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Standard Guide for
Preparing a Training Program for Environmental Analytical Laboratories[1]

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1. Scope

1.1 This guide is intended to assist the laboratories that analyze environmental samples with the development of a documented training program. The training program should develop and increase the competence of analysts and provide a means of recording the results of all proficiency testing.

1.2 Some of the functions within a laboratory that can be addressed using this guide are as follows:

1.2.1 Analysts,
1.2.2 Technicians,
1.2.3 Quality assurance (QA),
1.2.4 Sample receiving and control, and
1.2.5 Sample procurement (sampling).

2. Referenced Documents

2.1 *EPA Standards:*
EPA Method 150.1[2]
SW 846 USEPA Test Methods for Evaluating Solid Waste—Physical/Chemical Methods, 9040 and 9045[2]

3. Summary of Guide

3.1 This guide is summarized in the following steps:
3.1.1 Define the training needs;
3.1.2 Prepare training materials;
3.1.2.1 Develop training objectives;
3.1.2.2 Develop performance evaluation materials;
3.1.2.3 Develop a detailed training outline; and,
3.1.2.4 Develop a documentation form;
3.1.3 Identify trainers competent in the areas defined in 3.1.1;
3.1.4 Determine need and frequency for retraining;
3.1.5 Assemble and store training materials; and,
3.1.6 Assign responsibility for training program.

4. Significance and Use

4.1 Training is a key component in the development of a competent staff in the environmental laboratory.

4.2 This guide will assist in providing both the organizational structure and the direction for a laboratory training program.

4.3 This guide will result in a documentation effort that will satisfy the requirements of environmental auditing groups.

5. Defining the Need for Training

5.1 Each individual who handles or analyzes environmental samples must be knowledgeable in the proper procedures for performing one's job function. Any deficiencies must be corrected by training. Training also may be extended to include those individuals who accept and record information prior to receipt of a sample or who are responsible for generating a report detailing the results of the analyses. Those involved with quality assurance functions need specialized training as well.

5.2 The first step in developing a training program is to identify the procedures or methods within the laboratory for which an individual is responsible. These may range from basic activities to very complex manipulations or interpretations.

5.2.1 Basic activities might include: pH measurement, pipetting, titrating, unloading sample shippers, or data entry.

5.2.2 Complex activities might include: operating an inductively coupled plasma (ICP), cleaning the source of a mass spectrometer, or data validation.

5.2.3 Within each activity certain tasks will have to be learned. A detailed analysis of these tasks must be performed before specific training courses can be developed.

5.2.4 Before beginning actual training, the level of training should be determined using the task analysis.

5.3 Before starting a training program, an approved Standard Operating Procedure (SOP) must be available for each method or activity.

5.3.1 A detailed manual or training video may serve as an SOP.

5.3.2 Published or externally prepared materials must be followed explicitly or an in-house document should be prepared. It is often difficult to follow commercially prepared materials due to differences in the equipment, work areas, sample type, or even level of training of the analyst. For this reason, it is advisable to prepare SOPs that detail the actual

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[2] Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

situation that will be encountered by the trainee.

6. Preparation of Training Materials

6.1 An effective training program for environmental laboratories should use training courses that include, as a minimum, the following components. See Appendix X1 for an example of a training course employing these elements.

6.2 *Training Objectives*:

6.2.1 Each method or procedure for which training will be conducted must have a set of objectives;

6.2.2 Each objective should deal with specific aspects of the training process that require a demonstrated response; and,

6.2.3 An objective should be written to include the following components:

6.2.3.1 A statement of the desired result of the training. This statement will often take the following form: "After completing this training course on (specific topic), the trainee will be able to (specify result)." The specified result may be as simple as a new appreciation for the topic or the more difficult development of a specialized skill or the complex ability to perform problem solving activities.

6.2.3.2 A statement of the way in which the expected result will be demonstrated needs to be made. This might include discussion with a trainer, completing a written exercise, demonstrating a skill, or performing an operation without assistance. This statement should be very specific both for the trainee and the trainer. Ambiguity may lead to significantly different expectations and make the training process less effective.

6.2.3.3 A statement of the expected level of performance of the result detailed in 6.2.3.2. For discussions this may be more subjective and left up to the discretion of the trainer. For written exercises this can often be stated as the number of correct responses (7 out of 10) or as percentage of an expected score (80 %). For demonstration of skills it may be the performance on a sample of known composition within specified limits (80 to 120 % of true value).

6.3 *Performance Evaluation Tools*:

6.3.1 After a set of objectives has been formulated that clearly defines the goals of the training exercises, the tools necessary to measure the success of the training must be prepared. Often the development of these performance evaluation tools will aid in refining the objectives formulated in 6.2.

6.3.2 These tools should be carefully designed to measure exactly what has been defined in the objectives. For example, if the training objectives require the trainee to have a general knowledge of a process, a written exercise should not include a detailed discussion of that process. If the objective requires a complicated skill to be mastered, anything less than having the trainee perform that skill successfully will demonstrate inadequately the trainee's competence.

6.3.3 Performance evaluation tools must be prepared so that the trainee can use them for demonstrating competence without ambiguity or confusion.

6.3.3.1 Written exercises must be clear in their direction. Any questions must be worded in such a way that the desired response will be easily recognized by a properly trained individual.

6.3.3.2 Exercises requiring the demonstration of skills must be explicit in their directions. Any supplies or equipment called for must be readily available. Any hazards associated with the procedure must be clearly stated.

6.4 *Detailed Outline*:

6.4.1 Once objectives and performance evaluation tools have been selected, a detailed outline of each aspect of the process being trained must be developed. The development of this outline will help refine the performance evaluation tools indicated in 6.3. Much of this outline will be based on the task analysis (see 5.3). In all cases this outline must focus on accomplishing the stated objectives and providing a result that can be measured.

6.4.2 This outline should contain the general topics of:

6.4.2.1 Overview of task to be accomplished,

6.4.2.2 Definitions and terminology,

6.4.2.3 Theoretical considerations,

6.4.2.4 Safety issues,

6.4.2.5 Operational details,

6.4.2.6 Quality assurance,

6.4.2.7 Reference materials,

6.4.2.8 Documentation requirements,

6.4.2.9 Maintenance procedures, and,

6.4.2.10 Troubleshooting.

6.4.3 The amount of detail included with each of these topics will depend on the complexity of the procedure identified in the task analysis. Some topics may have only one or two items requiring training. Others may have much longer lists with several subheadings. Procedures involving modern computer driven equipment may require more detailed outlines than those processes involving only manual operations. Explicit SOPs in these areas can also reduce the amount of detail necessary in the outline.

6.5 *Documentation Form or Checklist*:

6.5.1 Following the completion of a detailed outline, develop a form to document the completion of items listed on the outline and to record the results of the performance evaluation.

6.5.2 A straightforward way of preparing this form is to use the major headings from the outline. Since this form also could be used as a training checklist, one may want to go into more detail. Space for recording the scores of oral or written examinations, or both, and performance on skills-based exercises should be customized to each task.

6.5.3 This form should have spaces to be initialed by both the trainer and the trainee and dated to show that both parties involved are in agreement as to the status of the training process. Following the completion of each item on the form or checklist and the performance evaluation, a formal statement describing the level of competency should be signed and dated by both the trainer and trainee.

6.5.4 Failure to reach agreement on the successful completion of a training element may require the intervention of a supervisor. Not everyone being trained for a particular process may be able to meet all the criteria successfully and should be considered for alternate job assignments. The standard of success should not be set at a level exceeding that necessary for the job in question.

6.5.5 All forms and scores should be placed in the individual's training or personnel file.

6.6 *Supplementary Material*:

6.6.1 Whenever a method or procedure requires information not readily available in SOPs, method manuals, or instrument operational materials, supplementary materials should be supplied.

6.6.2 These materials may consist of published textbooks, journals, etc., or information prepared specially for this training exercise. Enough information should be provided to allow the trainee to understand the method or procedure being taught. One should resist the temptation, however, to make the training course an end in itself, losing sight of the ultimate goal of an analyst performing competently.

6.6.3 These materials also may include regulatory information that gives a background for the use of an analytical method. Knowing how the results are going to be used can often emphasize the importance of performing an analysis properly.

7. Trainers

7.1 *Identification of Trainers*:

7.1.1 Trainers should meet the minimum qualifications as follows:

7.1.1.1 Demonstrated competence in method or process to be trained;

7.1.1.2 Education necessary to understand and explain the concepts involved in the method or procedure;

7.1.1.3 Ability to communicate effectively. Depending on the training needs this may require writing skills, speaking skills, or the use of other creative means to communicate concepts and activities to the trainee;

7.1.1.4 Ability to be objective;

7.1.1.5 Understanding of the training program may require training sessions for the trainers in the philosophy, goals, and practices of the training program. Trainers who are able to perform the activities outlined in this guide become more useful in assisting the ongoing development of a successful program;

7.1.1.6 Willingness to put forth the effort necessary to see that the trainee follows through to the completion of the training; and,

7.1.1.7 Sensitivity to the needs of the trainee and a willingness to adapt to meet those needs. Many of those needs will depend on a trainee's learning style.

7.1.2 In addition to those items listed in 7.1.1, effective trainers should also exhibit the following general characteristics:

7.1.2.1 Interest in training,

7.1.2.2 Be a positive role model,

7.1.2.3 Be considerate of others,

7.1.2.4 Be comfortable with people,

7.1.2.5 Be willing to listen, and,

7.1.2.6 Be a problem solver.

7.2 *Training of Trainers*:

7.2.1 If available, effective trainers should be aware of and use the following:

7.2.1.1 Leadership techniques,

7.2.1.2 Proper training techniques,

7.2.1.3 Learning styles and evaluation techniques, and,

7.2.1.4 Concepts of interpersonal relationships.

7.2.2 Effective trainers should be familiar with resources that can aid in the training process. These may include:

7.2.2.1 Standard operating procedures (SOPs),

7.2.2.2 Published methods,

7.2.2.3 Instrument manuals,

7.2.2.4 Reference materials, including books and audio or video tapes, and,

7.2.2.5 Training courses and seminars.

7.2.3 Trainers should be committed to the concepts of training and regularly participate in classes, workshops, seminars, or trade journals to improve their own effectiveness.

7.2.3.1 Many of the concepts listed in 7.2.1 may be unfamiliar to technically trained individuals. Each trainer should become familiar with these concepts through organized sessions designed to develop these skills relative to the specific training needs of the laboratory.

7.2.3.2 Technical improvement also should be encouraged among trainers. As they become more comfortable with new concepts, it will give them more confidence with the trainee.

8. Retraining

8.1 Once an individual has completed a training course and has demonstrated competency, one should be certified to perform that job for a specified period of time. Periodic review of the individual's performance should indicate the need for any additional or remedial training. If a deficiency exists, immediate action should be taken to retrain in the areas of the deficiency.

8.2 If no deficiencies are noticed over an extended period of time, for example, one year, a formal process should be in place that requires an updated set of performance data be placed in the individual's training personnel file.

8.2.1 These data may be from routine performance evaluation samples run by the laboratory.

8.2.2 If a specific set of performance evaluation tools is used to determine continued competency, the individual must be notified of the need to complete it and the required proficiency and time frame.

8.2.3 If a deficiency is noted based on any of the tools specified in 6.3, retraining should be instituted until competency can again be demonstrated.

9. Storage of Training Materials

9.1 It is recommended that the master copy of all training materials be stored in a central location. It should be available for copying and distribution at all times, but it should not be used for routine training purposes. This master file may be electronically maintained.

9.2 As new materials are prepared, they should be distributed to the appropriate trainers and the master copy placed in the central storage location.

10. Responsibilities

10.1 *Preparing Training Materials*:

10.1.1 Anyone can prepare training materials in accordance with Section 6.

10.1.2 All materials should be reviewed and approved by someone competent in the method or process and by someone familiar with the training program and its requirements. Only materials meeting both sets of requirements should be used.

10.1.3 In some laboratories, a full-time position may be created with responsibility for developing training materials, including performing the task analyses, writing the objectives, developing the evaluation tools, the training outline, the documentation form, and assembling supplementary material.

10.2 *Using the Training Materials*:

10.2.1 It is the responsibility of the laboratory management to assure that each individual within the laboratory receives the training necessary to competently perform one's job function.

10.2.2 It may be desirable to designate the QA department or a designated training director to monitor the training progress and notify individuals of their need for retraining.

10.2.3 Laboratory management should be provided with regular reports on the progress of training within the laboratory. Many organizations may want to establish training goals to keep everyone's focus on the need to improve.

11. Keywords

11.1 environmental laboratories; guide; training

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE TRAINING COURSE—MEASUREMENT OF pH

X1.1 *pH Electrometric Methods Objectives*—After the completion of training for pH electrometric measurement-Tables X1.1-X1.4, the trainee should be able to:

X1.1.1 Explain the use of pH in sample testing and demonstrate proficiency by achieving a minimum score of 80 % on a written or oral evaluation to be given by the trainer;

X1.1.2 Perform a pH test measurement on a given sample of known pH with a ±0.05 unit error;

X1.1.3 Use the pH meter according to the manufacturer's manual to analyze a batch of samples, meeting the stated criteria of the SOP including quality control (QC) and any written documentation; and,

X1.1.4 Troubleshoot problems commonly encountered with a pH meter and various sample conditions.

X1.2 *Supplemental Reading for pH*—pH is a convenient measure of hydrogen ion concentration. Specifically, it is defined as the logarithm of the reciprocal of the hydrogen ion concentration, expressed in molarity. Thus a 10^{-3} M solution of hydrogen ions has a theoretical pH of 3. A 10^{-9} M solution has a theoretical pH of 9. Since the pH scale is logarithmic, a change of 1 pH unit means a ten-fold change in hydrogen ion concentration. A pH change of about 0.3 means a two-fold change in hydrogen ion concentration.

X1.2.1 The definition of pH is based on the dissociation of water, which produces hydrogen ions and hydroxide ions.

$$H_2O = H^+ + OH^-$$

Pure water has equal concentrations of hydrogen and hydroxide ions and a pH of 7. Solutions with a pH of 7 are called *neutral*. Solutions with excess hydrogen ions have a low pH and are *acidic*. Solutions with excess hydroxide ions have a high pH and are *basic* or *alkaline*.

X1.2.2 *Occurrence—Natural, Anthropogenic*—Carbon dioxide is the principal corrosive agent in natural water. It dissolves in the water to produce carbonic acid, which lowers the pH. Equilibrium between rainwater and atmospheric carbon dioxide results in a pH of about 5.7. Deionized water in the laboratory also often has a pH near this value. As rainwater infiltrates the soil, the low pH causes minerals such as limestone to dissolve. This tends to raise the pH to higher values. Unpolluted surface waters normally lie in the pH range 6.5 to 8.5. There are many factors, however, which may change the pH. Oxidation reactions (those which consume oxygen) generally lead to a decrease in pH. This can be observed in the bottom parts of deep lakes where reduction reactions such as photosynthesis, denitrification, and sulfate reduction tend to raise the pH. Photosynthesis can result in diurnal (day/night) pH changes, reaching to a pH of 9 or even 12 in poorly buffered waters. Algae and other microorganisms break down carbonate and bicarbonate when there is no other source of carbon dioxide. This also results in an increase in pH. Evaporation can affect the pH. Basins without outlets may accumulate alkaline substances resulting in pH greater than 12.

X1.2.2.1 Most groundwaters in the United States have a pH of 6.0 to 8.5, but water with lower pH is not unusual in thermal springs and in waters affected by sulfur oxidation. Groundwater unsaturated with respect to calcium carbonate (limestone) causes caves to form.

X1.2.2.2 Rain will absorb gases other than carbon dioxide. In particular, sulfur dioxide and nitrogen oxides are common air pollutants produced as by-products of the combustion of fossil fuels. These gases will dissolve in rain to form sulfuric and nitric acids. This causes very low pH and the phenomenon is known as *acid rain*. Acid rain with a pH of less than 2 has been measured.

X1.2.2.3 In areas with little or no limestone, the water remains acidic unless there are other minerals present that are capable of neutralizing the acid. In areas susceptible to acid rain, such as the Northeast United States and Scandinavia, lakes and streams can easily have pH below 4.5.

X1.2.2.4 All acids will release hydrogen ions in water and all bases will consume hydrogen ions. The pH of natural waters, therefore, can be affected by leaks and spills of industrial chemicals, as well as by the discharge of improperly treated wastes. Examples include discharges from the timber and wood industry, pulp and paper mills, acid mine drainage (for example, from coal mines), and pickling liquors from steel mills. Many natural systems will contain a certain buffering capacity, which means that, unless excess of certain chemicals occur, the system tends to resist changes in pH. *Buffering* will

- I. Reading
  - A. Objectives for training
  - B. SOPs
  - C. Methods
    - 1. SW846 Method 9040 and 9045
  - 2. EPA Method 150.1
  - D. Instrument Manual
- II. Theory of Operation
  - A. Basic understanding of pH. Use the supplemental material that has been provided.
  - B. Instrument
  - 1. How it detects
  - 2. Why it is used rather than titration, pH paper
  - C. Buffers
    - 1. Definition
  - 2. Use in calibration
  - D. Use of pH in the laboratory
  - 1. As a parameter
  - 2. Use for other parameters
    - a. Leaching/extracting procedures
    - b. Acidity procedures
    - c. Alkalinity
    - d. Where pH will interfere with analyses
- III. Safety
  - A. Safety wear
  - 1. Laboratory coat
  - 2. Safety glasses
  - 3. Disposable gloves
  - B. Sample handling
  - C. Instrument
- IV. Procedures
  - A. Instrument operation
  - 1. Set-up
  - 2. Function keys
  - 3. Calibration
  - B. Buffer usage
  - 1. Initial calibration
  - 2. Continuing calibration
  - C. Sample preparation
  - 1. Waters
  - 2. Soils
      - a. Calcareous
  - b. Non-calcareous
  - D. Sample analysis
  - 1. Calibration
  - 2. Run order
  - 3. QC and control limits
  - E. Documentation
  - 1. Logbook
  - 2. Standards log
- V. Quality Control (QC)
  - A. Theory
  - B. QC elements
  - 1. Initial calibration
  - 2. Continuing calibration
  - 3. Duplicates
  - C. Reporting
  - 1. Standards logbook
  - 2. Calibration
- VI. Detection limits
  - A. Instrument
  - B. Reporting
- VII. Troubleshooting
  - A. Meter
  - 1. Programming
  - 2. Connections
  - B. Electrodes
  - 1. Temperature probe
  - 2. pH probe
  - 3. KCl solution
  - C. Matrix problems
  - 1. Oily materials
  - 2. Particulate matter
  - 3. Alternate method(s)
- VIII. Maintenance
  - A. Cleaning
  - 1. Probes
  - 2. Instrument

FIG. X1.1 pH Electrometric Method Training Outline

Name: ____

Description of Method or Process: pH—Electrometric Method

Start of Training: ____

Completion of Training: ____

Trainer(s): ____

	Completion Date	Trainer's Initials	Trainee's Initials
I. Reading/References			
A. Objectives for Training			
B. SOP(s)			
C. Method(s)			
D. Instrument Manual			
II. Theory			
A. Understanding of pH			
B. Instrument			
C. Buffers			
D. Use of pH in the Laboratory			
III. Safety (Method Specific)			
A. Safety Wear			
B. Sample Handling			
C. Instrument			
IV. Procedures			
A. Instrument Operation			
B. Buffer			
C. Sample Preparation			
D. Sample Analysis			
E. Documentation			

IX. Competency Demonstration
- A. Written/Oral Evaluation explaining the use of pH (80 %) (Objective #1)
- B. Three Performance Evaluation Scores with ±0.05 pH unit error (Objective #2)
- C. Complete Batch Analysis (Objective #3) (Includes all quality control samples, data entry, scheduling)
- D. Troubleshooting (Objective #4)

I certify that _____________ (name of trainee) is competent to perform pH—Electrometric Methods

___________________________ ___________________________

Trainer Date

I acknowledge that I have been trained in pH—Electrometric Methods and I feel adequately prepared to perform the above procedure(s)

___________________________ ___________________________

Trainer Date

	Completion Date	Trainer's Initials	Trainee's Initials
V. Quality Control			
A. Theory			
B. Quality Control Elements			
C. Reporting			
VI. Detection Limits			
A. Instrument			
B. Reporting			
VII. Troubleshooting			
A. Meter			
B. Electrodes			
C. Matrix Problems			
VIII. Maintenance			
A. Cleaning			

FIG. X1.2 Sample Competency Training Checklist/Documentation Form

1. How is pH defined? (2 pts.)
2. What significance does pH have in the laboratory? (3 pts.)
3. What is the usual numerical range for pH? (2 pts.)
4. How is the pH meter calibrated? (4 pts.)
5. What safety precautions are needed to perform a pH test? List three. (3 pts.)
6. What may cause an incorrect pH reading? List two. (2 pts.)
7. What are three common interferences when testing pH? (3 pts.)
8. What is a buffer and what is it used for? (2 pts.)
9. Define calcareous (2 pts.)
10. When would the pH meter need to be recalibrated? List at least two. (2 pts.)
11. At what pH should most electrodes be stored? (1 pt.)
12. After how many samples should a continuing calibration verification (CCV) be run? (1 pt.)

FIG. X1.3 Sample pH—General Evaluation (27 pts.)

1. pH is the measurement of hydrogen ion concentration.
2. It measures how much acidity or basicity a substance has in a water solution.
3. 0–14
4. By using a 2 point calibration made of two buffers and checked against a third buffer.
5. Electricity if using the electrometric methods, proper clothing, care in sample-handling.
6. Poor calibration, buffer contamination, bad electrode, temperature, KCl solution low, or a clogged reference electrode junction.
7. Oily matrices, high salinity, particulate matter.
8. A solution that controls pH at a specific level.
9. Solids that contain limestone.
10. If a buffer doesn't read correctly, or when it has been turned off.
11. 7
12. After every twenty samples.

Trainer's Use Only

PERFORMANCE SAMPLE EVALUATION SUGGESTIONS FOR pH

Water sample A (Electrometric)	4.88
Soil sample A (Electrometric)	11.44
Water sample B (Paper)	7.0

FIG. X1.4 Sample Answers to pH Evaluation (For Trainer's Use Only)

be discussed further in a later section.

X1.2.3 *Health and Environmental Significance*—Extremes of pH are toxic to plants, animals, and microorganisms. Damage to surface structures results and low pH inhibits enzyme activity. A pH between 6.5 and 9.0 is generally considered to be safe. A pH less than about 3.5 or greater than about 11 is lethal to most fish species. Some species, such as trout and salmon, are very sensitive and can be harmed by pH below 6 or above 9. Another consequence is that biological treatment of wastes is difficult or impossible without the proper pH.

X1.2.3.1 Sudden changes in pH can also have harmful effects, even if the pH always remains within safe ranges. Small changes in pH can result in a competitive advantage for some species and their eventual domination over others that were originally present in the system. Large changes in pH can cause total destruction of fish and other populations.

X1.2.3.2 Chemical speciation is highly dependent on pH. For example, unionized ammonia is present at alkaline pH and ammonium ion is present at lower pH. Ammonia is much more toxic than ammonium ion, so that even a moderate increase in pH can result in greatly increased toxicity. Complexation of metals by agents such as hydroxide, chloride, sulfate, bicarbonate, and fluoride is also affected by pH. At low pH, the free metal ions are usually present. As the pH increases, various complexes begin to form. The free metal ions are usually much more toxic than the complexes. The toxicity of metals, therefore, depends on pH. Low pH can also displace trace metals from adsorption sites on soil and sediment particles, leading to increased toxicity.

X1.2.3.3 Extremes of pH are irritating to the skin (such as bathing, swimming) and produce undesirable effects on food and beverages. Water with a low pH maybe corrosive to pipes and other fixtures.

X1.2.4 *Other Effects*—Proper pH is important in many waste treatment processes. Biological treatment depends on the health of various microorganisms, which are sensitive to pH. Metals are typically removed from waste streams by precipitating them as hydroxides. Maximum precipitation of metals is usually obtained if the pH is about 8.0 to 8.3. If the pH is too low or too high, then removal is less efficient; the metals redissolve at either extreme.

X1.2.4.1 The pH affects many chemical reactions. For example, reduction of hexavalent chromium to trivalent chromium occurs rapidly at low pH, but not at high pH. Many chemical processes used in industry depend on tight control of pH, since the chemical reactions they utilize proceed slowly or not at all if the pH is incorrect.

X1.2.5 *Regulatory Limits*—The pH of wastewater discharges is regulated under the United States Environmental Protection Agency (USEPA) Clean Water Act; the limits are usually 6.0 to 9.0. A secondary drinking water standard of 6.5 to 8.5 has been established for drinking water supplies. As a result of concern over acid rain, controls on sources of sulfur dioxide and nitrogen oxides have been proposed. pH is used under United States Resource Conservation and Recovery Act (USRCRA) regulations as one definition of corrosivity and is also one of the "indicator parameters" used in groundwater monitoring.

X1.2.6 *Analytical Methods*—The most common way of measuring pH is with an electrode. The electrode suffers from sodium effect at high pH. Samples with low ionic strength will cause sluggish response. The electrode is also temperature sensitive. It may also become coated with oil and greases destroying its sensitivity to pH.

X1.2.6.1 There are also various indicators that can be used to measure pH. These are organic dyes that change color in response to changes in pH; they can be used in liquid form or impregnated into absorbent strips. Although they are convenient to use, indicators are less accurate and are subject to numerous interferences. The electrode method is most accurate and is the method preferred by most laboratories.

X1.2.6.2 It should be noted that pH measurements are usually meaningful only for aqueous solutions; nonaqueous samples are first extracted with water using defined phase ratios and the pH of the resulting extract is measured. Dilution effects must be taken into account when interpreting the data.

X1.2.6.3 Also, the pH will change in a sample after collection due to chemical changes that occur when the water is removed from its environment. These include oxidation/reduction reactions, biological processes, and equilibration with atmospheric carbon dioxide. A change in pH of 1 unit or more between the field and laboratory is not unusual. The pH measured in the laboratory will almost certainly be different than the pH at the time of sampling.

X1.2.7 *Notes on pH*—From the definition of pH and the equilibrium constant for dissociation of water, it can be shown that:

$pH + pOH^- = 14$
or
$[H^+] \times [OH^-] = 1 \times 10^{-14}$ assuming that ion activity equals concentration.

X1.2.7.1 It is defined for aqueous system only. Although it is entirely possible to speak of hydrogen ion concentration in nonaqueous solvents, many of the conventional wisdoms do not apply. For example, neutral pH is defined as the point where $[H^+]$ and $[OH^-]$ are equal. In aqueous systems, this is pH 7 (based on the ion product of water). For nonaqueous systems, this may not be true. It is also difficult to measure pH in nonaqueous systems.

X1.2.7.2 The pH scale is logarithmic. A change of 1 pH unit means a ten-fold change in hydrogen ion concentration. A pH change of about 0.3 means a two-fold change in hydrogen ion concentration.

X1.2.7.3 *pH Electrode*—A pH electrode is constructed from specially made glass (for example, lithium silicates doped with lanthanum and barium). These types of glass have active sites that are selective almost exclusively for hydrogen ions. In a typical electrode, a thin-walled bulb of pH-sensitive glass is sealed to a thick-walled stem of non-responsive glass. This is to prevent complications arising due to changes in the depth of immersion of the electrode.

X1.2.7.4 The bulb of the pH electrode is filled with a constant pH buffer solution (usually pH 7), which is in contact with an internal solid electrode. This is connected in turn to a lead that can be connected to the pH meter.

X1.2.7.5 Hydrogen ions in the internal buffer solution diffuse into the inner surface of the glass membrane and eventually reach an equilibrium. Hydrogen ions in the sample diffuse into the outer surface of the membrane and reach a separate equilibrium. If the sample has a lower pH than the filling solution, the outer surface will have more hydrogen ions than the inner surface. If the pH is higher than the internal solution, there will be fewer hydrogen ions on the outer surface. This results in a voltage across the membrane that depends on the concentration of hydrogen ions in the sample.

X1.3 *Importance of pH:*

X1.3.1 *Natural Waters*—The most important buffering system in natural waters is that formed with carbonic acid (carbon dioxide), bicarbonate, and carbonate. In this system, carbonic acid is the predominant form present below about pH 4.5. Between 4.5 and 8.3, predominant form is bicarbonate. Above pH 8.3, it is carbonate.

X1.3.2 Water exposed to the atmosphere will absorb carbon dioxide and the following reactions occur:

$$H_2O + CO_2 \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2}$$

These reactions lower the pH of the water. Water in equilibrium with atmospheric carbon dioxide will have a pH of about 5.6, depending on temperature, atmospheric pressure, and other factors. Thus, rain is naturally slightly acidic.

X1.3.3 When rain falls and comes into contact with minerals in the soil, these minerals begin to dissolve. Limestone, which is a form of calcium carbonate, is a common mineral and neutralizes the carbonic acid in rain water.

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{+2} + 2HCO_3^-$$

This is the mechanism by which caves are formed.

X1.3.4 *Acid Rain*—Rain will also absorb other gases; in particular, sulfur dioxide and nitrogen oxides are common pollutants and dissolve in rain to produce acid rain. Examples of these reactions are:

$$2H_2O + 2SO_2 + O_2 \rightarrow 2H_2SO_4$$
$$NO_2 + NO + H_2O \rightarrow 2HNO_2$$
$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Acid rain with a pH of less than two has been measured. In areas with little or no limestone, the water remains acidic unless there are other minerals present that are capable of neutralizing the acid present. With little limestone, lakes and streams can easily have pHs below 4.5. Areas particularly vulnerable to acid rain include the Northeast United States and Scandinavia.