BECKMAN

Φ™31 pH METER

Beckman Instruments, ullerton, CA 92634
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Φ™ 31 pH METER

BECKMAN INSTRUMENTS, INC., SCIENTIFIC INSTRUMENTS DIVISION, IRVINE, CA 92713

Beckman Instruments, Inc., Fullerton, CA 92634

April 1984 832154 015-246204 Printed in U.S.A.

Warranty

Your Φ™ (pHI™) 31 pH Meter is warranteed to be free of manufacturing defects for one (1) year from the date of purchase. This does not include any defects that are the result of abuse or misuse of the instrument. Beckman Instruments, Inc., will, at Beckman's option, repair or replace your instrument with a comparable unit. This is a limited warranty. You may have additional rights under your state laws.

Writer: R. O. Brace
Art Director: Donald Exelby
Technical Advisors: Lindon Baker, Alice Tanibata, and L. M. Willmott

CONTENTS

Contents serve as a convenient summary of the organization of the instruction manual. For a specific item of interest, please refer to Section Thirteen, Cross Index.

ILLUSTRATIONS

CONTENTS

SECTION ONE INTENDED USE AND GENERAL DESCRIPTION

The Φ™ (pHI™) 31 pH Meter is a precision, digital-display pH meter designed for accurate measurements in a wide range of industrial and biomedical applications. The digital display of this pH meter reads to 0.01 pH unit or to 1 mV. The instrument provides simultaneous digital display of sample or ambient temperature.

NOTE

Read these instructions before operating the instrument.

1.1 INSTRUMENT PACKAGE

The instrument package comprises the pH meter and the following items:

1. Electrode holder and rod.
2. Instruction manual.

Figure 1. pHI 31 pH Meter

SECTION TWO INSTRUMENT SETUP

2.1 UNPACKING INSTRUMENT

Each instrument is packaged to guard against damage during shipment. Carefully inspect the instrument and the items included as soon as they are received.

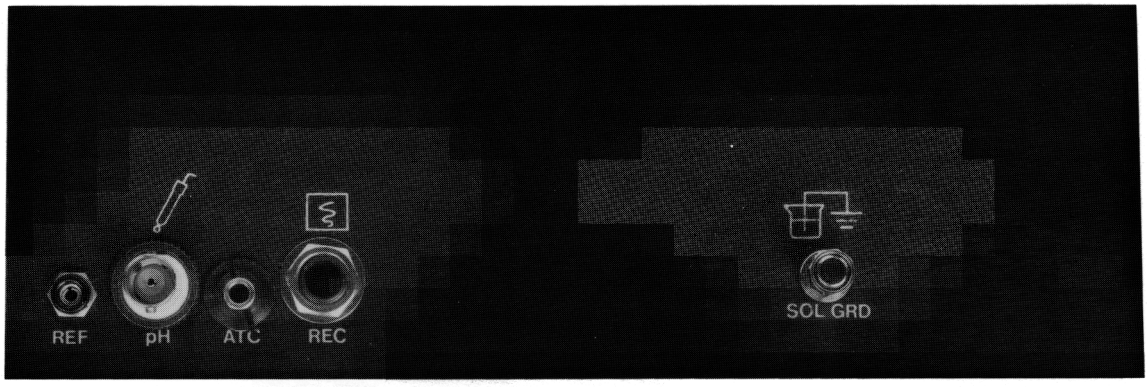


Figure 2. Back Panel of Instrument

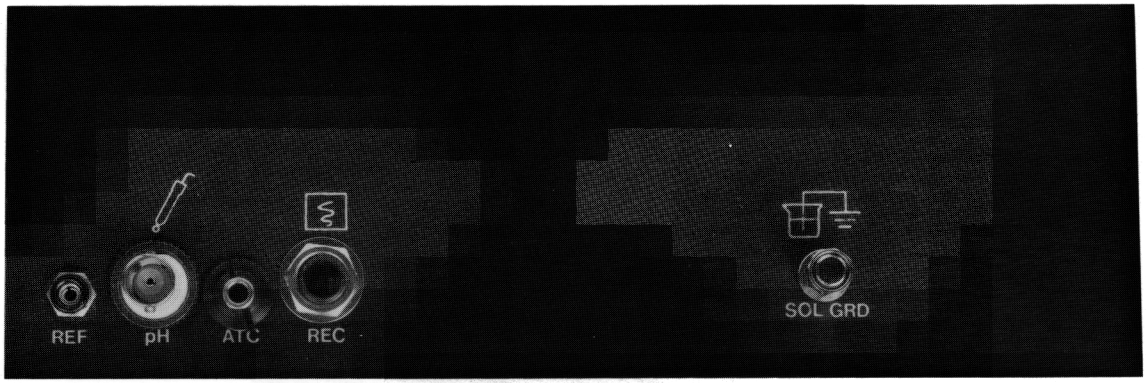
2.2 BATTERY REQUIREMENTS

The instrument is battery-powered by six Size D alkaline cells. Their predicted life is three years under normal use. When the batteries are low, the BATTERY Symbol appears in Display, indicating that the cells should be changed. About 35 minutes after the last depression of a key, the instrument shuts off automatically, thereby extending battery life.

Refer to Figure 3 for battery replacement instructions. When batteries are replaced, be sure to observe the correct polarity.

CAUTIONS

1. *Do not* attempt to recharge batteries.
2. *Do not* dispose of batteries in fire.
   In either case, the batteries may explode or leak.
3. *Do not* substitute carbon-zinc cells. Use only size D alkaline cells



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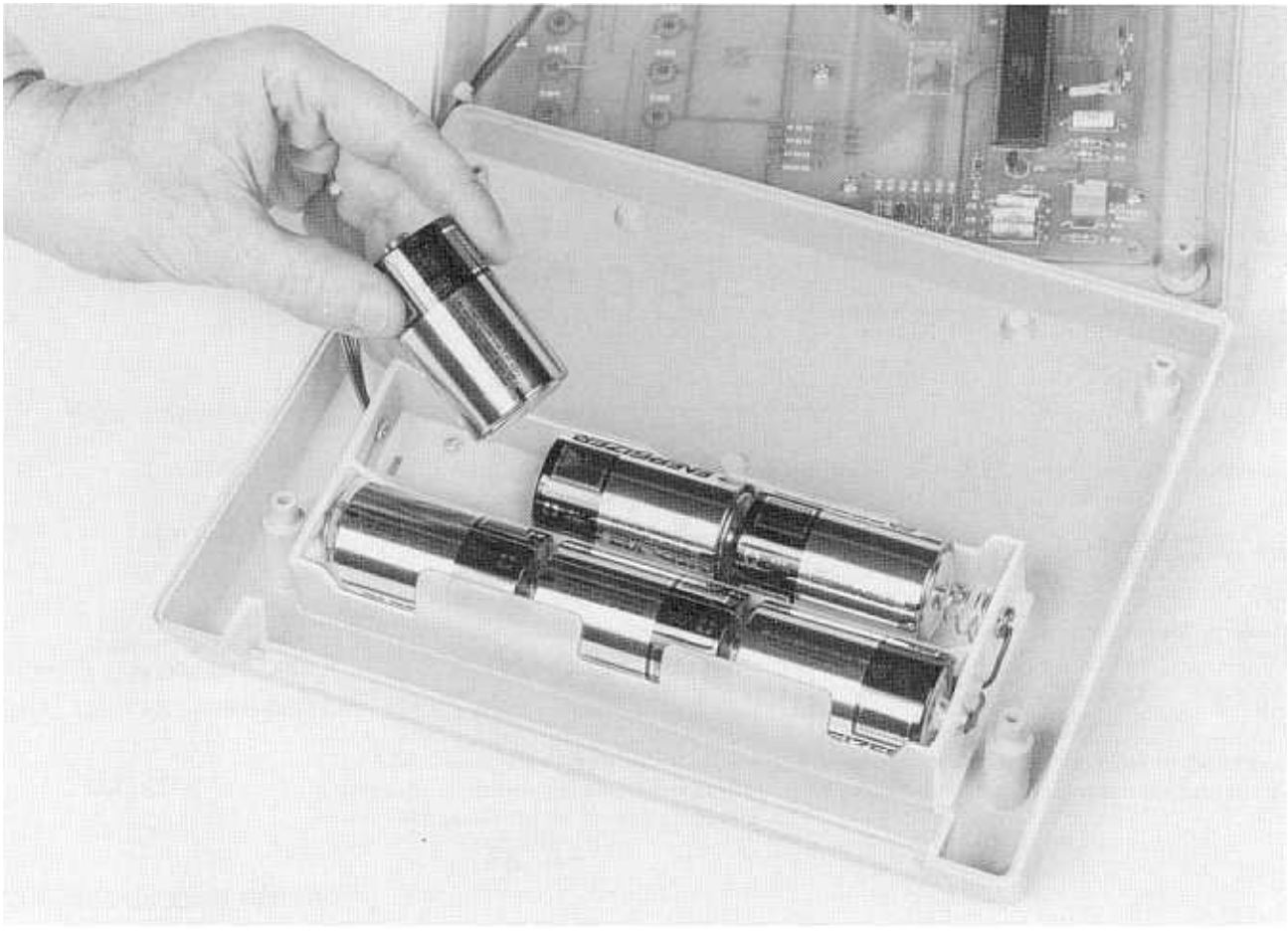


Figure 3. Battery Replacement

2.3 ASSEMBLING ELECTRODE STAND

The electrode rod supplied with the instrument is designed to screw-fit into the socket on either the top left-hand or the top right-hand side of the instrument. See Figure 2. Remove one of the caps and screw the rod in firmly so it is stable in use.

2.4 PREPARATION OF ELECTRODES

Prepare electrodes in accordance with the appropriate electrode instruction manual. For best results, the electrodes should be soaked for approximately one hour in Electrode Soaking Solution or tap water before initial use. Between successive buffer or sample measurements, wash electrodes with the next solution to be measured, or with deionized water, and blot dry.

SECTION THREE OPERATING CONTROLS

3.1 DISPLAY PANEL SYMBOLS

Not all symbols shown in Figure 4 appear at the same time. Only those symbols appear that properly define current instrument status.

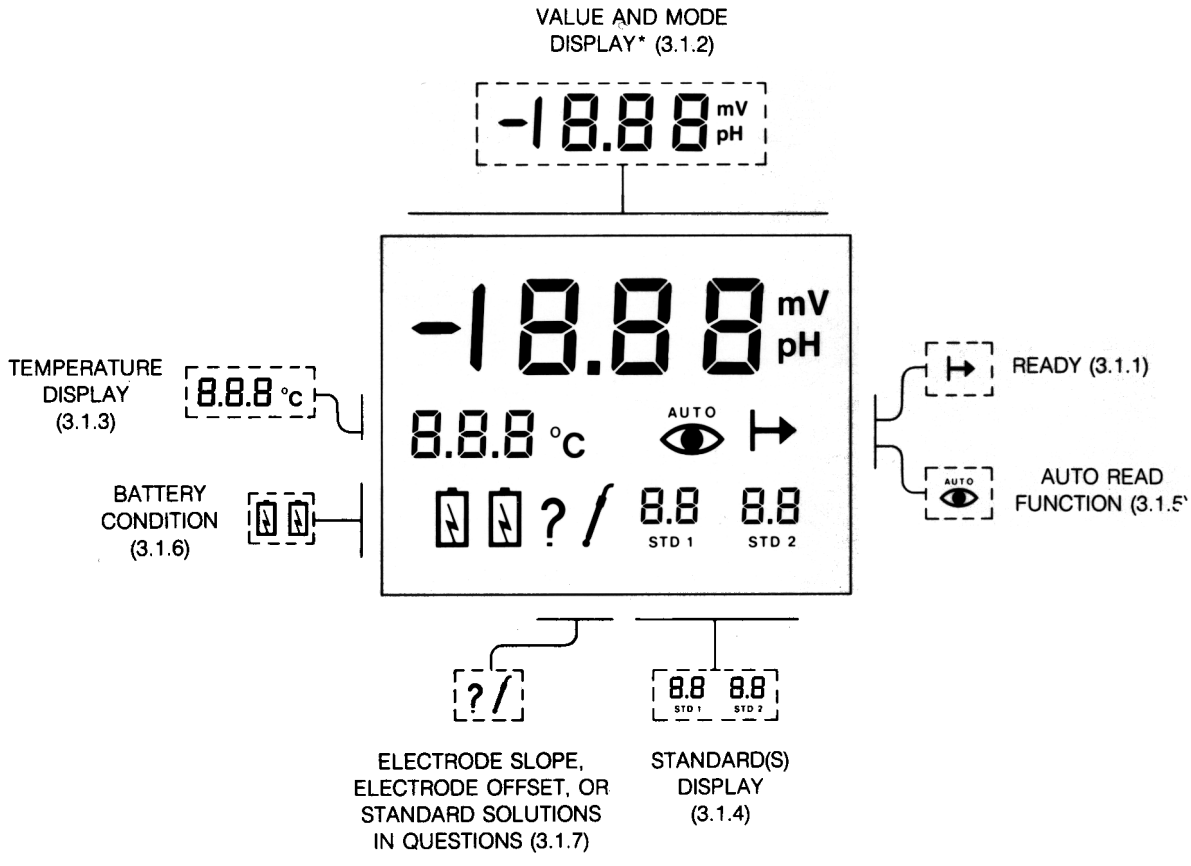


Figure 4. Display Panel Symbols: An Overview
(For details, refer to the paragraphs cited in parentheses.)

In this and the following sections, a dotted frame indicates an area in Display; a solid frame indicates a control key.

3.1.1 READY SYMBOL

Indicates the instrument is in the Ready State—or in Ready—and ready for new operation. Display is locked, retaining whatever was last displayed.

If the READY Symbol is off, the instrument and Display are active. The instrument is said to be in READ.

3.1.2 VALUE AND MODE DISPLAY

Values of pH readings or millivolt readings appear in this display. In addition, the mode of the reading—pH or mV—is indicated by the appropriate symbol.

This display serves another purpose—that of indicating status or error messages. When the instrument is cleared, "Clr" appears; when error condition 1, 2, or 4 occurs, "Er 1", "Er 2", or 'Er 4" appears in Display.

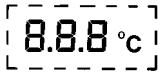
ERROR MESSAGES

Er Electrode input potential exceeds permissible limits—±1999 mV in mV Mode or ±1000 mV in pH Mode.

Er 2 Computed slope outside 50% to 140% of normal value. Clear instrument and begin again. Also check for a faulty electrode or improper buffers.

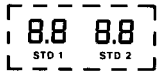
Er 4 Temperature, whether from an ATC probe or from the sensor within the instrument, is outside the specified 0°C to 99.9°C operating range.

3.1.3 TEMPERATURE DISPLAY



If an ATC (Automatic Temperature Compensator) probe is not plugged in, the value of the ambient temperature appears in this display. If an ATC probe *is* plugged in, the temperature displayed is the temperature sensed by the probe.

3.1.4 STANDARD(S) DISPLAY

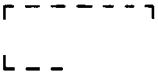


The approximate value of the standard or standards appears in this display. During standardization, the exact pH value of a buffer appears in the large Value and Mode Display. During sample readings, this smaller display serves as a reminder of the buffer standard or standards used. Consequently, only the first two significant figures appear. Examples follow.

When the instrument is standardized on only one standard (as in this example), its value appears in this display with the identification, STD 1. The instrument uses 99% of ideal slope, corrected for temperature, and offset has been corrected automatically.

When the instrument is standardized with two standards (as in this example), both values appear in this display with their identification, STD 1 and STD 2. The instrument has automatically computed a slope, which was corrected for temperature(s). Offset has also been corrected automatically.

INSTRUMENT STATUS AS INDICATED BY ON, OFF, OR FLASHING STANDARD SYMBOLS OR VALUES

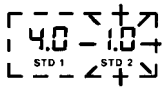


Both STD 1 and STD 2 Symbols off. No standard yet established. No standardization in progress.

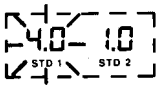
STD 1 Symbol and Value flash. No standard yet established. A standardization is in progress. Instrument is indicating that it will correct offset only.

STD 1 Symbol and Value on. One standard previously established. Offset is corrected. No standardization is in progress.

STD 1 Value on and STD 1 Symbol flashes; STD 2 Symbol and value both flash. One standard previously established. A two-point standardization is in progress. The instrument is indicating that it will correct both slope and offset. (No sample reading was made between STD 1 and STD 2.)



STD 1 Symbol and Value on. STD 2 Symbol and Value flash. Two standards are in use. The second standard is being restandardized. Slope will not be recomputed. (A sample reading was made between the last standardization and this standardization.)*



STD 1 Symbol and Value flash. STD 2 Symbol and Value on. As in the example immediately preceding, except that STD 1 is being restandardized.*

STD 1 Symbol and Value on. STD 2 Symbol and Value on. Two-point standardization is complete.

AUTO READ FUNCTION

Displayed to indicate that Auto Read is used; flashes off and on while the reading approaches stabilization.

Displayed when the instrument has determined that the electrode output is stable, and has locked the reading. Locking of Auto Read automatically puts the instrument in Ready. Note that when this symbol and the Ready Symbol appear together, *all* information in Display—including the temperature value—is locked.

BATTERY CONDITION

When this symbol appears in Display, change the batteries. Install six Size D alkaline cells.

ELECTRODE SLOPE, ELECTRODE OFFSET, OR STANDARD SOLUTIONS IN QUESTION

Activated if offset exceeds ±1 pH unit or if a slope computed in two-standard operation falls outside the range 85% to 105%. The instrument continues to operate normally. Either the electrode response is poor or the standard solutions are incorrect.

When the Auto Read Function is used, the "questionable electrode" flag begins to flash on and off if Auto Read does not lock within three minutes.

*After two-point standardization, if another standard, such as pH 7, is used, the instrument will discard the "older" standard—that is, the one that was least recently standardized.

3.2 INSTRUMENT CONTROLS

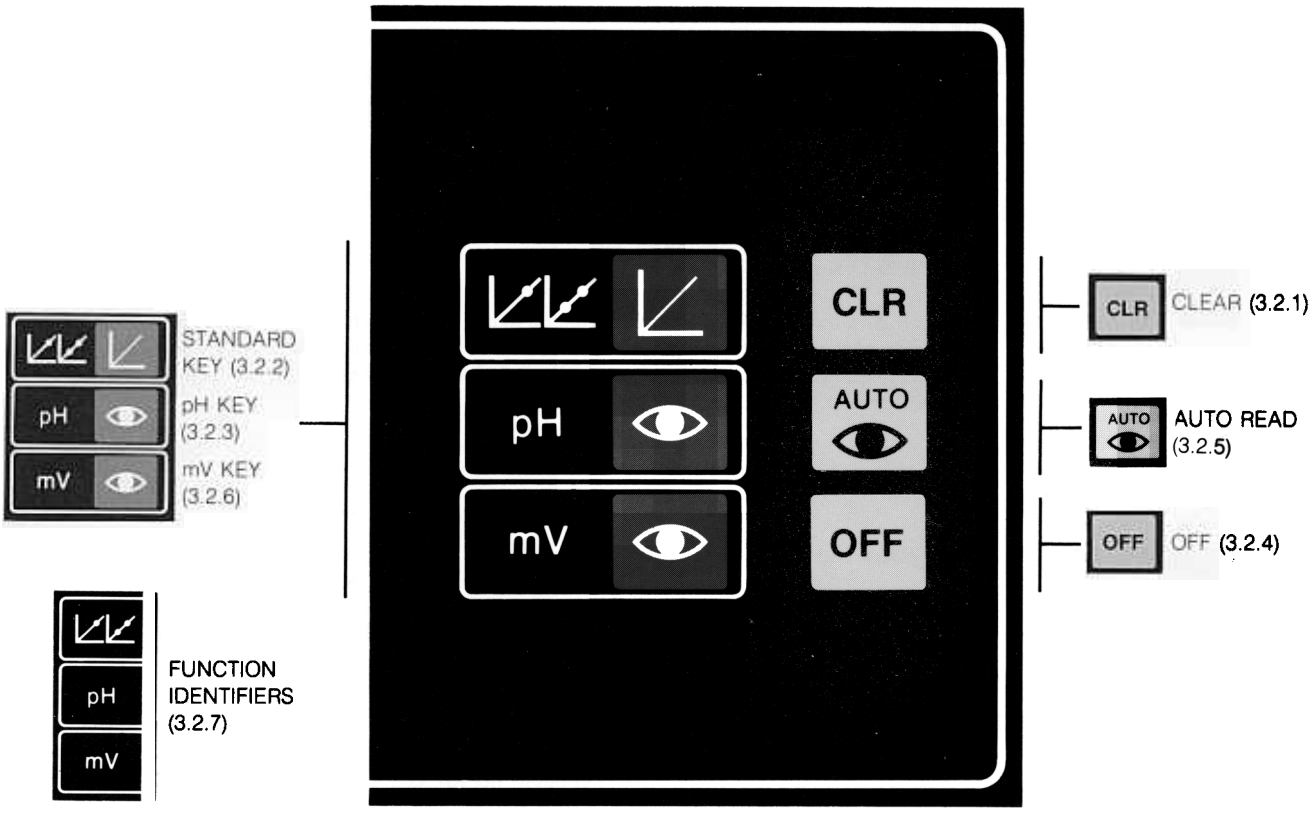


Figure 5. Instrument Controls of the pHI 31 pH Meter: An Overview
(For details, refer to paragraphs cited in parentheses.)

3.2.1 CLEAR KEY

CLEAR Key

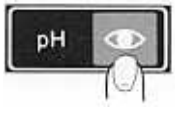
Depress to reset the instrument. Erases all stored data from microcomputer memory. Display indicates 'Clr'. If this key is depressed while the instrument is off, it will turn on automatically.

3.2.2 STANDARD KEY

STANDARD Key

Depress to initiate automatic standardization using the Auto-Find™ Standardization System. One or two points, in any order, any temperatures; slope and offset automatically computed. Accuracy, ±0.01 pH. Acceptable buffers are pH 1.68, pH 4.00, pH 7.00, pH 10.01, or pH 12.45. Also refer to the note at the end of Paragraph 5.3.1. If this key is depressed while the instrument is off, the key will be ignored.

3.2.3 pH KEY



pH Key

Depress to initiate measurement and display of sample pH. Sample temperature will be displayed if an ATC (Automatic Temperature Compensator) probe is in use. If there is no ATC probe, the instrument will default to ambient temperature as measured by an internal sensor. If this key is depressed while the instrument is off, it will first be turned on and then will begin to measure and display.

OFF Key

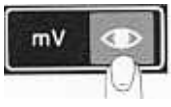
Depressing this key cancels any activity in progress and places the instrument in the power-down state. All stored data are retained. Display is off. *To ensure longer battery life the instrument will also shut off automatically 35 minutes after the last keystroke.*

AUTO READ ON/OFF KEY

AUTO READ Key

Depress to turn the Auto Read Function from on to off, or vice versa. The Auto Read Function detects the stability of the signal from the electrodes. Refer to Paragraphs 5.3.3 and 5.4 for details. Note that when the instrument is cleared, it automatically defaults to Auto Read on. If this key is depressed while the instrument is off, the key will be ignored.

3.2.6 MILLIVOLT KEY



MILLIVOLT Key

Depress to initiate measurement and display of sample mV. If this key is depressed while the instrument is off, the instrument will first be turned on and then will begin to measure and display.

2.7 FUNCTION IDENTIFIERS

On the Control Panel, the STANDARD Symbol, the pH Symbol, and the mV Symbol are not keys. They do not activate any instrument function, but serve only to identify related keys.

Glass electrodes for the measurement of pH generate a voltage output proportional to pH. In an ideal electrode pair, the output is 0 millivolt at pH 7.00, and it linearily tracks the pH at about -59 millivolts per unit increase in pH value at 25°C. Ideal electrode response is illustrated in Figure 6.

A simple, battery-powered pH meter is essentially a very high resistance millivoltmeter that translates the voltage output of the pH electrode into pH units. Since actual pH electrodes may not always precisely follow the ideal model, which is illustrated in Figure 7, an accurate pH measurement requires the pH meter to compensate for the electrode characteristics. Two compensatory programs, referred to as one-point standardization and two-point standardization, are used in the pHI™ 31 pH Meter.

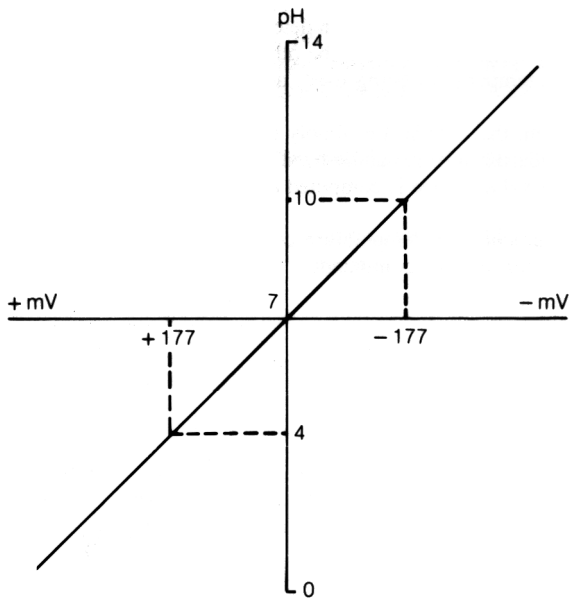


Figure 6. Ideal Electrode Response

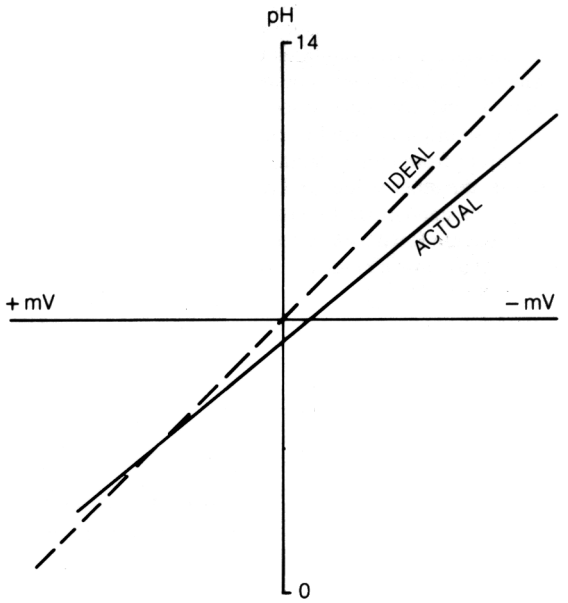


Figure 7. Ideal and Actual Electrode Responses

4.1 ONE-POINT STANDARDIZATION COMPENSATES FOR OFFSET

One-point standardization allows the pH meter to compensate for any offset in the electrode output from the ideal pH 7.00 = 0 mV. The microcomputer within the pHI 31 pH Meter will carry out the offset correction whether or not the first standard is pH 7.00. The instrument assumes that the electrode has 99% of the ideal slope response at 25°C, but it goes on to temperature-correct this slope before using it to complete the offset correction. Sample measurements can then be based on this standardization. (The 99% slope value is adopted because it more nearly represents actual electrode response in one-point standardization.)

4.2 TWO-POINT STANDARDIZATION COMPENSATES FOR BOTH OFFSET AND SLOPE

Two-point standardization consists of two steps: standardization with the first standard and standardization with the second standard. *The second step must always be performed immediately after the first, with no intervening sample measurements.*

The microcomputer notes the millivolt output for each of the two buffer standards, as well as their known pH values and temperatures. From this information, the microcomputer constructs a line connecting two points—one based on the first standard and one based on the second standard. The slope of this line, which is a measure of the response of an electrode in millivolts per pH unit, is referred to simply as *slope* at several points in this manual. The slope computed by two-point standardization is expressed as percentage of ideal slope, which is often termed % Slope. When slope has been constructed, the microcomputer has both and offset in memory. Accordingly, the millivolt output of the electrodes for any sample can be expressed in pH units.

4.3 SAMPLE MEASUREMENT

Once two-point standardization has been completed, the electrode and meter agree on the values of two buffers, and the instrument has compensated for both offset and slope. Accurate measurements can be made within 1.5 to 2 pH units of either standard value if proper temperature compensation is employed. Since solutions change pH as their temperature changes, proper data reporting should include mention of the sample temperature at the time of measurement.

4.4 TEMPERATURE COMPENSATION

At a given pH, the output voltage from a pH electrode changes with temperature. For temperature compensation of pH readings and of pH standardization, the instrument uses whatever type of temperature data is available—temperature information provided by an ATC (Automatic Temperature Compensator) probe or, if an ATC probe is not used, automatic default to ambient temperature of the instrument. If ambient differs markedly from the temperature of the standard(s) or sample, use an ATC probe.

4.5 FUNCTIONS OF THE AUTO-FIND STANDARDIZATION SYSTEM

The Auto-Find™ Standardization System, a special feature of the instrument, performs several important functions. These include automatic recognition of and automatic standardization to pH 1.68, pH 4.00, pH 7.00, pH 10.01, or pH 12.45 buffer. Each of these values appears accurately in the large Mode and Value Display and approximately in the smaller Standard(s) Display.

Auto-Find performs automatic standardization with one standard, compensating for offset, or automatic standardization with two standards, compensating for offset and slope. In either case, no input of buffer pH value is necessary. When the standard key is depressed, the Auto-Find Standardization System determines in which of the acceptable standard buffer solutions the electrode is immersed. Then it calculates the corrected pH value of the buffer at the temperature being used.

When two-standard operation is desired, again depress the standard key; the instrument will again determine in which of the acceptable standard buffer solutions the electrode is immersed. In the event that the solution is found to be other than that used for the first standard, the instrument computes the correct pH value of the buffer at the temperature being used, accepts the buffer as a second standard, and computes slope.

If the solution is found to be the same as a previously used standard solution, that standard is simply restandardized. If the solution is different from either standard, the instrument retains the most recently standardized or restandardized of the two existing standards, discards the other value, and replaces the discarded value with the new buffer value. Slope is computed *only* if two different standards have been standardized *consecutively*.

When Auto Read locks on a stable reading, Auto-Find standardizes the instrument to the temperature-corrected pH value of the buffer and the instrument returns to the Ready State, indicating that it is prepared for another command.

SECTION FIVE INSTRUMENT OPERATION

This section includes: Paragraph 5.1, an introduction to the use of your instrument; Paragraph 5.2, an explanation of Ready and its meaning in operation of the instrument; and Paragraph 5.3, which lists options in pH measurement. All are illustrated with drawings that show the control keys and the symbols that appear in Display. Paragraph 5.3.4 also provides a decision path, which is a guide to the selection of pH measurement options that are appropriate to your application. Then Paragraph 5.4 describes Auto Read and Paragraph 5.5 explains restandardization.

For the most part, the first five paragraphs concern pH measurements. The instrument is also used for millivolt measurements and temperature measurements; these topics are discussed in Paragraphs 5.6 and 5.7, respectively.

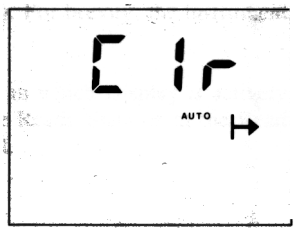
5.1 pH MEASUREMENTS: A SIMPLE AND COMMON PROCEDURE

The following standardization procedure is the easiest method for operating the instrument in the pH Mode. The required accessories and equipment are: a combination pH electrode; a Keeper Cable; one or two buffers (must be pH 1.68, pH 4, pH 7, pH 10, or pH 12.45); and several beakers.

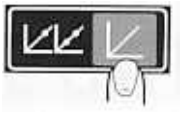
In the example that follows, pH 4 buffer is used first and pH 10 buffer is used second. In practice, any two of the five acceptable buffers can be used in any order. Three of the buffers, which are listed in Paragraph 11.2 are color-coded for easy identification by the operator—red for pH 4, green for pH 7, and blue for pH 10.*

As an introduction to the instrument, follow the steps outlined below.

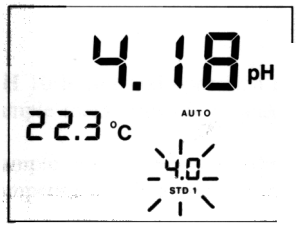
Depress the CLEAR Key to clear the instrument. Display will look like this.



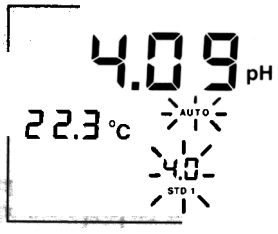
Rinse the electrode(s) with distilled water or pH 4 buffer and immerse in pH 4 buffer. (This symbol does not appear on the instrument. It indicates rinsing.)



Depress the STANDARD Key. The instrument recognizes this entry as the first standard. Display will look much like this, with Temperature Display indicating the measured temperature,** 22.3°C. *The actual pH reading, which changes as the electrode(s) stabilize, varies depending upon analytical conditions and upon the electrode used.* Both the STD 1 Symbol and STD 1 Value flash. For details regarding behavior of the Standard(s) Display, review Paragraph 3.1.4.

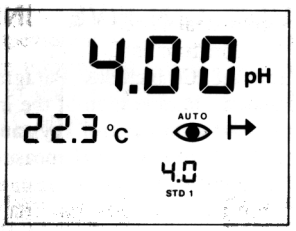


Shortly, the AUTO Symbol will begin flashing, indicating that the electrode(s) are approaching stabilization. *STD 1 Symbol and Value continue flashing.*

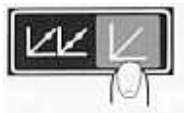


*These two buffers—pH 4 and pH 10—are selected for illustration only. The best results are obtained when the pH values of the two buffers bracket anticipated sample pH values.
**For a discussion of temperature compensation options, refer to Paragraph 5.3.1.

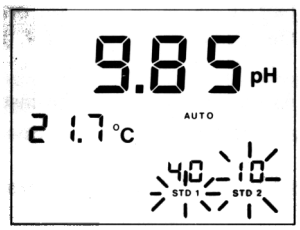
When input from the electrode(s) is stable, Auto Read will lock, the instrument will automatically standardize on the pH value of 4.00 pH buffer at the measured temperature, 22.3°C, and the STD 1 Symbol will appear in Display along with 4.0, the approximate value of the pH 4.00 buffer. Note that with this particular buffer the pH value at 22.3°C is the same as it is at 25°C—the usual temperature specified in describing buffer characteristics.



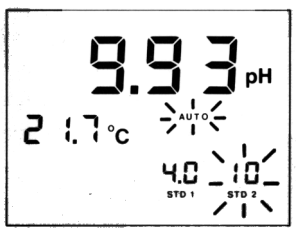
Now rinse the electrode(s) with distilled water or pH 10 buffer, blot, and immerse in pH 10 buffer.



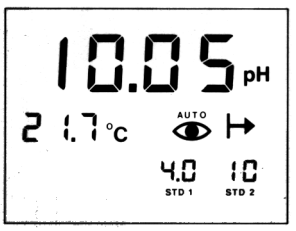
Depress the STANDARD Key again. The instrument recognizes this entry as the second standard. Display will look much like this, with Temperature Display indicating the measured temperature, 21.7°C. *Once again, the pH value shown may be different. And once again, it will change as the electrode(s) stabilizes.* The STD 1 Value is on and the STD 1 Symbol flashes; the STD 2 Symbol and Value both flash. For details, refer to Paragraph 3.1.4.



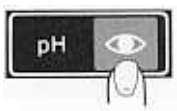
The AUTO Symbol will again flash after a short time. *This flashing indicates that the Auto Read Function of the instrument has detected that the electrode(s) are nearing stabilization.* STD 1 and STD 3 Symbols and Values behave as in the preceding stage.



When input from the electrode(s) is stable, Auto Read will lock, the instrument will standardize on 10.05 pH, the pH value of 10.01 pH buffer at the measured temperature, 21.7°C, and the STD 2 Symbol will be on, along with 10, the approximate value of the second buffer. The STD 1 Symbol and STD 1 Value also remain on. *When both STD Symbols and STD Values are on, as in this example, the instrument has completed two-point standardization on the indicated standard buffers.*

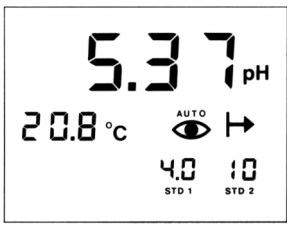


The instrument is now ready to make a pH measurement. Select a handy solution as the sample, rinse the electrode(s) with distilled water or the selected sample, blot, and immerse in the sample.



Depress the pH Key. Display will again activate. As the electrode(s) approach stability, the AUTO Symbol flashes, then Auto Read locks. Temperature Display indicates the measured temperature.

This sequence is repeated for all sample measurements. That is, depress the pH Key, wait for Auto Read to lock, and note the pH value.



Review what Display shows: Sample pH is 5.37, assuming that temperature is 20.8°C, the measured temperature. The instrument is in two-standard operation, using pH 4 and pH 10 buffers as the standards. Auto Read is employed and the instrument is in Ready, waiting for another sample or a new entry.

A great deal more has happened than would first appear. Since there was an Automatic Temperature Compensator (ATC) probe plugged in, the instrument accepted the temperatures sensed by the probe. Temperatures for STD 1, STD 2, and sample were 22.3°C, 21.7°C, and 20.8°C, respectively. Accordingly, these three values appeared successively in Temperature Display at the appropriate times, and in each case the pH value, whether of standard or sample, was corrected for temperature.

The Auto-Find™ Standardization System*, a special function of the instrument, provides for recognition of pH 1.68, pH 4.00, pH 7.00, pH 10.01, or pH 12.45 buffer. After the first buffer is measured, the instrument decides the correct buffer value. In this example, when input from the electrode is sufficiently stable to allow Auto Read to lock, the instrument places itself in Ready and standardizes the first point to the correct pH value of 4.00 buffer *at 22.3°C.* If the temperature were other than 22.3°C, Auto-Find would have used an appropriately adjusted value for pH 4.00 buffer.

When the electrode(s) are standardized in the second buffer—pH 10—the same sequence of events takes place, with the instrument standardizing to the correct pH value of pH 10.01 buffer at 21.7°C. But when Auto Read locks, the instrument automatically compensates for the unique slope—or response—of the electrode *without* disturbing the first standardization on pH 4 buffer.

And finally, during sample measurement, the instrument reads pH 5.37, the pH value of the sample at 20.8°C, the temperature measured by the ATC probe. *Note that in the absence of the probe, the instrument would, in each case, standardize at the ambient temperature of the instrument—as measured by an internal sensor.*

5.2 READY: DISPLAY FUNCTIONS

READY Symbol

Before proceeding further, one instrument function needs to be explained because it reflects the state of the instrument. When the READY Symbol is displayed, the instrument is in an idle state, ready to accept your command; it is not reading the value from the electrode(s). For brevity, the instrument is said to be in Ready.

When the READY Symbol is off, the instrument is in the Read Mode, in which Display is actively monitoring electrode response. Note that the instrument is in either the Ready State or in the Read Mode, as indicated by the presence or absence of the READY Symbol.

5.3 pH MEASUREMENT OPTIONS

Now that you have made some measurements and understand the meaning of Ready, look at options available for your specific application. This paragraph lists and discusses the following options:

1. Automatic Temperature Compensation by an ATC probe or operation at ambient temperature of the instrument, as detected by a thermistor.
2. Single-point standardization, two-point standardization, or no standardization.
3. Auto Read or operator determination of electrode stability.

5.3.1 TEMPERATURE COMPENSATION OPTIONS

The simple procedure in Paragraph 5.1 assumed two-point standardization with a pH 4 buffer and a pH 10 buffer and operation at the indicated temperatures. The instrument then uses each temperature value in standardization and sample measurements to make temperature compensations.

It is possible to standardize the instrument using two standards at different temperatures and make sample measurements at other temperatures. The various temperature values are retained by the instrument and used for temperature compensation. Examples of the options that are given below should be reviewed to determine which is best for your application.

1. Ambient Temperature of the Instrument
   The instrument adopts ambient temperature when there is no Automatic Temperature Compensator (ATC) probe connected to the instrument. Display shows the value of the ambient temperature when this assumption is being made. When ambient temperature is used, temperature compensation is based upon the temperature of the instrument's surroundings, as sensed by an internal thermistor. *Note that for best results this option for temperature compensation should be used only if ambient is close to the temperature of the standard(s) and samples.*

2. Temperature Compensation by an ATC Probe
   An Automatic Temperature Compensator (ATC) probe can be used to provide the temperature input automatically. (Refer to Paragraph 12.1, Accessories, for the part number.) When the probe is connected (plugged in), Temperature Display indicates the temperature sensed by the probe.

*Refer to Paragraph 4.5 for a complete description of the Auto-Find Standardization System.

The following table lists the pH value as a function of temperature for acceptable buffers. This information is provided 1) as a convenient reference, and 2) to emphasize the importance of temperature in pH measurement.

BUFFER VALUES AT VARIOUS TEMPERATURES
(for Beckman Buffers*)

TEMP	BUFFERS				
°C	pH 1.68	pH 4.00	pH 7.00	pH 10.01	pH 12.45
0	1.67	4.00	7.12	10.32	13.42
5	1.67	4.00	7.09	10.25	13.21
10	1.67	4.00	7.06	10.18	13.00
15	1.67	4.00	7.04	10.12	12.81
20	1.68	4.00	7.02	10.06	12.63
25	1.68	4.00	7.00	10.01	12.45
30	1.68	4.01	6.99	9.97	12.29
35	1.69	4.02	6.98	9.93	12.13
40	1.68	4.03	6.97	9.89	12.04
35	1.70	4.04	6.97	9.86	11.84
50	1.71	4.06	6.97	9.83	11.70

*The Auto-Find Standardization System operates properly only if the buffers used have the same temperature/pH characteristics as the corresponding Beckman Buffers.

5.3.2 STANDARDIZATION OPTIONS

Standardization options include the following: standardization with one standard solution, standardization with two standard solutions; or—for rough approximations—operation without using any standard at all. The latter assumes that the electrode has 99% of ideal slope. These options are discussed immediately following and should be reviewed to determine which is best for your application.

1. One-Point Standardization
   One-point standardization corrects for electrode offset but not for slope. One-point standardization is useful when samples are close in pH value to the buffer standard pH value and therefore corrected slope is not critical. For example, with samples in the pH range between pH 3.5 and pH 4.5, the instrument should be standardized using a pH 4 buffer.
   When standardizing at only one point, select a buffer that is close to the expected pH value of the sample. The instrument assumes 99% of temperature- compensated ideal slope, corrects for electrode offset, and indicates one-point standardization on the display.

2. Two-Point Standardization
   Two-point standardization corrects for offset and computes slope. It should be used when greater accuracy is required and when the sample pH values vary over a wide range and the electrode slope is critical. For example, with samples that vary over a pH range of 3 to 8, an initial standardization could be performed using a pH 4 buffer and the slope adjustment (second standard point) could be performed using a pH 7 buffer to complete the standardization. Remember that Paragraph 5.1 is a detailed example of two-point standardization.
   To go from one-standard to two-standard operation, the two-point standardization must be done consecutively without any sample readings between the first and second standardization. Two-standard operation computes slope and corrects offset. Paragraph 5.1 provides an example using Auto-Find on pH 10 and pH 4 buffers to demonstrate the steps involved to obtain a two-point standardization.

3. No Standardization
   When no standardization is employed, the instrument computes pH by assuming 99% of ideal slope and no offset. The instrument returns to this condition when cleared. If standardization is not used, depress the pH Key to take a reading. This is the least accurate method since electrodes seldom have both ideal slope and no offset. It should be used only for rough approximations.

5.3.3 AUTO READ ON/OFF OPTION

The Auto Read Function is another primary option that needs to be considered. It applies to standardization as well as to sample measurements. Auto Read has been used during all the previous examples.

The Auto Read Function may be disabled at any time by a single depression of the AUTO READ Key. The instrument will then continue to read data until it is placed in another mode, until it is turned off or cleared, or until time runs out (Paragraph 2.2). Auto Read locks if 10 successive updates (10 seconds) are within a ±1.0 millivolt range.

5.3.4 pH MEASUREMENT OPTIONS: A DECISION PATH

DECISION 1

IS MEASUREMENT PRECISION BETTER THAN 0.2 pH REQUIRED?

If the answew is YES, choose two-point standardization, or one-point standardization if all sample pH values are within ±0.5 pH of the standard buffer pH value. Both are described in Paragraph 5.3.2. Then go on to Decision 2.

If the answer is NO, one-point standardization, will probably suffice. See Paragraph 5.3.2, and go on to Decision 2. Note, however, that two-point standardization also provides an automatic electrode performance check. See Paragraph 3.1.7.

DECISION 2

ARE SAMPLES AND STANDARDS ALWAYS AT AMBIENT TEMPERATURE?

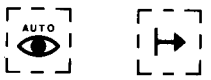
If the answer is YES, then use ambient temperature as the basis for temperature compensation. An ATC probe is not required

If the answer is NO, use an Automatic Temperature Compensator (ATC) probe.

5.4 AUTO READ

Auto Read, an automatic feature of the pHI 31 pH Meter, applies to standardization as well as to sample measurements.

The Auto Read Function is used to help obtain consistent results. The instrument checks each displayed value to see if the electrode output is stabilizing. When the readings are changing by no more than ±2.5 millivolts* in eight seconds, the AUTO Symbol of the Auto Read indicator flag begins to flash. When readings are changing by no more than ±1.0 millivolt** in ten seconds, Auto Read locks. *Because the two time intervals may overlap to some degree, the time for locking Auto Read will often require less than the sum of eight seconds and ten seconds. Indeed, in some instances both flashing and locking will be completed in a total of ten seconds.*



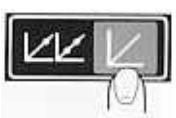
When the electrode(s) have stabilized, the Auto Read lock indicator is activated. The final reading remains in numeric display, the instrument automatically returns to Ready, and the READY Symbol in Display is activated.

The Auto Read Function can, if necessary, be disabled by depressing the AUTO READ Key. This turns off the AUTO Symbol. The instrument reads data until the operator terminates measurements by depressing the OFF Key, by allowing the instrument to shut off automatically, or by placing the instrument in another mode.

5.5 RESTANDARDIZATION

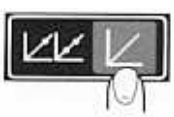
Restandardization of a single standard corrects offset only, even in two-standard operation. Consecutive restandardization on both standards corrects offset and recomputes slope as a percentage of ideal slope, or % slope. In order to return to one-standard operation after performing a two-point standardization, the instrument must be cleared. Refer to Section Four, Principles and Theory, for a discussion of one-point standardization and two-point standardization. After measuring samples, you can now perform a complete restandardization in either one-point or two-point operation. Follow these steps, returning to the original automated procedure in an abbreviated form.

Rinse the electrode(s) with distilled water or pH 7 buffer, blot, and immerse in pH 7 buffer.



Depress the STANDARD Key and wait until the instrument returns to Ready. *The instrument recognizes this entry as the first standard.*

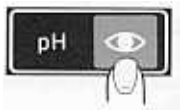
Rinse the electrode(s) with distilled water or pH 4 buffer, blot, and immerse in pH 4 buffer.



Depress the STANDARD Key and wait until the instrument returns to Ready. *The instrument recognizes this entry as the second standard.*

*At room temperature, a reading of 2.5 mV is about 0.042 pH unit.
**At room temperature, a reading of 1.0 mV is about 0.017 pH unit.

Rinse the electrode(s) with distilled water or the sample, blot, and immerse in the sample



Depress the pH Key and wait until the instrument returns to Ready before recording the reading. *This is the sample pH value.*

Remember that the temperature options and number of standards are options that apply to any procedure. Now clear the instrument and develop the procedure specific to your application, selecting any options that you consider pertinent.

5.6 MILLIVOLT (mV) MEASUREMENTS

Millivolt measurements are made with metallic or ion-selective electrodes. Measurements with metallic electrodes may be referred to as oxidation-reduction potentials (ORP or redox potentials), E_h, or EMF values. With ion-selective electrodes, millivolt measurements are taken and translated into ion concentrations of solutions. In recording millivolt measurements it is important to report the reference electrode used and the temperature. For example, 123 mV vs SCE @ 25°C means that the value obtained was 123 millivolts, measured against a saturated calomel reference electrode at 25°C.

5.6.1 PROCEDURE FOR MILLIVOLT MEASUREMENTS

Rinse the electrode(s) with distilled water or the sample solution, blot, and immerse in the sample solution.

Depress the mV Key. When the value in Display stabilizes, the Auto Read Function will lock Display on the sample millivolt value.

5.7 TEMPERATURE MEASUREMENTS

This instrument can be used as a digital thermometer when an ATC probe is connected. In this application, the ATC probe becomes a thermometer. The temperature sensed by this probe is displayed continuously. Note, however, that when Auto Read locks, the displayed temperature also locks. Thus, for *continuous* monitoring of temperature, Auto Read must be turned off. This is also true of the temperature sensed by the internal sensor in the ambient temperature mode, in which the ATC probe is not plugged in. Remember that the instrument will automatically shut off 35 minutes after the last keystroke.

SECTION SIX RECORDING

The recorder output, indicated in Figure 2, can be used to continuously monitor pH versus time or millivolt values versus time on a recorder. Use a high-impedance recorder for this application.

The recorder output provides a one-to-one input to output ratio. That is, if the electrodes are producing 10 millivolts, then output to the recorder is 10 millivolts. This is convenient when monitoring millivolts but difficult to interpret when monitoring pH. Therefore, the two modes have different requirements.

Output to the recorder is a reflection of the electrode input only. Thus any temperature compensation or standardization potential shift does not affect the recorder output.

The recorder output continues to operate when the instrument is off if a recorder is plugged in. This is useful when long-term recordings are to be made.

6.1 CONNECTING THE METER TO THE RECORDER

1. *Millivolt Mode*
   In the millivolt mode, a recorder cable (Recorder Cable A)*, which is a direct connection between the pH meter and the recorder, may be used. Thus a 100-millivolt recorder with the zero adjusted to midscale would provide ±50 mV recording. The recorder zero control is used to offset this span to a different range.
2. *pH Mode or for Large Millivolt Readings*
   When reading pH, or when large millivolt ranges must be displayed on a fixed gain recorder, a different recorder cable (Recorder Cable B)*, is used. This cable has a span adjustment built-in. If the direct cable is used, a pH span of approximately 1.8 units is displayed across the 100-millivolt recorder span. Consequently, a span adjustment is necessary.

6.2 SPAN ADJUSTMENT AND ZERO ADJUSTMENT: AN EXAMPLE

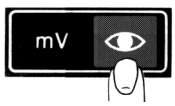
Setting up the pH meter and recorder so that a specific pH range is displayed fullscale on the recorder requires *span adjustment* and zero adjustment. The span adjustment is done first. Then a zero offset is made, using the recorder zero adjustment to shift to the range of interest. For example, a 1 pH-unit span adjustment can be made between pH 6 and pH 8 and then the recorder zero offset can be adjusted to record between pH 1 and pH 4 if desired.

Span *Adjustment*

Rinse the electrode(s) in distilled water or pH 7 buffer and immerse in pH 7 buffer.

2. Depress the mV Key and wait until the READY Symbol is displayed. Make a notation of the millivolt value.

3. Rinse the electrode(s) in distilled water or the second buffer that is within the *span* desired and immerse in that buffer. For example, if a 5 pH-unit span is desired, a pH 4 buffer could be used to adjust span, because it is within the desired span. (For best accuracy, a pH 2 buffer would be used because both extremes of the 5 pH-unit span would then be based upon standards. However, since no recognized pH 2 standard buffer is available, a pH 4 standard buffer is used.)



4. Depress the mV Key and wait until the READY Symbol indicates that the displayed value is stable. Make a notation of the millivolt value.

$mV_2 - mV_1$

5. Determine the difference between the millivolt readings for the two buffers (mV_2—mV_1) where mV_2 is the larger value. This difference corresponds to the pH change between the two buffers. For example, if the reading for pH 7 is 15 milli volts and that for pH 4 is 184 millivolts, the 3 pH-unit change corresponds to 169 millivolts.

*Part numbers of the recorder cables are in Paragraph 12.1, Accessories.

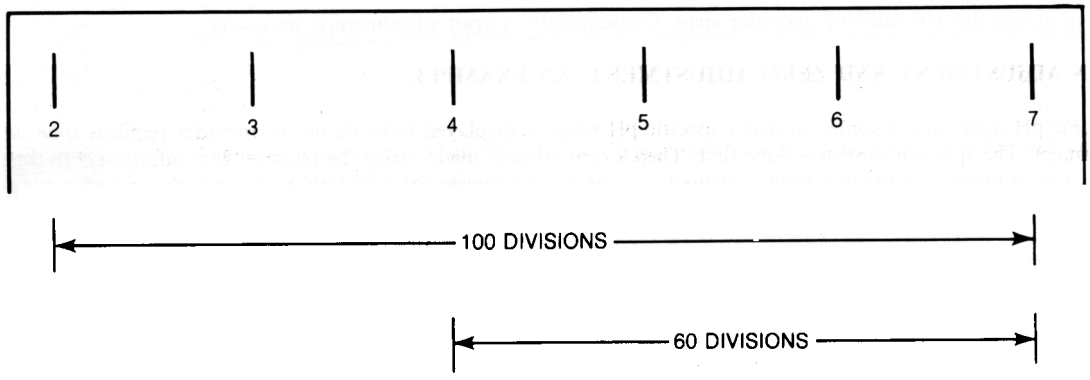
6. Short the recorder inputs by making a direct connection between the inputs and adjust the pen to one side of the chart paper, using the recorder zero control. (On some recorders, input can be shorted by depressing a ZERO Pushbutton. If this is not available, use a shorting strap.)

7. From the meter to the recorder, connect the recorder cable with built-in span adjust (Recorder Cable B)*.

8. Depress the mV Key. With the electrode(s) in the second buffer, adjust the span adjust in Recorder Cable B until the pen is at the appropriate position on the recorder chart for the millivolt value of the second buffer. If Auto Read causes Display to hold during this operation, depress the mV Key again to reactivate Display.

   For example, using the values listed below, the pen would be adjusted to the position representing 65.3 divisions. Calculations follow showing how the 65.3-division value is determined.

Calculations:
Display a pH range of 5 —pH 2 to pH 7—fullscale on 100-division paper.



Establish recorder zero on the extreme right-hand side, where pH 7 is to be located. On this scale, pH 4 is 60 divisions from pH 7. Calculate mV_2 - mV_1 from the results obtained in Step 5, immediately preceding, in which mV_2 (for the pH 4 buffer) is 184 and mV (for the pH 7 buffer) is 15.

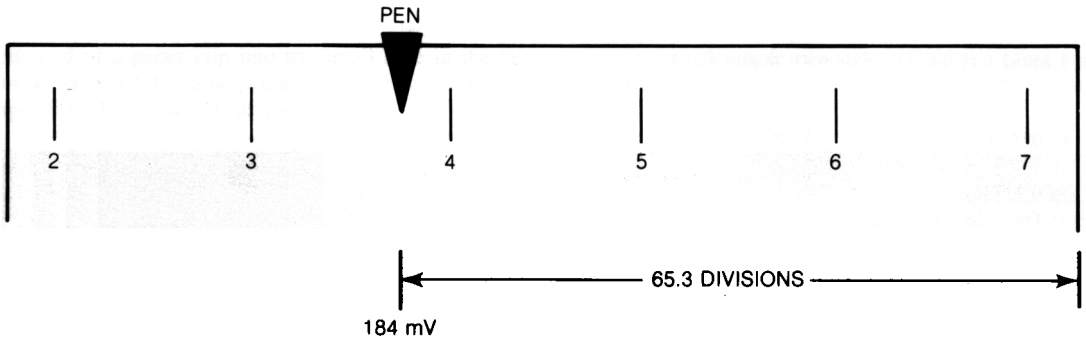
$mV_2 - mV_1 = 184 - 15 = 169$ mV
and
divisions/mV = 60/169 = 0.355

To determine the position corresponding to 184 mV

mV x divisions/mV = divisions
or
184 x 0.355 = *65.3 divisions*

*Part numbers of the recorder cables are in Paragraph 12.1, Accessories.

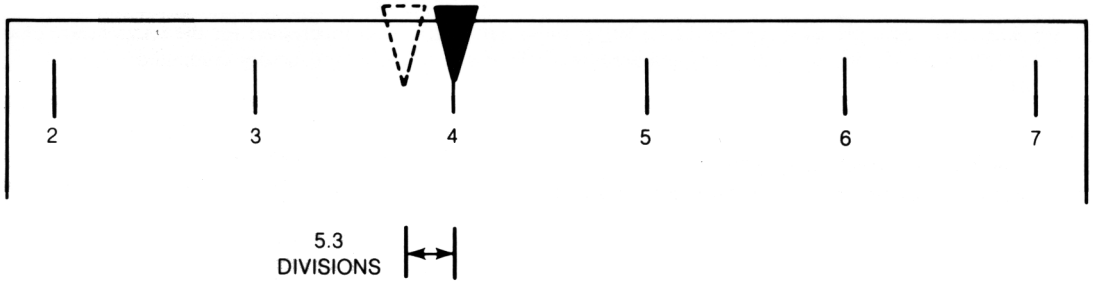
Consequently, *to establish span*, adjust span adjust on Recorder Cable B so that a pH 4 buffer reads 65.3 divisions from the recorder zero. Remember that recorder zero is on the extreme right-hand side, where pH 7 is to be established.



At this point, recorder span corresponds to the 5 pH-unit range, but zero adjustment is required so that the pen position agrees with the pH value on the 5 pH-unit recorder chart.

Zero Adjustment

Zero adjustment is made by rotating the *recorder zero control* until the pen reads at the appropriate division for the buffer value. Thus, in this example, pH 4 at 184 millivolts is shifted to the 60-division line while a pH buffer is being measured in the millivolt mode. As an alternative, pH 7 at 15 millivolts could be shifted to the recorder zero position.



SHIFT BY RECORDER ZERO CONTROL
(WHILE MEASURING A pH 4 BUFFER)

NOTE

Much the same span adjustment procedure would apply to another pH range, pH 8 to pH 13, for example. In that case, it would be better to establish pH range with pH 7 and pH 10 buffers. This will accommodate differences in electrode response in the basic pH range. A pH buffer within the pH 8 to pH 13 range—pH 10, for example—would then be used for zero adjustment.

SECTION SEVEN PERFORMANCE CHARACTERISTICS AND SPECIFICATIONS

CATALOG NUMBER
Beckman Part 123115

DISPLAY
Multifunction Liquid Crystal Display with status flags

RANGE
pH 0 to pH 14; 0°C to 99.9°C; and ±1999 mV

DISPLAY RESOLUTION
0.01 pH unit; 0.1°C; and 1.0 mV

pH ACCURACY (INSTRUMENT)
±0.01 pH

mV ACCURACY
±1.0 mV ±0.1% of reading, absolute mV only

TEMPERATURE ACCURACY
±0.5°C (System including temperature probe)

TEMPERATURE COMPENSATION

ATC only: ±0.5°C (System including temperature probe)
Range: 0°C to 99.9°C, with default to ambient temperature without ATC

AUTO STANDARDIZATION WITH EITHER ONE OR TWO STANDARDS
With pH 1.68, pH 4.00, pH 7.00, pH 10.01 *or* pH 12.45 buffer only, automatically compensated for the temperature characteristics of the buffers. One or two points, in any order, any temperatures; slope and offset automatically computed.
Accuracy ±0.01 pH.

AUTO READ
±2.5 mV for 8 seconds gives coarse range indication;
±1.0 mV for 10 seconds gives fine range indication and locks answer or standardization. *An Auto Read On/Off key is provided.*

OPERATING TEMPERATURE RANGE
15°C to 40°C. The instrument will function at lower temperatures at low (non-condensing) humidity.

POWER
Battery-operated, using six size D alkaline cells.

SECTION EIGHT CHECKOUT AND CALIBRATION

The following procedures may be used to help verify correct operation of your system.

Meter

1. Depress the CLEAR Key and disconnect the electrode and ATC probe (if one is being used).
2. Insert one end of a paper clip into the small hole in the center of the meter electrode connector. Hold the other end of the clip to the inside barrel of the same connector, as shown in Figure 8. This short circuits the instrument input, effectively making instrument input 0 millivolt, which is about 7.0 pH.

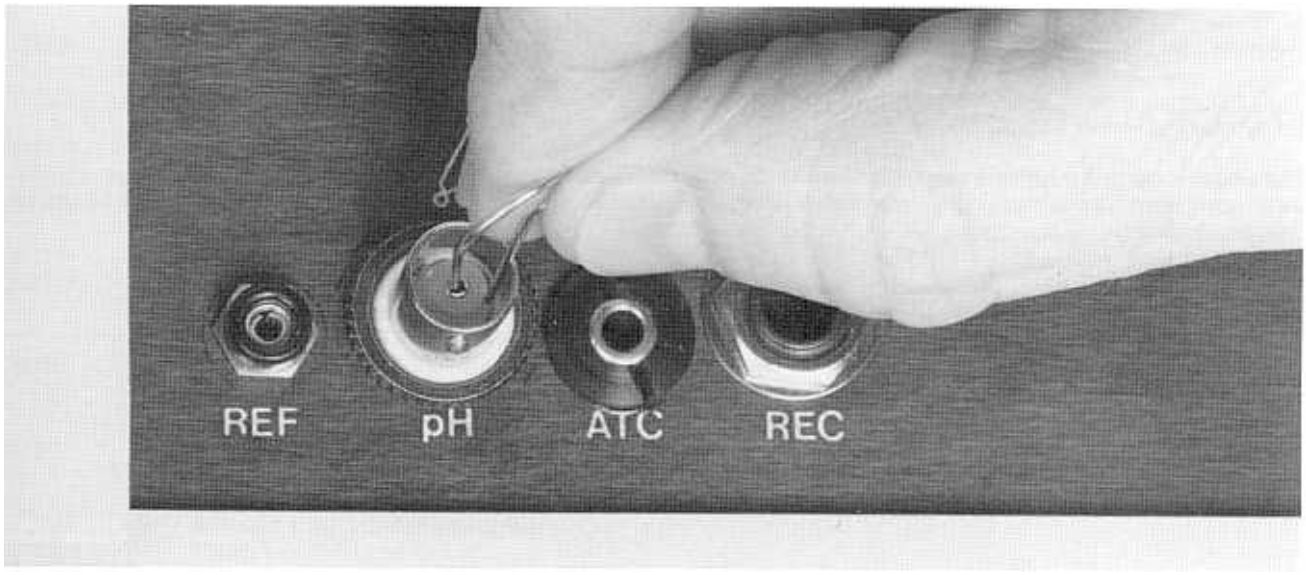


Figure 8. Shorting the Instrument Input

3. Depress the STD Key. The instrument should stabilize at 7.00 ±0.01 pH and lock, indicating a one-point standardization. If the instrument passes this test, go on to Item 4. If the test fails, refer to Section Eight, Service.
4. Remove the paper clip. Depress pH Key. The instrument reading should drift. If it is steady near 7.00 pH, the instrument has an internal short. Refer to Section Eight, Service. Note that in drifting, the reading may drift out of range and an Er1 display would result.
5. Most sources of instrument malfunctions will be revealed by the two tests immediately preceding. If instrument behavior is still suspect, refer to Section Eight. However, first eliminate the electrode as a trouble source by successfully completing the procedure that follows.

Electrode

1. For electrode preparation and checkout, refer to the electrode instruction manual.
2. Verify electrode performance by completing Paragraph 5.1, A Simple and Common Procedure, in this manual. If the measuring system completes this procedure satisfactorily, both instrument and electrode are functioning properly.
3. If the electrode continues to be suspect, substitute an electrode that is known to be good and repeat Step 2.

1-800-854-8067 Outside California
(714) 833-0751 Within California

SECTION NINE SERVICE

Should your instrument need service:

1. Follow the directions in Section Seven, Checkout and Calibration.
2. If repair or replacement is necessary, service is available at the National Service Center. Be sure to send the entire measuring system (including cable and electrode), and include a return address and the name and phone number of a contact. If you feel that the instrument should be covered under warranty, include a copy of your sales order.

Beckman Instruments, Inc.
National Service Center
167 West Poplar Avenue
Porterville, CA 93258
(209) 784-0800, Ext. 365

SECTION TEN OPERATIONAL PRECAUTIONS AND LIMITATIONS

The following operational precautions and limitations are cited so that the operator may avoid those actions that can damage the device, disrupt a series of determinations, or adversely affect the validity of a quantitative or qualitative determination.

1. READ THIS INSTRUCTION MANUAL BEFORE OPERATING THIS INSTRUMENT.
2. Do not subject the instrument to mechanical shock.
3. Care should be taken not to transfer body capacitance to glass electrodes when rinsing electrodes. Blot only, DO NOT WIPE. Drift of reading will be experienced if charge is transferred. If glass electrodes obtain charge, wait for discharge before proceeding.
4. Slowly lower electrodes into solution so as to prevent breakage of electrodes on bottom of beaker.
5. Standardize pH measuring system periodically. For either one-point or two-point pH standardization, use acceptable buffers only; that is, use pH 1.68, pH 4.00, pH 7.00, pH 10.01, or pH 12.45 buffer.

SECTION ELEVEN HAZARDS

Because the instrument is battery-powered and because the power is extremely low, under normal operating conditions there is no electrical hazard to operator safety. Simply observe good laboratory practice when measuring corrosive or acidic samples. Note the cautions regarding batteries.

CAUTION

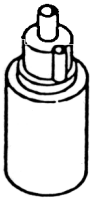
1. *Do not* attempt to recharge batteries.
2. *Do not* dispose of batteries in fire. In either case, the batteries may explode.
3. *Do not* substitute carbon-zinc cells. Use only size D alkaline cells.

SECTION TWELVE SUPPLIES AND ACCESSORIES

12.1 ACCESSORIES

BECKMAN PART NO.	DESCRIPTION
597578	Futura* II BNC Combination Electrode Keeper Cable, 1-meter
597579	Futura II BNC Combination Electrode Keeper Cable, 2-meter
597580	Futura II BNC Combination Electrode Keeper Cable, 6-meter
592328	Futura I BNC Combination Electrode Keeper Cable, 30-inch (0.76-m)
592329	Futura I BNC Combination Electrode Keeper Cable, 5-foot (1.5-m)
	Futura I BNC Combination Electrode Keeper Cable, 20-foot (6.1-m)
592379	BNC Shorting Plug
598115	Thermocompensator, 1-meter cable (ATC for use with Standard 5-inch [13-cm] Electrodes)
592380	Thermocompensator, Flexible (ATC for use with Long Electrodes and Test Tube Electrodes)
	Extension Cable, 5-foot (1.5-m) (for use with Thermocompensators to Increase Cable Length)
	Recorder Cable, Direct (Recorder Cable A)
592356	Recorder Cable, with Span Adjust (Recorder Cable B)
	Electrode Holder

Futura I Connector



Futura II Connector

12.2 SUPPLIES

BECKMAN PART NO.	DESCRIPTION
582517	Buffer, Six-Pack Pints, 473 mL, Red, pH 4.00 at 25°C
582521	Buffer, Six-Pack Pints, 473 mL, Green, pH 7.00 at 25°C
582525	Buffer, Six-Pack Pints, 473 mL, Blue, pH 10.01 at 25°C
566468	Reference Filling Solution, saturated KCl (used with Calomel Internal), Four-Pack, 100 mL
566467	Combination Filling Solution or Reference Filling Solution, 4 moles/L KCl (that is, 4 molar KCl) saturated with AgCl (used with Ag/AgCl Internal). Four-Pack, 100 mL
566576	Electrode Soaking Solution, Four-Pack, 100 mL
897715	Alkaline Cell, 1.5 Volt D-size, Eveready E95 or equivalent, six required

See the Handbook of Applied Electrochemistry, listed in Paragraph 12.3, Literature, for information on selecting electrodes.

12.3 LITERATURE

Bulletin 7739 The Beckman Handbook of Applied Electrochemistry

Available on request, this handbook contains helpful information on pH measurements, including measurement techniques, care and maintenance of electrodes, tips on buffers, and an orderly approach to troubleshooting. Other sections describe common topics such as pH measurement of troublesome samples, nonaqueous pH measurements, and the measurement of oxidation-reduction potentials.

*Futura is a trademark of Beckman Instruments, Inc.

SECTION THIRTEEN CROSS INDEX