DQM Information Paper 3.1.4
Acidity (pH) Measurement Principles and Methods

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1.0 About this Information Paper

(This section is essentially common to all DQM Information Papers. If you have seen it already, please skip to Section 2 below). This Information Paper is a new type of guidance. It has been created for our new integrated system of guidance and tools for water quality monitoring called "the Data Quality Management (DQM) System". DQM is implemented by the Clean Water Team (CWT) where needed to support collection of **reliable** data of **known quality** in a fully documented, **scientifically defensible** manner. Most DQM materials are delivered in Parameter-Specific Folders, which provide both the traditional "protocol" materials and new, expanded guidance in three types of inter-related documents: Fact Sheet, Information Paper, and Standard Operation Procedures. Background information on the ecological significance of each parameter and the regulatory benchmarks that have been developed for it is summarized in the FACT SHEET. The technical information on measurement methodology provided in this IP with its method-menu. Then there are several detailed standard operating procedures (SOPs) that provide step-by-step instructions for each instrument or kit, as well as instrument-specific Quality Assurance/Quality Control and CCRR directions and data validation checklists.

This Information Paper (IP), a part of the Parameter-Specific Folder for pH, provides "big picture" technical information on pH measurement methodology. If you are a Trainer or a Technical Leader of any monitoring project, this may help you select a good method to measure pH in your water body.

Section 2 of this IP introduces a "method menu" table with a list of kits and instruments commonly used by citizen monitoring groups, agency staff, or laboratory technicians, with information on the limitations, approximate cost, measurement range and resolution, and associated labor of each device. Next (Section 3), a description of the different physical or chemical principles underlying the commonly used methods to measure pH is provided. Section 4 provides practical tips and advice on pH measurements, calibration, and Standard Buffers; this information is based on our cumulative experience (The Clean Water Team and others). This section is meant to be updated as we learn more. Finally, the "Sources & Resources" section (Section 5) provides a list of available SOPs as well as contact and website leads into further information.

2.0 Ways to Measure pH

Table 3.1.4-1 provides a lead into the major types of commonly used methods for measuring pH; it cannot include all available kits and instruments and the user is encouraged to seek more information. You can look at it for selection of a device based on available resources and operators' skill, e.g., during the initial phases of your group's monitoring activities.

Table 3.1.4-1: Selected Methods and Devices for Field Measurements of pH

Code *(Note a)*	Device	Range	Resolution (pH units)	Cost	Labor	Limitations	Extent & Sources of Error (pH units)
PHLQ	Liquid pH kit	2-10	2	$4 /50 tests	2 min	Daylight only	±2; Aging of indicator
PHLQ	Liquid pH kit	5-10	0.5	$8 /50 tests	2 min	Daylight only	±1 Aging of indicator
PHST	Universal pH strip *(Note b)*	1-14	1	$12 /100 tests	3 min	Daylight only	±1 Aging of indicator, slow response
PHST	"Environmental" pH strip *(Note b)*	5-10	0.5	$12 /100 tests	3 min	Daylight only	±0.5 Aging of indicator, slow response
PHST	"Physiological" pH strip *(Note b)*	6.5-10	0.3	$12 /100 tests	3 min	Daylight only	±0.3 Aging of indicator slow response r
PHEL	Pocket meter with dry electrode	1-14	0.1	$60	10 min cal, 3 min measure	Need to rehydrate	±0.3 Standard buffer drift, slow response
PHEL	Multi-meter pH probe	1-14	0.1	variable	10 min cal, 3 min measure		±0.3
PHP	Sonde/datalogger probe	1-14	0.01	~$4,000 for entire Sonde	10 min cal, 3 min measure		±0.1

Notes: (a) The Codes on the left are consistent with the Instrument codes used in all other DQM materials
(b) Litmus papers impregnated with (unbound) pH indicators are NOT suitable for measurements of pH in environmental samples.

Once you have formulated the monitoring question, decided which parameters you need to measure, developed your sampling design, and determined how much error you can tolerate in your measurements, you can refer to this menu again and find the device that will work for you.

3.0 Principles and Applications of pH Measurement Methods

Materials dissolved in water confer acidic or basic reaction to the water, depending on the balance between different substances. The extent of reaction is expressed by the pH scale, which is a derivative of the concentration of hydrogen-ions (H+, or "protons"; in fact, the pH value is the negative decimal logarithm of proton concentrations). In the "molecular reality", the pH value reflects the balance between acidic and basic materials present in the water: the lower the value, the higher the acidity. Low pH value in the range of 0 to 7 represent acid conditions, pH 7 is neutral, and solutions with a pH value of above 7 are basic. pH values can be measured by pH electrodes. pH conditions can also be gleaned from the response of special color indicators (see below) . As mentioned above (Section 2), there is an assortment of methods and the "method menu" table (Table 3.1.4.1) is intended for use as a selection tool in response to the specific needs, measurement quality objectives, level of operator skill, and safety concerns of each individual Project. The principles of the methods listed are described below.

3.1 Indicators

Many organic pigment molecules are pH INDICATORS: they change their color in response to the balance between acidic and basic materials present in the water (for example, tea changes color in response to addition of lemon). A myriad of pH Indicators that are sensitive to minute shifts in the balance have been selected or synthesized for different ranges of pH, and they are used in a variety of combinations. Each combination used in a commercial kit has created a color scale that has been correlated with the numerical pH values by the kit manufacturers, so the color hue "translates" to numbers – pH values – that are reported as the measurement Result (and are compatible with measurements made by electrodes). The most commonly used are soluble indicator kits and color-fast indicator kits.

Soluble indicators are used in **Liquid pH kits (DQM code PHLQ),** which are comprised of mixtures of indicators in concentrated solutions. The concentrate is added to a water sample and the resulting color is compared to a color scale that "translates" the color to pH units. They are also used in some litmus papers made of absorbent paper impregnated with indicator – which bleeds out when wet. These types of "non-linked", or "bleeding" litmus papers are useful only with strong acid and bases (i.e., in chemistry labs) and are NOT suitable for environmental samples. Therefore, they are not included in the menu table as an option for water monitoring. Liquid pH kits providing various ranges and resolution are available in aquarium stores or from vendors of monitoring equipment. When shopping for a PHLQ kit make sure that the color panels, or gradations, vary in hue (and not merely in intensity of the same hue).

Colorfast indicator strips (non-bleeding pH strips, **DQM code PHST**) are made of absorbent paper to which the indicator molecule has been linked by a chemical bond, and does not "leave" when wet. These strips are good for measuring pH in environmental samples, and are available at a variety of pH ranges

3.2 pH Electrodes

A pH electrode is made of metal wires in a glass tube, filled with electrolytes. The wires have a semi permeable connection to the "outside" and can sense differences in proton concentration inside and out; this difference is translated to pH units. The electrode always works in a liquid environment; however there are "dry" pH electrodes that can be stored without liquid and those are often used for field work. Because the salts may form a hard crust on the semi-permeable connection area upon prolonged dry storage, it is mandatory to rehydrate these electrodes before use (i.e. soak in water till the electrode responds properly; please see SOP-3.1.4.3 for more detail; see section 5 and pages following).

4.0 General pH Measurement Tips

4.1 Quality "Control, Check, Record, and Report" (CCRR) guidance for pH

(This paragraph is essentially common to all DQM-IPs. If you have seen it already, please skip to the second paragraph in this Section) The DQM guidance and tools provide ways to "Control, Check, Record, and Report" (CCRR) the quality of numerous water quality measurements. Essentially, **"Control"** is about things we can do to affect and improve data quality. **"Check"** is about testing how good a measurement actually is. **"Record"** is about the language we use to express the results of our quality checks and about entering our findings into the "placeholders" on DQM forms or spreadsheets. **"Report"** is about the way we calculate the measures of quality, i.e., the data quality indicators, so they can be shared with others. Specific CCRR procedures are added on top of the generic quality assurance procedures such as keeping everything clean, waiting for stabilization of the reading, and keeping good records. Because each type of instrument or kit requires its unique CCRR actions (that cannot be generalized for all measurement devices), the step-by-step instructions for these actions are provided in the instrument-specific standard operating procedures (SOP).

As far as pH measurements are concerned, we can control – i.e., diminish - the measurement error for all methods by using the right kind of Standard buffer for accuracy control or accuracy checks (see section 4.2 below). However, there is a basic difference between pH indicators and pH electrodes in the way we control accuracy: we can adjust the reading of a pH electrode but we cannot tweak the output of an indicator kit. To diminish and quantify electrode error, it is recommended to calibrate pH electrode often, and to record the reading **both before and after** calibration (so we know how much the electrode had drifted from the calibrated state while we were doing our measurements). Many groups now calibrate it before and after a sampling event. To diminish pH indicator error, it is essential to protect the indicator solutions and comparator color charts from direct sunlight, because that kind of radiation destroys pigments. To quantify pH indicator error, it is recommended to conduct accuracy checks often, using a colorless Standard Buffer (see section 4.3 below). If a pH kit that employs an indicator is found to be "off", it should be discarded. Under desperate situations the user may record how far off it was from the Standard value and correct the data for that bias.

4.2 All about Standards and NIST-traceable (Certified) Standards

(These four paragraphs are common to other Parameter-Specific DQM IPs that refer to Standard Solutions. If you have seen them already, please skip to the last – fifth - paragraph of this Section). Instrument calibration is adjustment of the output to reflect the reality, as defined by a "Standard". Instrument accuracy checks – done for devices for which you cannot tweak the output – provide for "correction" of the output based on comparison with reality, as defined by a "Standard". In both and all other cases, the accuracy of any measurement depends on the Standard that is used to assess how close the measurement was to the "True Value" (i.e., as close as it gets to the absolute truth. But how do we protect and assess the accuracy of the Standard itself? Standard solutions do change and deteriorate over time.

Another unfortunate fact is that different manufacturers of Standard solutions and buffers sell solutions that sometimes differ in their conductivity or pH value to begin with. The only way to cope with this is to assign a unique Standard ID to each bottle, to carefully document all the information related to that Standard, and to specify the Standard ID when recording instrument calibrations (see DQM Project File for placeholders and SOP-9.2.1.2(Calib) for detailed instructions). It also helps to bring your instruments and "Resident" Standards to regional inter-calibration events (a.k.a. "instrument calibration parties") and compare them with "External" Standards.

We are still left with the question "How do we know which Standard is more accurate?" for which we need to refer to the National Institute for Standards and Technology (NIST), American Society for Testing and Materials (ASTM), and other organizations dealing with Standards. Fortunately, NIST has developed a set of Standard solutions (that everyone refers to as "the truth") and highly-detailed recipes for preparation of these Standards. Today, many Standard manufacturers make Standards that are "NIST-traceable" or ASTM-traceable" by using these recipes to the letter and/or by comparing the batches of solutions they make with Standard solutions distributed by NIST or ASTM. Thus,
"**Certified Standards**" include any Standard that is traceable to NIST or ASTM. Resident and External Standards can all be Certified Standards as well. A Certified Standard is considered the "ultimate authority" if valid, i.e., if the bottle was (a) used before the expiration date; (b) has been stored tightly capped; and (c) has not been exposed to extreme temperatures or other chemicals.

The CWT Coordinators are using Certified Standards when participating in instrument calibration events, and our DQM Project File has placeholders for the NIST or ASTM reference information. Certified (NIST-traceable or ASTM-traceable) Standards can also be purchases directly, but they are more expensive than the generic Standards. Making your own Certified Standards using recipes is a good option only if you have access to a laboratory with analytical balance, Reagent-grade salts, high purity water, and an expert chemist who knows how to handle anhydrous reagents through desiccators & temperature shifts and do the right calculations with formula weights of hydrated salts. Note: Distilled water that is sold in the store usually has trace levels of nutrients and other chemicals.

Standard pH buffers, used for calibration standards are made of different substances for different ranges of pH. Some buffers are made with organic substances; these are less stable and may be subject to microbial degradation once a bottle has been opened. It is very important to protect Standard buffers from exposure to extreme conditions and to use within expiration time. Some monitoring programs are using single-use buffer packages (ampoules or sachets with 20 ml of buffer) to avoid using buffers subject to deterioration after a bottle has been opened.

Note from Southern California Marine Institute reviewers: "A pH buffering system in a solution effectively acts as a "sponge" that absorbs excess acid or base, enabling the solution to resist fluctuations in pH. In natural systems, freshwater has minimal buffering ability. As ions and organic molecules are dissolved in water, the buffering capacity increases. The bicarbonate-borate system is very effective in maintaining a relatively constant pH in ocean waters. The pH usually varies in the ocean surface waters between 7.5 and 8.5 depending on the relative importance of photosynthesis versus respiration. Human blood has a very narrow pH range centered around 7.4 due to the bicarbonate buffering system in blood."

4.3 Manual versus automatic calibration

Calibration (i.e., adjustment of the reading) of a pH meter while immersed in a standard buffer solution is fairly simple, involving turning a calibration screw. Automatic calibration is more complex, and care should be given to assuring that the Standard used indeed has the value that has been specified by the manufacturer.

4.4 Color indicators

As mentioned above, it is possible for the user to calibrate (i.e., adjust the reading of) a pH electrode according to a Standard buffer, whereas pH measurement devices that involve indicators cannot be calibrated in a similar way. However, the Standard buffers are still essential to provide "accuracy check" for the indicator, i.e., to check if it gives the color it is supposed to give. Some buffers are sold with a pigment added to the solution, often color-coded to "label" the liquid for ease of identification or for warning against accidental ingestion. These standard buffers are NOT useful for accuracy checks of indicators because they interfere with the color.

5.0 Sources and Resources

This IP is an integral part of the Data Quality Management (DQM) System implemented by the Clean Water Team, the Citizen Monitoring Program of the California State Water Resources Control Board.

For an electronic copy, to find many more CWT guidance documents, or to find the contact information for your Regional CWT Coordinator, visit our website at www.swrcb.ca.gov/nps/volunteer.html

If you wish to cite this IP in other texts you can use "CWT 2004" and reference it as follows: "Clean Water Team (CWT) 2004. Acidity (pH) measurement principles and methods, DQM IP-3.1.4 (pH). in: The Clean Water Team Guidance Compendium for Watershed Monitoring and Assessment, Version 2.0. Division of Water Quality, California State Water Resources Control Board (SWRCB), Sacramento, CA."

Available SOPs (2004 Compendium)

- DQM-SOP-3.1.4.1 Determination of pH with liquid indicators.
- DQM-SOP-3.1.4.2 Use of non-bleeding pH indicator strips for pH measurements.
- SOP-3.1.4.3 Measuring pH using a pocket meter with "dry electrode".