within the control limits determined for the particular test. For new methods developed at UMass or for modifications of existing methods, we will have to establish criteria on acceptable control limits. In general, a test will not be deemed useful if its precision or accuracy is found to be equal to or greater than 20% of the highest values observed. Where possible, external performance standards will also be run. This serves as a measure of accuracy both for the analysis and for standard preparation.

Data generated by the QA program will be incorporated into a Quality Control (QC) archive that is used to monitor the fluctuations in precision and accuracy so that chance or assignable causes of error can be determined. Control charts such as X-charts for simple successive samples or cumulative sum techniques may be employed to record both precision and accuracy data (Taylor, 1987).

General Procedures

General sample collection and handling will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All previously established analytical methods used in laboratory research will follow approved methods in the standard compilations (e.g., ,APHA et al., 1999; USEPA-EMSL, 1990, or ASTM, 1994).

Reagent grade chemicals or higher quality when needed will be used throughout the research. Laboratory-grade water (purified by reverse osmosis, deionization, and carbon adsorption) will be used for preparation of reagents, sample blanks, and dilution water. Where necessary, this water will be further purified using batch UV irradiation. All glassware used in the experiments and in analytical analyses will be thoroughly cleaned with a chromium-free sequence of detergent, oxidant and acid to prevent interferences from trace contaminants.

Data Quality Indicators

A wide range of data quality indicators are normally calculated for the purpose of assessing method performance. Some of these are defined below.

Precision

Precision may be expressed as the relative percent difference (RPD) from duplicate measurements (C_1 and C_2) of the same sample:

$$RPD = \frac{|C_1 - C_2| x100\%}{(C_1 + C_2)/2}$$

When three or more replicates are available, the relative standard deviation (RSD) should be used:

$$RSD = \left(\frac{s}{\bar{y}}\right) x100\%$$

where the standard deviation (s) is determined from:

$$s = \sqrt{\sum_{i-1}^{n} \frac{(y_i - \bar{y})^2}{n-1}}$$

Accuracy

Accuracy is best assessed by analysis of a standard reference material (SRM) prepared in the matrix of interest. It is quite rare that such materials are available, so two possible compromises may be used instead. These are the laboratory-prepared matrix spikes, and the independent SRM prepared in a standard matrix. One or both may be analyzed and the percent recovery (%R) calculated as a measure of accuracy.

$$\%R = \left(\frac{S - U}{C_{sa}}\right) x100\%$$

where:

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

$$\%R = \left(\frac{C_m}{C_{srm}}\right) x100\%$$

and:

C_m = measured concentration of SRM

C_{srm} = actual concentration of SRM

Method Detection Limit (MDL)

The method detection limit (MDL) will be defined as:

$$MDL = s_7 \bullet t_{(n-1,1-\alpha=0.99)}$$

where:

s_7 = standard deviation of 7 replicate analyses where the mean is no more than 10 times the MDL

$t_{(n-1,1-\alpha=0.99)}$ = Students' t-value for a one-sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Linearity

The calibration curve linearity (L) is defined as the ratio of the slope using the highest standards (S_U) divided by the slope determined from the lowest standards (S_L) as follows:

$$L = \frac{S_U}{S_L}$$

The highest standards shall be all those that fall within the top 50% of the calibration range including the 50% standard if it is used. If only one standard falls within that range, the S_U shall be calculated based on the top two standards. The lowest standards are all those that fall within the bottom 50% of the calibration range including the 50% standard if it is used. Least squares linear regression is used to determine slopes.

Sampling Custody

In most cases analyses will be performed immediately upon return from the field or after preparation of samples in the laboratory. Problems with sample custody are minimized, because the same people who receive (or sometimes, collect) the samples also analyze them. In general sample collection, handling, and preservation will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All samples must be fully labeled with the sample identity, date, and name of researcher.

Sample Collection and Storage

Samples are collected and stored in clean borosilicate (e.g., Pyrex, Kimax) glass containers. Containers must be capped with either Teflon-lined septa or ground glass stoppers. Exceptions are made for large volume samples which may be stored and shipped in clean polyethylene carboys. Glass containers are cleaned with detergent, followed by 5% sulfuric acid soak, and final rinsing with reagent-grade water. These containers are dried in a 150ºC oven.

Samples for TOC analysis must be acidified and kept in a refrigerator from the time of collection to the start of analysis. Some organics are biodegradable, so care must be taken to minimize this type of loss.

Data Reduction, Validation and Reporting

To ensure the accuracy and permanency of collected data, all research data are recorded with permanent ink in bound notebooks and all QC data (precision, accuracy) are recorded in instrument log notebooks. Summary QC graphs and tables are reviewed at least quarterly by the Faculty QC officer to observe noteworthy trends or inconsistencies. These are maintained in loose leaf notebooks for subsequent use in preparing progress reports, final reports, and theses. Major concerns and conclusions are reported to the external Project Officer via the progress reports.

Pages from the laboratory data books are regularly duplicated so that a file copy of raw data can be placed in safe storage in the event that the book is lost or destroyed. At the end of the project, all bound data books and any loose leaf data will be stored by the project team for at least ten years. Summary data files will be put on magnetic media so that statistical analysis of the data can be done. Our laboratory has several personal computers that can be used for this purpose.

Procedures specific to pH Measurement

General Analytical QC

Many types of QC procedures are required as indicated under standard method xxxx. The guidelines below are prepared assuming that samples are run in groups, whereby a "daily" frequency refers to once every day that the analytical method is being used.

Table 5. Summary of QC Elements as Applied to TOC Analysis

Types of Samples or Standards	§ in Std. Meth.	Purpose	Frequency	Timing	QC data
Laboratory Performance Check Standard (LPC)		To establish basic analyzer performance			Noise, response
Laboratory Reagent Blank (LRB)		Test lab conditions and quench for interferents			Response
Field Reagent Blank (FRB)		Test all field conditions for interferents			Response
Calibration Standards		To provide a basis for determining the concentrations in unknowns			Calibration curves including slopes and intercepts
Continuing Calibration Check Standards (CCC)[3]		To verify the accuracy of the calibration standards			
Challenge standard[4]		To test the method with a "difficult" compound			% recovery
Unknowns or "samples"		This is what you really want to measure			Relative standard deviations
Low I standard		To test system for accuracy with low ionic strength waters			

[3] Prepared from the calibration solution (eg., KHP stock)
[4] these are compound that are not as easily oxidized, such as caffeine, dodecylbenzene sulfonic acid, and chondroitin sulfate. Sometimes standard solutions of humic substances can be used.

Table 6 shows a recommended sequence for a typical run of about 16 samples. The first two samples require immediate attention, as they are simple indicators of unacceptable QC.

Table 6: Typical Testing Sequence for pH Analysis

Test #	Sample type	QC objectives
1-2	Calibration Samples	To calibrate offset and slope of response
3	Water Blank	To check on IC condition
4-15	Analytical Samples	
16	Calibration standard (one intermediate)	Final check to verify that calibration hasn't changed during run

QC Criteria

Any quality control data must be analyzed as soon as possible. The best practice is to have the QC data tabulated and evaluated as the work is being done. However, it is recognized that there will be times when this is impossible.

Should there be a problem meeting QC criteria, the graduate and faculty QC officer along with the analyst will then work out a plan for returning the analysis to acceptable levels of QC. Table 7 lists some typical corrective actions, however the actions taken may differ depending on the particular circumstances. Excursions from QC criteria can be quite complex, and many analytical characteristics and conditions must be considered before a decision can be made on the most effective steps to be taken.

Table 7: Quantitative Criteria for Judging Data Acceptability

Types of Samples or Standards	Frequency	Timing	QC data Acceptance Criteria	Typical Corrective Action
Low I pH standard	Depends on nature of samples being tested	Mixed throughout day	Mean % accuracy = ±0.1 log units	❖ Re calibrate and re-run low I standard ❖ Clean electrode, and re-run ❖ Replace electrode and re-run

Literature Cited

McQuaker, Neil R., Paul D. Kluckner, and Douglas K. Sandberg, 1983 "Chemical analysis of acid precipitation: pH and acidity determinations", Environ. Sci. Technol. 17(7)431-435.

Appendix

Standard Method 4500-H^+ B. :

(20th edition, 1999)