HORIBA

pH Meter

D Series

Operation Manual

Measuring pH and mV

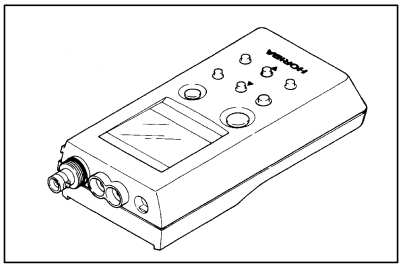
D-21

D-22

D-23

D-24

D-25



Thank you for purchasing one of the HORIBA D−20 Series of handy pH meters.
The HORIBA D−20 Series of handy pH meters are designed with a compact body that can be held in one hand and features a water−resistant construction Note 1.
A large−sized LCD display is employed for easy viewing; simple operation enables use of a wide range of functions; and best of all, the compact size of the HORIBA D−20 Series of handy pH meters makes them convenient to use on−location.
Carefully read this operation manual, entitled "Operation Manual: Measuring pH and mV," before using the pH meter.

Note 1: The water−resistant construction of this pH meter conforms to IP−67 of IEC 529, entitled "Water−resistant testing and protection against penetration by solid matter for electrical machinery and equipment." To maintain the water−resistant construction of this pH meter, following the instructions provided in this operation manual when using the meter.

IP−67 standards

- Dust does not penetrate into internal parts.
- Water does not penetrate into internal parts when the device is submerged under one meter of water for 30 minutes, at a temperature differential between the water and the device of 5°C or less.

HORIBA's Warranty and Responsibility

Your D−series pH meter is covered by HORIBA's warranty for a period of one (1) year, under normal use. Although unlikely, if any trouble attributable to HORIBA should occur during this period, necessary exchange or repairs shall be conducted by HORIBA, free of charge. The warranty does not cover the following:

- Any trouble or damage attributable to actions or conditions specifically mentioned to be avoided in the operation manuals
- Any trouble or damage attributable to use of the pH meter in ways or for purposes other than those described in the operation manuals
- If any repairs renovations, disassembly, etc. are performed on this pH meter by any party other than HORIBA or a party authorized by HORIBA

- Any alteration to the external appearance of this pH meter attributable to scratches, dirt, etc. occurring through normal use
- Wear and tear to parts, the exchange of accessories, or the use of any parts not specified by HORIBA

HORIBA also shall not be liable for any damages resulting from any malfunctions of this product, any erasure of data, or any other uses of this product.

CE Marking

CE

This product is in conformity with the following directives and standards:

Directives: The EMC Directives 89/336/EEC as amended by 91/263/EEC, 92/31/EEC and 93/68/EEC, in accordance with the Article 10 (1) of the Directive.
The Low Voltage Directive 73/23/EEC

Standards: EN61326: 1997+A1:1998
(EMISSION: Class B, IMMUNITY Category: General)
EN61010-1: 1993+A2:1995

Installation Environment

This product is designed for the following environment.
– Installation Categories II
– Polution degree 2

FCC Warning

This equipment has been tested and found to comply withthe limits for a Class A digital device, pursuant to part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference in which case the user will be required to correct the interference at his own expense.

Unauthorized reprinting or copying of this operation manual

No unauthorized reprinting or copying of all or part of this operation manual is allowed. The utmost care has been used in the preparation of this operation manual. If, however, you have any questions or notice any errors, please contact the HORIBA customer service center printed on the back cover of this operation manual.

❑CONTENTS

❑CONTENTS (cont.)

❑Overview of pH meter (Basics)

This table lists only the following information, to serve as an overview of this pH meter.

If you're searching for information on...		See this section...	On page...
Basics	Part names for main unit	⇒ Part names	p.16
	Meaning of displays	⇒ Explanation of display	p.16
	How to insert battery	⇒ Charging/replacing dry−cell battery	p.23
	pH/ORP electrodes for D−20 Series	⇒ Electrode part names	p.19
	Connecting electrodes to main unit	⇒ Connecting electrodes	p.20
	Displays when POWER key is pressed to turn power ON	⇒ Explanation of measurement mode	p.26
Special functions	Changing Automatic power−OFF setting	⇒ Setting automatic power−OFF	p.54
	Using key−lock	⇒ Setting key−lock	p.50
	Lighting up all LCD displays	⇒ LCD check	p.52
	Checking battery voltage	⇒ Battery voltage check	p.52
Trouble	When error nos. are displayed	⇒ Troubleshooting	p.63

1. Overview of pH meter

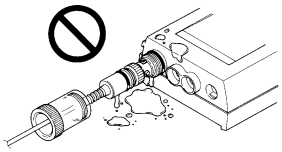
This chapter explains the names of the parts of this pH meter, how to connect the electrodes, how to replace the battery, and what to be cautious of when using this meter.

1 Overview of pH meter

1.1 Precautions

This operation manual explains how to make measurements using this pH meter and what to be careful of when using the meter. If an extended unit is connected to the pH meter, refer also to the operation manual entitled “Operation Manual: Extended Unit.” In addition, be sure to carefully read the operation manual that comes with the electrodes.

● Electrodes and connector



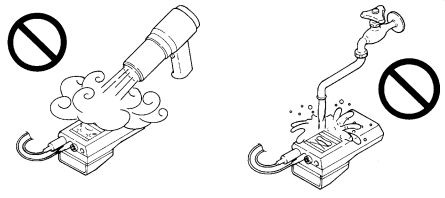
This pH meter is of water−resistant construction **when the main unit of the pH meter and an electrode are connected securely together or when the main unit is by itself.**

When the protective cover is not properly attached, do not allow water to contact the connection area and do not touch the connection area with your hands.

Regarding the electrodes, they are only water−resistant when connected securely to the main unit of special pH meters (meters that have the protective connector covers designed for the D−20 Series). Use electrodes according to their operation manuals.

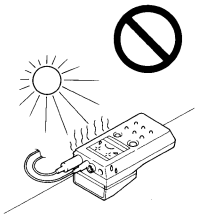
● Dropping the main unit into water

If the main unit of the pH meter falls into water or is otherwise made wet, **remove the liquid by wiping if off with a soft cloth**. Do not dry it with a hair drier. Also, be sure NOT to wash the main unit by allowing water to contact the unit directly from a water spout.



Note▶▶▶ This pH meter is not water−resistant when the extended unit is attached to it. When using the extended unit, do not submerse the pH meter in water. For details, refer to the operation manual for the extended unit.

● Battery cover and opening/closing the extended unit



If foreign substances (sand, dust etc.) adhere to the rubber packing of the battery cover, water may enter the internal parts of the pH meter if the meter gets wet. Close the battery cover only after removing all foreign substances from the rubber packing.

Also, be sure NOT to close the battery cover if it askew.

Note▶▶▶ It is recommended that the rubber packing for the battery cover be replaced once a year. When replacing the rubber packing, contact the HORIBA agent where the unit was purchased.

● Chemical resistance of main unit case

The case for the main unit of the pH meter is made from ABS resin, acrylic resin and various kinds of rubbers. Do not submerge the case in alcohol, organic solvents, or strong acidic or alkaline solvents.

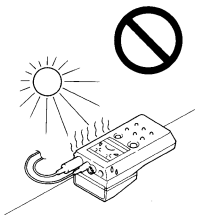
If the main unit of the pH meter becomes dirty, wipe the dirt off with a soft cloth containing water or a neutral detergent . Do not use paint thinner, benzene or alcohol.

- **Handling and storing electrodes**

Handle electrodes in accordance with their operation manuals.

Do not allow the electrode to come in contact with hard objects.

- **Do not allow the main unit to experience strong impact.**
- **Operate the keys using your fingers and not with any metal tools or other hard objects.**
- **Do not allow the pH meter to stand in the sun for long periods of time.**



This pH meter uses an LCD display. Extended exposure to ultraviolet light may cause deterioration in LCD performance.

- **Avoid operating the pH meter in the following kind of locations.**
  - Locations subject to ambient temperature of 0°C or below.
  - Locations subject to ambient temperature of 45°C or above.
  - Locations subject to strong vibration.
  - Locations subject to corrosive gas.

- **Dry−cell battery**

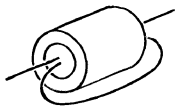
  If a dry−cell battery is misused, the liquid within may leak out and cause damage to surrounding parts. Be sure to follow/note the below points.

  - Dry−cell batteries cannot be recharged.
  - Remove the dry−cell battery from the pH meter when the meter will not be used for a longperiod of time.
  - If liquid leaks from a battery while in the pH meter, clean off any liquid adhering to the battery cover before placing in a new dry−cell battery.

- **Never use solvents to clean the meters.**

- **Use only the specified AC adapter (AC−10 adapter; optional).**

- **Set the ferrite core to the electrode cable**



In using the pH meter under strong electric wave, set the ferrite core to the electrode cable by winding the cable to the ferrite core as shown in the figure.

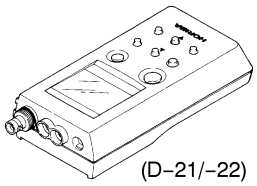
The recommended ferrite core is either of the followings:

・ZCAT3035−1330 (TDK CORPORATION)
・TFC−25−15−12 (KITAGAWA INDUSTRIALS CO., LTD)

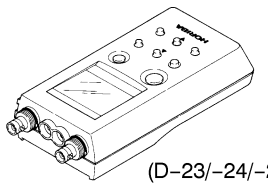
1.2 Removing packaging

The following items are contained within each HORIBA D−20 Series hand held pH meter package. Make sure all items are present. Accessories and electrodes come in separate packaging.

- **Meter (D Series pH meter, main unit) . . .** 1 unit

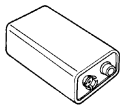


(D−21/−22)



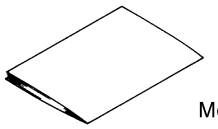
(D−23/−24/−25)

- **6F22 (NB) dry−cell battery . . . . . .** 1 battery



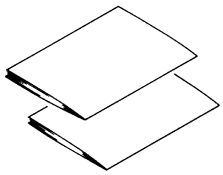
- **Operation manuals**

D−21/−22 **1 booklet**



Measuring pH and mV

D−23/−24/−25 **2 booklets**



Two booklets:

Measuring pH and mV 1 booklet
Measuring ions, conductivity, and dissolved oxygen . 1 booklet

- **Ferrite core (D−20 Series) . . . . . .** 1 package
- **Sensor adaptor (D−23/−24/−25) . . . . . .** 1 package

1.3 Functions

The D−20 Series features the following functions.

● Measurement items

The following table indicates what can be measured using the D−20 Series.

Measurable	Definition	Model of main unit					Required electrode/ standard solution
		D−21	D−22	D−23	D−24	D−25	
pH	Measures the pH of a solution	○	○	○	○	○	pH electrode pH standard solution
ORP (mV)	Measures the ORP(mV) of a solution		○	○	○	○	ORP electrode (pH,Ion electrode)
Ions	Measures the ion concentration of a solution			○			Ion electrode Ion standard solution
Conductivity	Measures the conductivity in a solution				○		Conductivity electrode
Dissolved oxygen	Measures the dissolved oxygen in a solution					○	DO electrode

Note▶▶▶ When using a D−23, D−24 or D−25 pH meter to measure ion concentration, conductivity or dissolved oxygen, refer to the operation manual entitled, “Operation Manual: Measuring ions, conductivity and dissolved oxygen.”

• Functions

An overview of the functions that can be used when measuring pH or mV with a D–20 Series pH meter is provided below.

Function	Explanation	Page
pH calibration	Enables the calibrated asymmetry potential/ sensitivity to be viewed.	p. 32
Displaying calibration history	Enables standard solution used for calibration to be changed to NBS and U.S. specification settings. (See p. 78 for standard solution values.)	p. 49
Calibration standard solution setting	Enables changes of NBS and US specification settings for calibration buffers.	p. 32
Data memory	Enables a maximum of 30 pieces of measurement and temperature data to be stored. (See p. 48 for how to set memory numbers.)	p. 44
Data out	Calls up what is stored in data memory.	p. 46
Temperature compensation	Enables temperature compensation to be conducted in pH MEASUREMENT mode, either manually or using a temperature sensor.	p. 48
Setting calibration frequency	Counts the number of times measurement takes place using AUTO HOLD, since the last calibration took place. “ERR” is displayed if the count exceeds the set number. Can be used as a guide for when to calibrate.	p. 56
Key–lock	Disables all keys other than MEAS and POWER. This prevents other keys from being accidentally pressed during measurement.	p.50
Measuring relative mV	Enables the measurement of mV using the value indicated when the display of the measured potential is shifted to 0 mV. Enables the viewing of relative changes.	p. 39

In addition to the above, other functions can be used in CHECK mode. (See p. 51.)

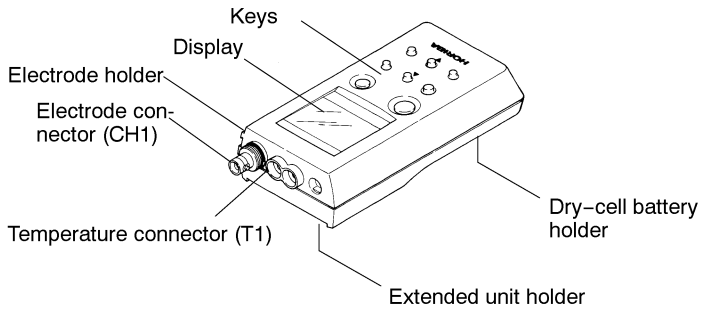
● Functions of extended unit (sold separately)

Function	Explanation
Clock	The day and time of calibration are displayed as calibration history.
Commercial power supply	Enables the use of commercial power, using an AC adapter (sold separately).
RS−232C communications	Enables communication with a computer, using RS−232C.
Printer output	Prints the contents of the memory (printer sold separately).
Recorder output	Enables analogue output of measured values. This requires a special cable (sold separately).

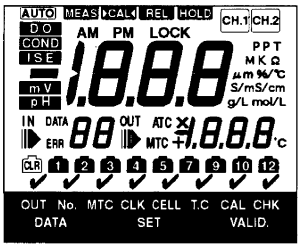
Important: Refer to the operation manual for the extended unit.
RS−232C communications and the printer cannot be used simultaneously.

1.4 Part names

The D Series of hand held pH meters are comprised of the following parts.



1.5 Explanation of display



← Differs according to model.

MEAS: Displays when in MEASUREMENT mode (p. 26)

>CAL<: Displays when in CALIBRATION mode (p. 32)

REL: Displays in mV MEASUREMENT mode, when relative mV is being set (p. 42)

HOLD: Displays when electric potential is stable and data is being maintained on display; flashes until potential is stable (p. 26)

AUTO: Displays when automatic power−off function is ON (p. 54)

DO: Displays when measuring dissolved oxygen
COND: Displays when measuring conductivity
ISE: Displays when measuring ions
mV: Displays when measuring mV (p. 40)
pH: Displays when measuring pH (p. 31)
IN : Displays (for 3 seconds) when data is entered into memory
ERR: Displays when an error is generated (p. 63)
DATA: Displays when data no. is being set (p. 46)
OUT : Displays when calling up data (p. 46)
ATC: Displays during automatic temperature compensation (p. 48)
MTC: Displays during manual temperature compensation (p. 48)
%/°C: Displays when setting temperature conversion factor (only when measuring conductivity)
°C: Displays when displaying temperature (p. 48)

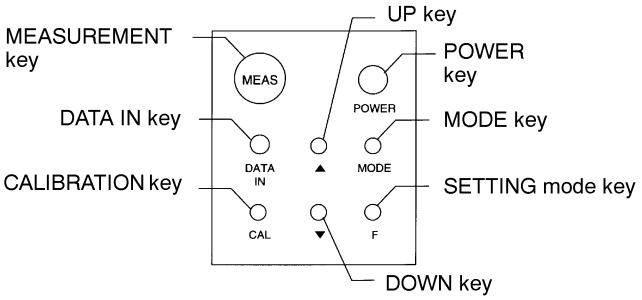
CLR : Calibration clear display
(only displays when measuring pH or ions) (p. 34)

1 – 12 : Calibration and display
(only lights up when measuring pH or ions)
Not lit when measuring mV, conductivity or dissolved oxygen

✔ : Special function mode display (p. 45)
AM/PM: Displays when calibration date and time are displayed and when setting the date (p. 49)
LOCK: Displays when key–lock in being used (p. 50)
CH.1: Displays when in input channel 1
CH.2: Displays when in input channel 2

1.6 Key names

POWER: POWER key
MEAS: MEASUREMENT key
MODE: MODE key
F: SETTING MODE key
▲ : UP key
▼ : DOWN key
DATA IN: DATA IN key (activates commands when in CHECK mode)
CAL: CALIBRATION mode key (changes channels when in CHECK mode)



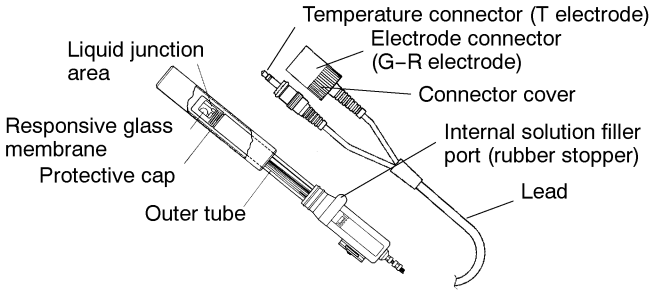
Note▶▶▶ The automatic power−off function is part of the default settings for this pH meter. The power is automatically turned OFF if no operation is performed for a period of approximately 30 minutes.

1.7 Electrode part names

Electrodes are not included when the pH meter is purchased alone. Please request the following electrodes that meet your requirements.

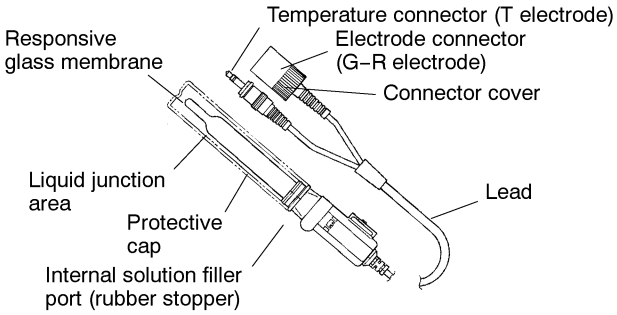
- **pH electrode (plastic body; 9620−10D)**

  Required for measuring pH.



- **pH electrode (glass body; 9610−10D)**

  Required for measuring pH.



- **ORP electrode (platinum; 9300−10D)**

  Required for measuring mV.

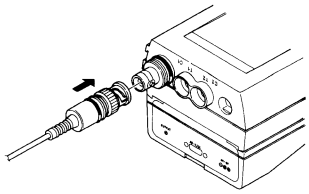
1.8 Connecting pH/ORP (oxidation−reduction potential) electrode

Connect the electrode to the pH meter , by following the below procedures. Use special care to ensure that no water or dirty hands come in contact with the connector during connection procedures.
(The explanatory drawings provided below show the pH meter with an extended unit attached.)

Note▶▶▶ Connect the pH/ORP electrode to C1. (For D−23 you can also connect to C2 by changing the CH setting.)

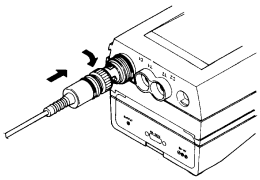
● Electrode connector (G−R electrode)

1. Insert the electrode connector, making sure to align the connector grooves with the pins in the connector sleeve on the main unit. Do not use undue force to push in the electrode connector when it is not properly aligned with the connector port.

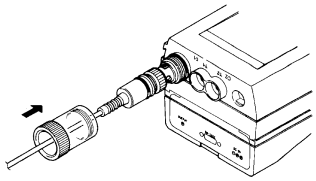


Note▶▶▶ Do not perform this step with wet or dirty hands.

2. Push the electrode connector into the connector port while turning it clockwise, following the grooves.



3. Place the connector cover on the connector. Then, push it vertically, until it comes in contact with the face of the main unit.



Note▶▶▶ The water−resistant construction of the pH meter assembly is not maintained if the electrode is not inserted properly.

● Temperature connector (T electrode)

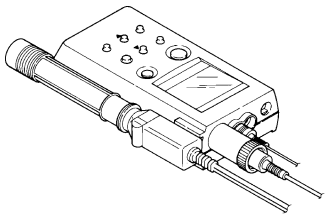
1. Insert the temperature connector into the jack on the main unit of the pH meter, while turning the temperature connector. Insert the connector all the way, until it is firmly attached and the O−ring on the electrode can no longer be seen.

C1: pH electrode connector (same for entire D−20 Series)
T1: Channel 1 temperature connector (same for entire D−20 Series)

Note▶▶▶ The water−resistant construction of the pH meter assembly is not maintained if the electrode is not inserted sufficiently. The temperature display on automatic temperature compensation (ATC) will show 25°C when a T electrode has not been inserted or has not been inserted completely.

- **The electrode can be attached to the main unit.**

  There is an electrode holder on the right side of the main unit of the pH meter.



1.9 Loading/replacing dry−cell battery

The dry−cell battery for this pH meter is not loaded in the pH meter before shipping. Load the battery by following the below procedures.
Note that if “ERR2” appears in the LCD display while using the pH meter, this indicates that the dry−cell battery is running down. In such a case, replace the battery promptly.

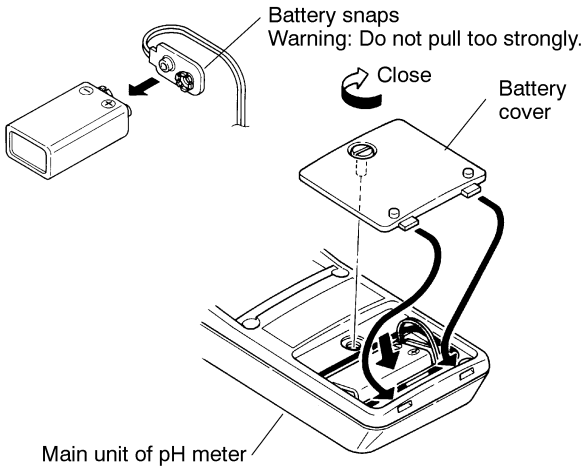
Type of dry−cell battery: 6F22 manganese battery or
6LR61 alkaline battery

Note▶▶▶

- Insert the battery correctly, paying attention to the orientation of the battery poles (“+” and “−”).
- Exchange the battery only after first turning OFF the power using the POWER key. Data saved in memory will not disappear.
- When the extended unit is attached to the pH meter, removing the battery will erase the clock data. If the clock data is to be saved, remove and replace the battery while the AC adapter (sold separately) is connected to the pH meter and plugged into a power source.
- Open and close the battery cover with dry hands and where no water can get on it or the pH meter.
- The battery included with the pH meter of purchase have a short time.

Procedures for replacing battery

1. Remove the battery cover stop screw, by using a coin or something that fits in the grove. The cover is constructed so that the screw cannot be removed.
2. Remove the battery cover by pulling up on the stop screw and sliding the cover out of the holes at the end of the main unit of the pH meter.
3. If there is an old battery inside, remove it.
4. Load the new battery into the pH meter, verifying the orientation of the poles ("+" and "–").
5. Insert the edge of the battery cover into the grooves on the pH meter, then tighten the stop screw.



Note▶▶▶ Be careful not to trap the cable in the battery cover. Also, be sure not to close the battery cover when the rubber packing is twisted. (If either of the above situations occurs, the water–resistant construction of the pH meter assembly will not be maintained.)

2. Measuring

This chapter explains how to make basic measurements.

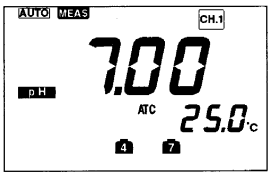
2 Measuring

2.1 Measurement modes

The D−20 Series of pH meters have an INSTANTANEOUS VALUE MEASUREMENT mode and an AUTO HOLD MEASUREMENT mode for all components of the solution being measured. Measurement data can be saved to memory using the data memory function.

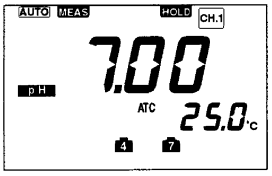
• Instantaneous value measurement

Instantaneous value measurement continuously displays the measurements, as they take place. The D−20 Series of pH meters perform instantaneous value measurement as the default measurement mode when the power is first turned ON and when AUTO HOLD measurement is cancelled or cleared.



• Auto hold measurement

Auto hold measurement maintains display of the value measured when the meter automatically judges that the measured value has stabilized. Press the MEAS key when in the INSTANTANEOUS VALUE mode to make “HOLD” flash in the display. When the measured value becomes stable, “HOLD” will stop flashing and remain steadily lit and the measured value will remain displayed. To clear the hold status or “stabilized” judgement (when “HOLD” is flashing), press the MEAS key again.

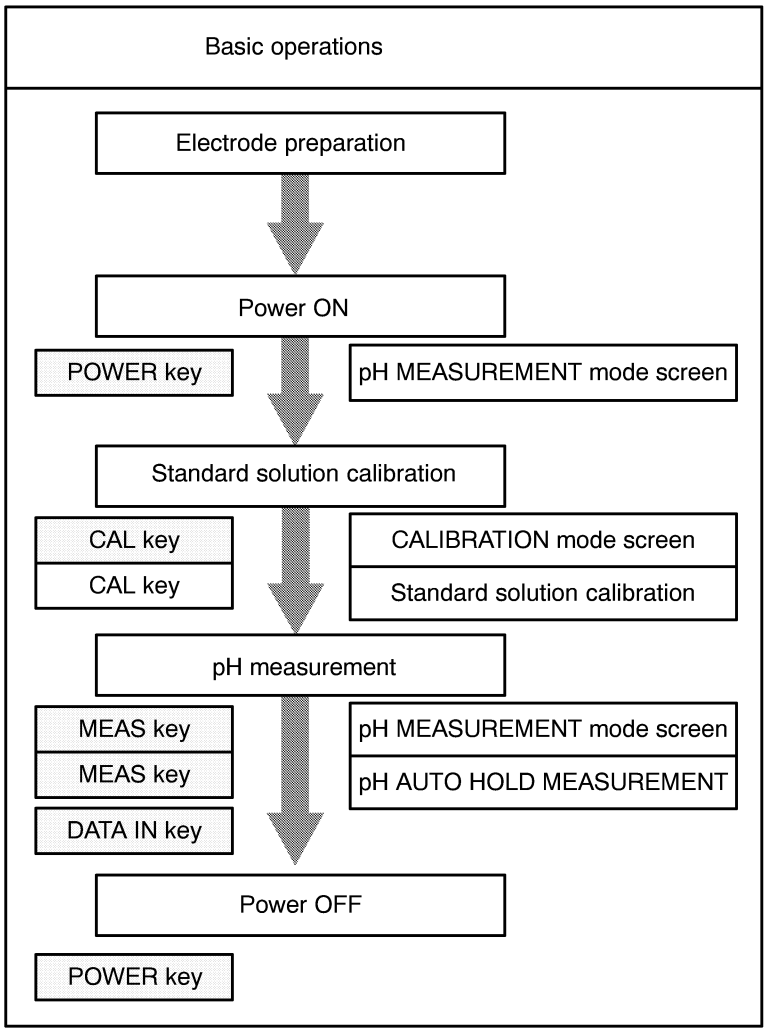


Ref.▶▶▶ The criteria for judging a measured value to be stabilized is a change in potential of 1 mV (approx. 0.02 pH) or less and a change in temperature of ±2℃ or less, for a 10-second period of time.

2.2 Measuring pH

If you're searching for information on...		See this section...	On page...
Basics	Your first pH measurement	⇒ Measuring pH: basic operations	p. 30
	Saving measurements to memory	⇒ Data memory function	p. 44
Special functions	Viewing measurements saved to memory	⇒ Data OUT mode	p. 46
	Viewing asymmetry potential and sensitivity	⇒ VALIDATION mode	p. 49
Applied measurements	pH measurement when measuring exact temperature	⇒ MTC SET mode ⇒ Calibrating temperature display	p. 48
	Limiting the number of AUTO HOLD measurements after calibration	⇒ Calibration frequency setting	p. 56
	When the extended unit (sold separately) is connected	⇒ CLOCK SET mode	p. 49
	When the extended unit and printer (both sold separately) are connected	⇒ Electrode ID no. setting	p. 54
	How to handle electrodes	⇒ Electrode maintenance	p. 60
	When an error number is displayed during measurement	⇒ Troubleshooting	p. 63
	Material about pH	⇒ Reference	p. 75

2.3 Measuring pH: basic operational flow



2.4 Measuring pH: basic operations

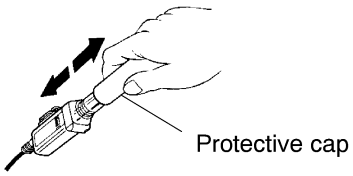
This section explains the basic operations involved in conducting pH measurement.

• Electrode preparation

Follow the below procedures to prepare the electrode, if it is to be used for the first time or after a long period of non−use.

Plastic−body pH electrode: 9620−10D
Glass−body pH electrode: 9610−10D

1. Turn and remove the protective cap from the pH electrode tip.

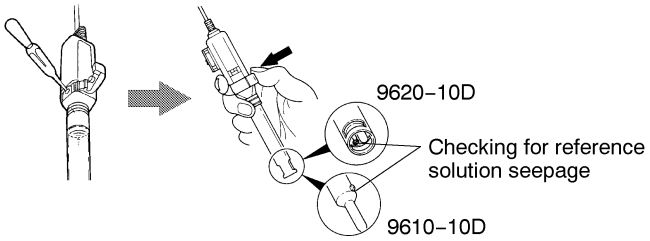


Chemical solution

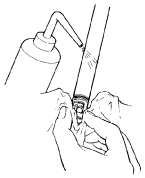
Warning

The liquid inside the electrode is highly concentrated potassium chloride (3.33 mol/L KCl).
If the internal solution in the electrode comes in contact with your hands or skin, wash immediately with water. If the internal solution comes in contact with your eyes, flush immediately with large amounts of water and seek treatment by a physician.

2. Fill the electrode with new internal solution until it nears the rubber stopper. Repeatedly close the opening with the rubber stopper to apply pressure to the reference solution and confirm that the reference solution is seeping from the liquid junction.



3. Wash the tip of the electrode well with pure (ion exchange) water and blot it with filter or tissue paper.



Glass fragments

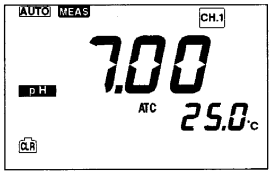
Warning

Glass fragments cause injury.

The outer tube of the electrode and the tip of the electrode are made from glass. Use care not to break them.

• Turning power ON

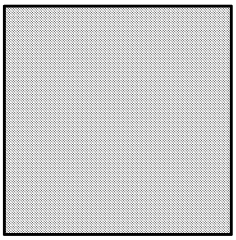
1. Press the POWER key. The INSTANTANEOUS VALUE MEASUREMENT screen will appear.



● Standard solution calibration

First, the pH meter must be calibrated using standard solution. When an extended unit is connected, the time at which calibration is conducted is saved. For this reason, it is recommended that the time setting be checked and adjusted if necessary (See p. 49.) prior to calibration.

This section will explain how to conduct a two−point calibration using pH 7 and pH 4 standard solutions. Perform a one−point calibration for making simple pH measurements; for more accurate measurement, perform at least a two−point calibration.



Note▶▶▶ Conducting calibration again, after returning to the pH MEASUREMENT screen, will clear all the calibration data. NBS specifications are used as the default settings for standard calibration solution.

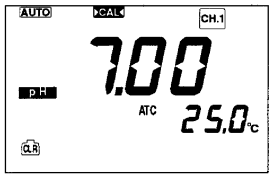
NIST (former NBS) : 2 4 7 9 12 bottle marks

U.S. specifications : 2 4 7 10 12 bottle marks

Refer to the reference material (See p. 78) for details on standard solution values.

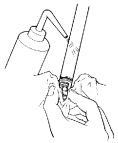
To modify standard calibration solution settings, press the MODE key while in CALIBRATION mode to change the MODE. Press the CAL key when the pH meter re−enters the CALIBRATION mode. Modes cannot be changed unless the calibration data has been cleared (when CLR is display).

1. Press the CAL key while in the pH MEASUREMENT mode to select the CALIBRATION mode. >CAL< will flash.

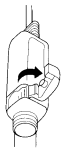


Note▶▶▶ The mode cannot be changed during AUTO HOLD measurement (while “HOLD” is flashing in the display).

2. Wash the tip of the electrode well with pure (ion exchange) water, then blot with filter or tissue paper.

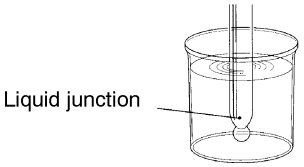


3. Open the internal solution filler port by removing the rubber stopper. Leave the rubber stopper off while calibration is taking place.



One–point calibration

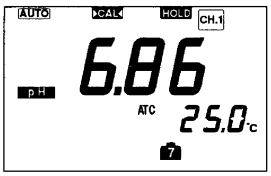
1. Immerse the tip of the electrode into a beaker containing pH 7 standard solution.



2. Press the CAL key to start calibration.

The measured value will be displayed. “HOLD” will flash in the display until the measured value stabilizes.
When the indicated value stabilizes, “HOLD” will stop flashing and remain lit and the calibrated value will be held on the display.

The number 7 bottle mark will be displayed, indicating that calibration was conducted with pH 7 standard solution.



Ref.▶▶▶ When the HOLD display is flashing
When calibration is forced: Fix the value using the DATA IN key.
When calibration is cancelled: Clear the hold by pressing the CAL key, again.

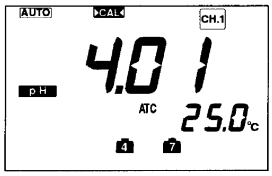
Two–point calibration

Continue by performing calibration using pH 4 standard solution.
Wash the electrode and the liquid junction area again using pure (ion exchange) water, then wipe with filter or tissue paper.

1. Immerse the tip of the electrode into a beaker containing pH 4 standard solution.
2. Press the CAL key to clear the hold, and check that the value indicates approximately pH 4.
3. Press the CAL key one more time to start calibration.

The measured value will be displayed and “HOLD” will flash in the display until the indication stabilizes.
When the indicated value stabilizes, “HOLD” will stop flashing and remain lit and the calibrated value will be held on the display.

The 4 bottle mark will be displayed, indicating that calibration was conducted with pH 4 standard solution.
This concludes the calibration procedures using pH 7 and pH 4 standard solutions. The numbers 7 and 4 bottle marks are displayed in the LCD.

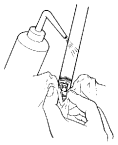


Ref.▶▶▶ Reference: Three–point calibration can be conducted by adding another point. To do so, repeat the calibration operations for the second point.

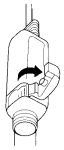
4. Press the MEAS key to return to the pH MEASUREMENT screen. Now, pH can be measured.

● Measuring pH

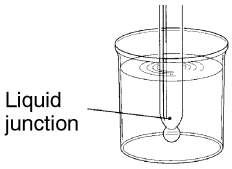
1. Wash the tip of the electrode well, using pure (ion exchange) water, then blot with filter or tissue paper.



2. Open the reference solution filling port by removing the rubber stopper. Leave the rubber stopper off while measurement is taking place.



3. Immerse the electrode in the sample all the way until the liquid junction is well submergel.

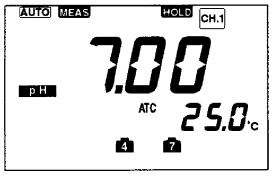


4. Press the MEAS key while on the INSTANTANEOUS VALUE MEASUREMENT screen.

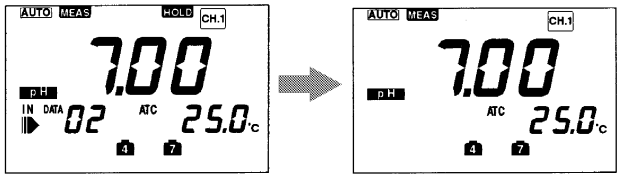
”HOLD” will flash on the display until the indicated value stabilizes.

When the indicated value stabilizes, “HOLD” will stop flashing and display steadily and the indicated value will be maintained on the display.

Once this is done, pH measurement has been completed.



If the data is to be saved to memory, press the DATA IN key. The memory number. will be displayed, then three seconds later the screen will automatically return to the INSTANTANEOUS VALUE MEASUREMENT screen.



Ref.▶▶▶ The data number automatically increments by one. If the data number stored in memory is to be changed, refer to “DATA No mode (Setting data no.)”, on page 47.

Ref.▶▶▶ Reference: When the DATA IN key is pressed to save data, the data will be printed if a printer is connected.
(The extended unit and printer are sold separately.)

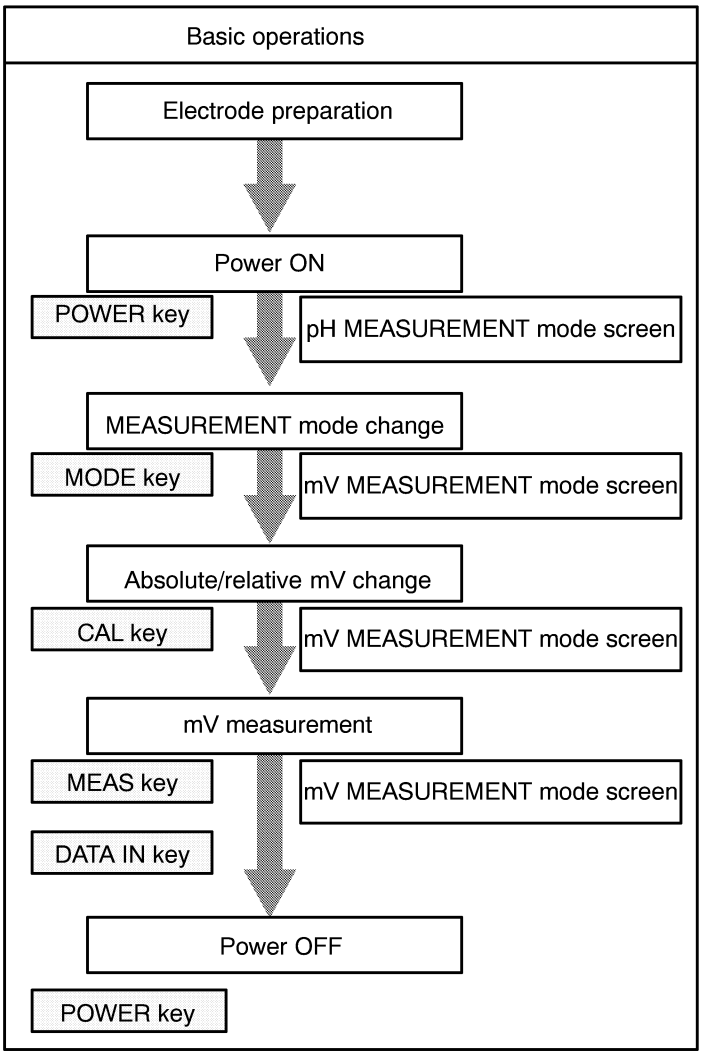
● Turning power OFF

1. When operation are finished, press the POWER key to turn OFF the power.

Note▶▶▶ The next time the power is turned ON, the pH meter will start on the pH MEASUREMENT (CH1) mode.

For information on handling the electrode, refer to the electrode operation manual or the section entitled “Electrode maintenance” (p. 60) of this operation manual.

2.5 Measuring mV: basic operational flow (not available with D–21)



2.6 Measuring mV: basic operations

This section explains how to perform basic mV measurement.

● Electrode preparation

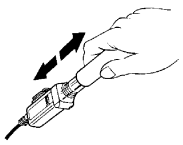
Follow the below procedures to prepare the electrode, if it is to be used for the first time or after a long period of non−use.

To measure the ORP (oxidation−reduction potential) of a solution, use a platinum electrode especially designed for that purpose.

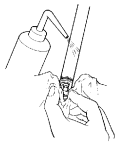
Using a glass electrode to conduct mV measurement enables the potential being measured to be checked and makes checking the performance of the electrodes possible without involving the calibrated value.

Platinum electrodes (ORP): 9300−10D

1. Remove the protective cap by turning it.

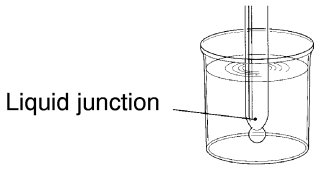


2. Wash the tip of the electrode well with pure (ion exchange) water then wipe it with filter or tissue paper.



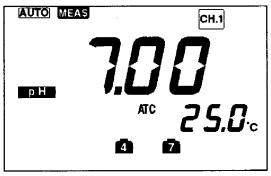
● Turning power ON

1. Immerse the electrode in the sample solution, all the way until the liquid junction.

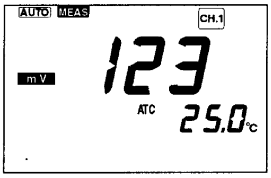


Note▶▶▶ If the power is turned ON when the electrode has not been totally immersed in the sample solution, the displayed value may move outside the display range.
For more accurate measurement, immerse the pH electrode in the sample, to at least three centimeters from the electrode tip.

2. Press the POWER key.
The pH INSTANTANEOUS VALUE MEASUREMENT screen will appear.



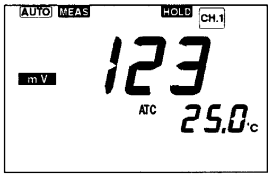
3. Press the MODE key, once.
The mV INSTANTANEOUS VALUE MEASUREMENT screen will appear.



4. Press the MEAS key while on the INSTANTANEOUS VALUE MEASUREMENT screen.

"HOLD" will flash in the display until the indicated value stabilizes.

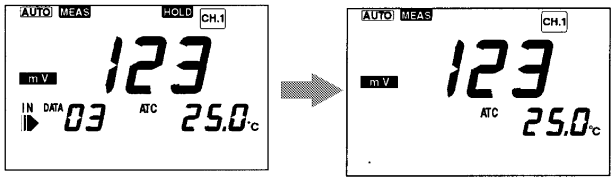
When the indicated value stabilizes, "HOLD" will stop flashing and display steadily and the indicated value will be maintained in the display.



Once this is done, mV measurement has been completed.

If the data is to be saved to memory, press the DATA IN key.

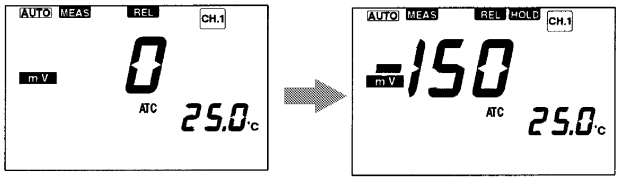
The memory number. will be displayed, then three seconds later the screen will automatically return to the INSTANTANEOUS VALUE MEASUREMENT screen.



● Measuring relative mV

The D–20 Series of pH meters can correct for relative mV, by applying offset electric potential to the measured electric potential to force the difference between the two to be shifted to 0 mV.
(Potential that has not been corrected is called “absolute mV.”)

1. Press the CAL key when mV instantaneous value measurement is taking place or when “HOLD” is steadily lit in the display to make “REL” light up.
The instantaneous value of the relative mV will be displayed, after the value displayed is corrected as the offset potential and held on the display as “0 mV” for approximately three seconds.



2. Press the CAL key again to return to the display of absolute mV.

Note▶▶▶ Correcting electric potential when measuring absolute mV does not affect the pH display. An operation check can be performed using a standard sample to verify whether or not the ORP electrode is defective. Refer to page 84 for details on ORP standard solution.

Ref.▶▶▶ With the D–23, the same amount of offset potential is applied for relative mV on CH1 and CH2.

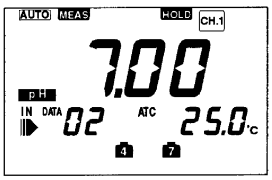
This chapter explains the various functions available on the D−20 Series pH meters.

3 Functions

3. Functions

3.1 Data memory function

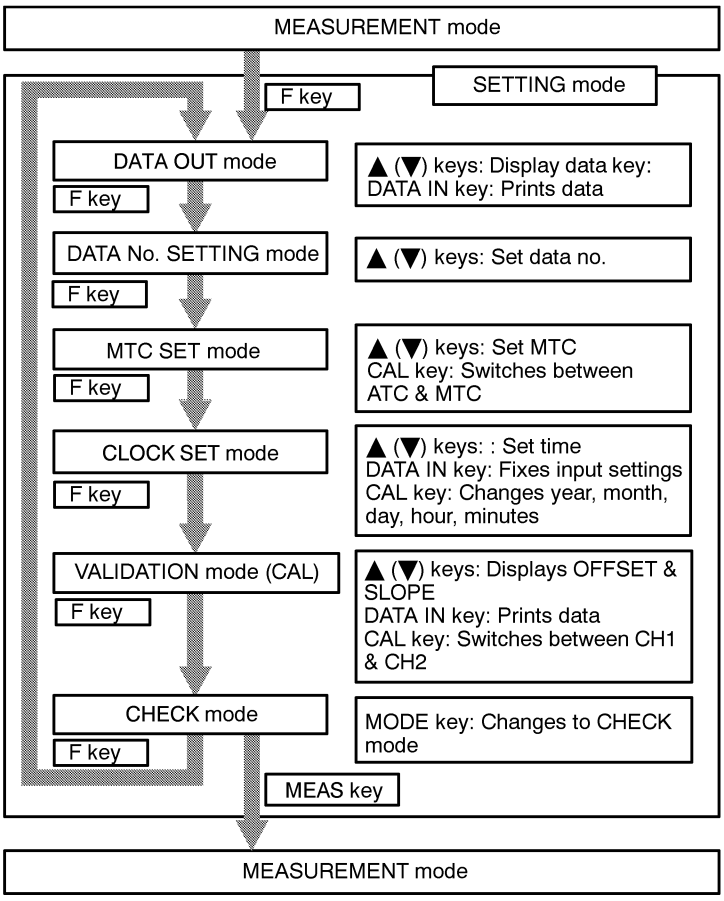
Press the DATA IN key when the measured value is being held in the display, during either instantaneous value or AUTO HOLD measurement, to save data to memory.
The pH, mV, relative mV, ions (only with the ion meter), conductivity (only with the conductivity meter), and dissolved oxygen (only with the dissolved oxygen meter) measurements will be saved to memory separately, according to and along with the temperature, date and hold/instantaneous value at that time. At this time, if there are any automatic or manual temperature compensation (ATC/MTC) indications and calibration points (only with pH and ion meters), they will be saved to memory along with the above data.
After the data number. appears on the screen, the meter will automatically return to the INSTANTANEOUS VALUE MEASUREMENT mode. A maximum of 30 pieces of data can be stored in memory. If the maximum memory capacity is exceeded, the data numbers will start over at data number 1 and the previously stored data will be overwritten.



Note▶▶▶ Data cannot be saved to memory when the meter is judging whether or not to hold or during CAL mode.

3.2 Setting mode: basic flow (for D–21/–22)

Press the F key when in the measurement mode (the ✔ mark at the bottom of the screen will illuminate) to select the setting mode according to the following flow chart.



Note▶▶▶ When in the CLOCK SET mode, settings can be made only with an extended unit (sold separately) is connected.

Printing is only possible when a printer (not sold by HORIBA) is connected.

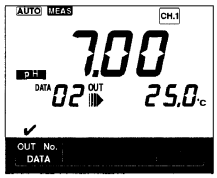
Ref.▶▶▶ The D–23, D–24 and D–25 have modes for setting ion, conductivity, and dissolved oxygen measurements, in between the CLOCK SET mode and the VALIDATION mode.

3.3 Setting mode

❑DATA OUT mode

Press the F key to select the DATA OUT mode.

DATA OUT mode (with data)



Select the data number and call up data from memory, by using the ▲ and ▼ (UP and DOWN) keys.

DATA OUT mode (without data)

" – – – " is displayed when there is no data.

- **Calling up data**

  Each time the ▲ (▼) key is pressed while in the DATA OUT mode, the data number increases (decreases) by one. After the maximum data number of 30 is reached, the numbers start over again from 1.

- **Clearing data**

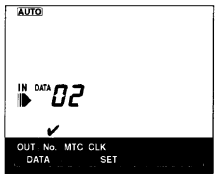
  Press the CAL key while in the DATA OUT mode to clear the data. This operation clears ALL data.

Note▶▶▶ If an error occurs while a data number is being displayed, the error number will NOT be displayed.

When an error is being displayed (when the value is flashing), press the DATA IN key to store that value in the memory. Note, however, that this data will not flash when called up from memory and displayed.
When using a printer (sold separately), press the DATA IN key while in the DATA OUT mode to print the data.

❑DATA No mode (setting data no.)

Press the F key to select the DATA No mode.



Use the ▲ and ▼ (UP and DOWN) keys to select the data number to be used next time.

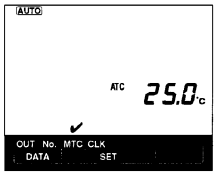
Note▶▶▶ If a data number that already has data saved on it is selected, the older data will be overwritten.

❑MTC SET mode (temperature compensation function)

Press the F key to select the MTC SET mode.

MTC SET mode (ATC)

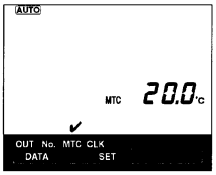
Automatic temperature compensation (when an electrode temperature sensor is used)
ATC lights up.



When a temperature connector is attached, the current temperature is automatically displayed.
(When no temperature connector is attached, the display shows 25°C)
Press the CAL key to switch between MTC and ATC.

MTC SET mode (MTC)

Manual temperature compensation (when an electrode temperature sensor is not being used and the temperature of the solution is known beforehand)



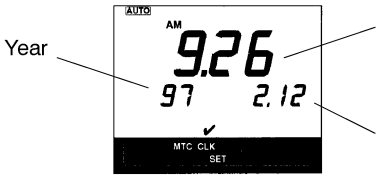
MTC lights up.

Set the temperature using the ▲ and ▼ (UP and DOWN) keys.
Setting range: 0.0 – 100.0°C

❑CLOCK SET mode (Setting time)

The date and time are displayed only when an extended unit is attached.

Press the F key to select the TIME SET mode.



The year, month, day, hours, and minutes will appear on the screen and the selected mode will flash.

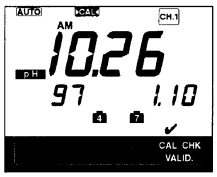
Press the CAL key to select the year month, day, hours, or minutes mode.

Use the keys to set the values, then press the DATA IN key to fix the settings. When the settings are fixed, the year display will flash again.

Note▶▶▶ The clock uses a 12–hour display.

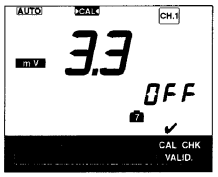
❑VALIDATION mode (calibration history)

Press the F key to select the VALIDATION mode.

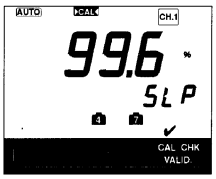


The most recently set year month and day will be displayed. "– – –" is displayed when no extended unit is connected to the pH meter.

Press the ▲ (UP) key to light up the 7 and display the offset value (asymmetry potential).



Press the ▲ (UP) key again to light up the 4 and 7 (when conducting a two-point calibration using pH 4 and pH 7) and display the slope value.



Press the ▲ (UP) key again, when conducting a three-point calibration, to light up the 7 and 9 and display the slope value.
Press the ▲ (UP) key again to return to the most recent date and time display.
Use the ▼ (DOWN) key to return to the most recent date and time screen in reverse order.

Note▶▶▶ The calibration history is limited to pH and ion measurements.

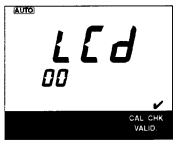
❑Setting key-lock

With the power OFF, press the POWER key while holding down the ▲ (UP) key, to turn the power ON and activate the key-lock function. The key-lock function allows only the MEAS and POWER keys to work. When the key-lock is activated, “LOCK” appears in the LCD. To clear the key-lock setting, turn the power OFF once, then turn it back ON again.

3.4 CHECK mode

❑CHECK mode start–up

Press the F key to display the LCD CHECK screen (item no. 00) and enter the CHECK mode.



Start–up screen for CHECK mode

❑Kinds of CHECK modes

The CHECK mode enables the following.

Item	Name	Explanation	Page
00	LCD check	Enables check for whether or not all LCD segments are displayed	p. 52
01	Battery voltage check	Enables simple check of battery voltage	p. 52
02	Temperature display calibration	Adjusts the display of the temperature sensor to the actual temperature.	p. 53
03	Automatic power–off setting	Turns ON/OFF the setting that automatically turns the power OFF if no keys are touched for a 30–minute period	p. 54
04	Electrode ID no. setting	Sets the electrode ID numbers that are output when the calibration history is printed, if an extended unit (sold separately) and printer (sold separately) are being used	p. 54
05	pH/ion CH setting (D–23 only)	Enables CH1 and CH2 to be used and both channels to be set for pH measurement (ion measurement)	p. 55
06	Initializing settings	Initializes all settings (See p. 86 for the values of default settings.)	p. 55

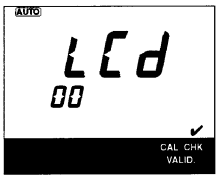
07	Conductivity units setting (D–24 only)	Enables the conductivity display units to be changed. Refer to the operation manual for the conductivity meter.	Separate booklet
08	Calibration frequency setting	Counts the number of measurements performed on AUTO HOLD since calibration was performed, and displays “ERR” is the set number of measurements is exceeded.	p. 56
09 (*)	Printing test	Conducts a printing test for the printer	p. 57
10 (*)	RS–232C output test	Conducts a test for RS–232C output	p. 57
11 (*)	Recorder output zero and span adjustment	Conducts fine adjustment of the recorder output	p. 58

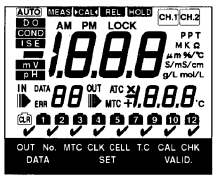
*: Valid only when an extended unit is connected.

- **LCD check (item no. 00)**

  Displays all segments of the LCD

  1. Press the DATA IN key.
     Confirm that all segments of the LCD are displayed.
  2. Use the MODE key to proceed to the battery voltage check (item no. 01).



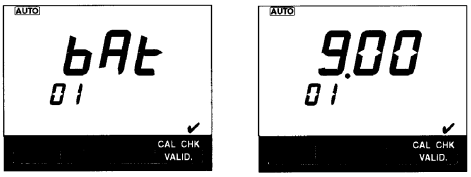


- **Battery voltage check (item no. 01)**

  Displays the battery voltage

  1. Press the DATA IN key.
     The battery voltage (V) is displayed.

2. Use the MODE key to proceed to the temperature zero adjustment (item no. 02).

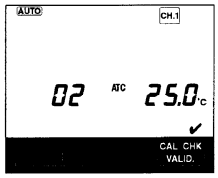


Note▶▶▶ The battery voltage alarm is set to approximately 6 V. When the battery voltage in this mode drops below 7 V, it indicates that the time for battery replacement is approaching. The current flowing from the battery is different at each terminal, so the voltage displayed in this mode is slightly lower than the actual voltage.

● Temperature display calibration (item no. 02)

This mode uses a known temperature to calibrate the temperature compensation value. This mode is used when calibrating the temperature of the thermometer.

1. Press the CAL key to switch between CH1 and CH2.
2. Use the ▲ (UP) and ▼ (DOWN) keys to set the temperature.
3. Press the DATA IN key. Save the zero factor to memory.
4. Use the MODE key to proceed to automatic power–off settings (item no. 03).



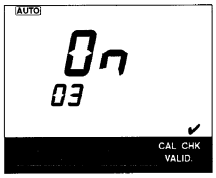
Note▶▶▶ The temperature sensor attached to the electrode maintains accuracy to within approximately ±1°C, even without

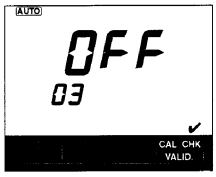
calibration. The above mode should be used when greater precision than ±1 °C is required.

• Automatic power–off settings (item no. 03)

Turns the automatic power–off mode ON and OFF.
When the automatic power–off mode has been set to ON, the power to the pH meter automatically turns OFF if there are no key operations for a 30–minute period of time.

1. Press the ▲ or ▼ (UP or DOWN) key to set the automatic power–off mode to ON/OFF.
2. Use the MODE key to proceed to electrode ID number. settings (item no. 04).

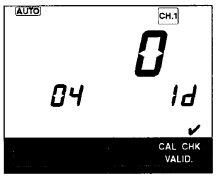




• Electrode ID no. settings (item no. 04)

Sets the Electrode ID no. When the printer is used to print out the calibration history, it is printed according to the electrode ID numbers.
Use this mode to control which electrodes have been calibrated.

1. Press the CAL key to switch between CH1 and CH2.
2. Use the ▲ (UP) and ▼ (DOWN) keys to set the electrode ID no.
3. Use the MODE key to proceed to initialization of settings (item no. 06)

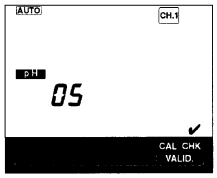


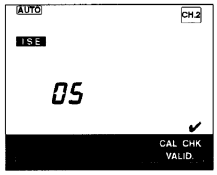
Note▶▶▶ Proceed to pH/ion channel setting range : 0 – 1999 (item no. 05) with the D–23 only.

- **pH/ion CH setting (item no. 05) (For D–23 only)**

  Changes the pH/ion CH (channel) to be changed to enable both channels to measure pH.

  1. Press the CAL key to switch between CH1 and CH2.
  2. Use the ▲ or ▼ (UP or DOWN) key to select the pH/ion measurement channel.
  3. Use the MODE key to proceed to initialization of settings (item no. 06)

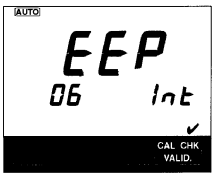


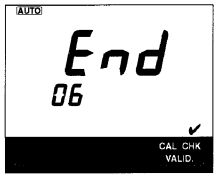


- **Initialization of settings (item no. 6)**

  This mode returns all settings to the default settings. Use this mode to return the pH meter settings to the same state as when the meter was purchased.

  1. Press the DATA IN key to initialized the settings.
  2. Use the MODE key to proceed to calibration cycle setting (item no. 8).





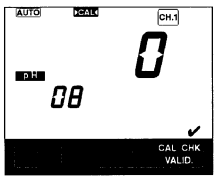
Note▶▶▶ Details about what is initialized are provided on page 86.

Note▶▶▶ Proceed to conductivity units setting (item no. 07) with the D–24 only.

• Calibration frequency setting (item no. 08)

This mode counts the number of measurements performed in AUTO HOLD since the time of the last calibration and enables display of “ERR08” when the number of measurements exceeds the setting. Use this mode to control calibration frequency according to the number of measurements conducted.

1. Use the ▲ and ▼ (UP and DOWN) keys to set the calibration frequency.
2. Use the MODE key to proceed to printer connection and printing test (item no. 09).

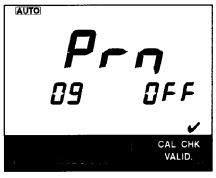


Note▶▶▶ When calibration frequency setting is ”0”,this mode doesn’t display of ”ERR08”.

• Printer connection and printing test (item no. 09)

This mode is valid only when an extended unit is attached. A printing test is conducted if a printer is connected.

1. Press the DATA IN key to start the printing test.
   When conditions are normal, “Print” is displayed. When conditions are not normal, “Err” is displayed.
2. Use the MODE key to proceed to RS–232C output check (item no. 10).



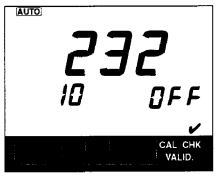
(This screen appears when no printer is connected.)

Note▶▶▶ For details on what is printed, refer to the operation manual for the extended unit.

• RS–232C output check (item no. 10)

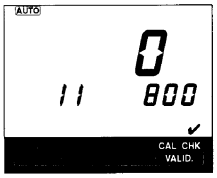
This mode checks the extended unit connection.

1. This mode connect an extended unit and displays “OFF” if the connect is not normal.
2. Use the MODE key to proceed to recorder output zero and span adjustment (item no. 11).



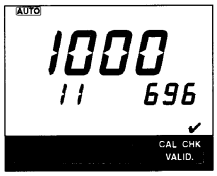
• Recorder output zero and span adjustment (item no. 11)

This mode is valid only when an extended unit is attached.
This mode adjusts the zero and span values of the recorder output
Use this mode to measure the output voltage from the tester, etc.



Zero adjustment (0 mV)

1. Use the ▲ and ▼ (UP and DOWN) keys to set the tester voltage to 0 mV.
2. Press the DATA IN key to set the zero adjustment.
3. Move to span adjustment.



Span adjustment (1000 mV)

4. Use the ▲ and ▼ (UP and DOWN) keys to set the tester voltage to 1000 mV.
5. Press the DATA IN key to set the span value.
6. Return to zero adjustment.
7. Use the MODE key to return to the LCD check (item no. 00).

Note▶▶▶ Be sure to adjust both zero and span.

Ref.▶▶▶ The above settings are for 100 mV/pH.
For 50 mV/pH, set the span adjustment to 500 mV.

Note▶▶▶ Press the MEAS key when in the CHECK modes to go back INSTANTANEOUS VALUE MEASUREMENT.

This chapter explains how to perform daily maintenance of the pH meter and how to deal with error messages. Daily maintenance is vital in assuring accurate measurement and preventing breakdowns before they occur. Maintenance of the electrodes is especially important; if ignored, various problems and erroneous measurements may result. This pH meter is equipped with a convenient error message function. If an error message is displayed be sure to take appropriate action.

4 Maintenance and troubleshooting

4. Maintenance and troubleshooting

4.1 Electrode maintenance

Maintain your electrodes by referring to the following information or to the operation manuals for the electrodes.

❑pH (ORP) electrode maintenance

Injury warning

Warning

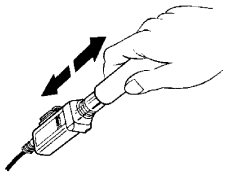
Glass fragments cause injury.
The outer tube of the electrode and the tip of the electrode are made from glass. Use care not to break them.

The following explanation is about pH electrodes (9620−10D) ORP electrodes should be cared for in the same manner.

- **Extended storage**

When an electrode is not to be used for a long period of time, store the electrode after performing the following procedure. Also, replace the reference solution every three to six months, using the method explained below.

1. Remove the electrode from the pH meter.
2. Remove the protective cap from the electrode.

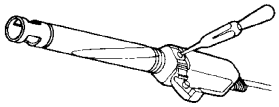


Chemical warning

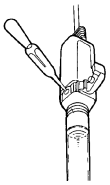
Warning

The liquid inside the electrode is highly concentrated potassium chloride (3.33 mol/L KCl).
If the internal solution in the electrode comes in contact with your hands or skin, wash immediately with water. If the internal solution comes in contact with your eyes, flush immediately with large amounts of water and seek treatment by a physician.

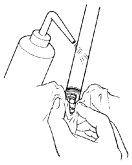
3. Open the internal solution filler port by removing the rubber stopper, then use a plunger to remove the reference solution.



4. Fill the electrode with new reference solution (#300), until it nears the rubber stopper.



5. Wash the tip of the electrode well with pure (ion exchange) water and wipe it with filter or tissue paper. If the liquid on the inside of the electrode cap has dried, wash the inside of the electrode cap with pure (ion exchange) water, then, after shaking out the water, fill the cap with enough pure (ion exchange) water to soak the sponge.



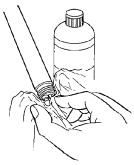
Note▶▶▶ If the solution inside the protective cap for the electrode has dried up and the electrode has not been used for an extended period of time, the response speed of the electrode may have slowed and its sensitivity may have decreased.

❑Washing electrodes

If the tip of the pH electrode is extremely dirty, the speed of its response may slow and it may cause errors in measurement. If the electrode is so dirty that it cannot be cleaned by rinsing with pure (ion exchange) water, wash the electrode using the method below that is most appropriate.

■ General dirt & oily grime

Wipe the dirt/grime off using cotton gauze that contains a neutral detergent.



■ Inorganic grime

Rinse using a hydrochloric acid solution of approximately 1 mol/L. Be sure not to soak the electrode in strong acid for a long period of time.

Note▶▶▶ 1 mol/L hydrochloric acid solution is made by diluting commercially available concentrated hydrochloric acid by a factor of ten.

4.2 Troubleshooting

The D−20 Series of hand held pH meters is equipped with a simply error−message function to notify the operator that an operation error or problem with the equipment has occurred. Errors or other problems that occur while in the MEASUREMENT mode are announced by an ”Error no.” appearing in the lower left−hand corner of the display.

❑Error message chart

Error no.	Message
ERR 01	Memory error
ERR 02	Battery voltage low
ERR 03	Electrode stability error
ERR 04	Asymmetry potential error
ERR 05	Electrode sensitivity error (pH)
ERR 06	Max. calibration points exceeded
ERR 07	Cannot identify standard solution
ERR 08	Calibration cycle error
ERR 09	Printer error

• ERR 01 Problem with memory

Explanation | Data cannot be read from or written to the internal memory.

Cause	How to solve problem
The internal IC is defective.	Seek repairs at your nearest retail outlet or HORIBA service station.

• ERR 02 The battery voltage is low

Explanation | The battery has insufficient voltage.

Cause	How to solve problem
The battery voltage is low.	Replace the dry−cell battery.
Dry−cell battery is not inserted correctly.	Insert the dry−cell battery (6F22) correctly.

• ERR 03 The electrode will not stabilize

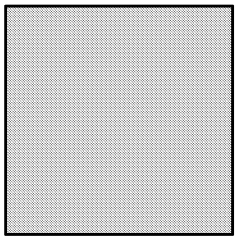
Explanation | The electric potential did not stabilize within three minutes.

Cause	How to solve problem
This is caused by the effect of the sample solution (when the sample solution is pure water or other solution with low conductivity or the pH concentration or temperature change).	Press the MEAS key again while ”HOLD” is either flashing or steadily lit in the display, to measure the sample using instantaneous value measurement.
The electrode is dirty.	Wash the electrode.
The electrode is cracked.	Replace the electrode.
The responsive glass membrane of the electrode has been dry for a long time.	Soak the membrane (on the electrode) in pure (ion exchange) water for 24 hours.
The temperature of the sample solution is fluctuating.	Measure after the sample solution temperature stabilizes.

• ERR 04 There is an error with the asymmetry potential

Explanation The asymmetry potential of the electrode is ±45 mV or more.

Cause	How to solve problem
The electrode is dirty.	Wash the electrode.
The electrode is cracked.	Replace the electrode.
The reference solution concentration is fluctuating.	Replace the internal solution in the reference electrode.
The electrode is not connected correctly.	Connect the electrode correctly.
Electrode is not submerged deeply enough to cover reference junction.	Immerse the electrode in the sample, to at least three centimeters beyond the electrode tip.
There is problem with the standard buffers.	Prepare the standard buffer anew.



- **ERR 05 There is an error in electrode sensitivity**

Explanation The electrode sensitivity is either 105% or more or 90% or less than the theoretical sensitivity.

Cause	How to solve problem
The electrode is dirty.	Wash the electrode.
The electrode is cracked.	Replace the electrode.
Calibration was not performed correctly.	Redo the calibration correctly.
There is a problem with the standard solution.	Use fresh standard buffer.
The electrode is not connected correctly.	Connect the electrode correctly.
Electrode is not submerged deeply enough to cover reference junction.	Immerse the electrode in the sample, to at least three centimeters beyond the electrode tip.

- **ERR 06 No more than three points can be calibrated**

No more than three kinds of standard solution can be used for calibration. Refer to the section entitled ”Standard solution calibration” (p. 32) of this operation manual.

• ERR 07 The pH meter cannot identify the standard buffer

Explanation If the automatic standard−buffer identification function of the meter cannot identify kinds of standard buffer, re−calibrate the meter after performing the appropriate measures, below.

Cause	How to solve problem
There is a problem with the standard solution.	Prepare the standard solution anew.
There is a problem with the standard solution setting.	Check the NBS or US standards settings and the kind of standard solution used for calibration, and make sure they match.
The responsive membrane is dry or dirty.	Measure after washing the responsive membrane and soaking it in pure (ion exchange) water for 24 hours.
The reference solution is contaminated.	Replace the reference solution with new solution.
The responsive membrane is damaged or worn out.	Replace the electrode.

• ERR 08 The number of measurements set for calibration frequency has been exceeded

Explanation This error appears when the number of measurements set for the calibration cycle has been exceeded since the last calibration was conducted.

The meter should be re−calibrated.

● ERR 09 There is a problem with the printer unit

Definition If a problem occurs with the printer unit, turn OFF the power to the meter, perform the appropriate measure below, then turn the power to the meter back ON.

Cause	How to solve problem
The printer paper is jammed.	Remove the jammed paper.
There is no printer paper.	Load new paper in the printer.
There is a problem with the printer unit connection.	Reconnect the printer after making sure the connector parts are okay.
The printer is defective.	Replace the printer.

4.3 More troubleshooting

This section explains how to respond to various symptoms of trouble that are not indicated by an error number.

• Nothing shows up on the display when the power is turned ON

Cause	How to solve problem
The battery is not loaded.	Place a battery in the meter.
The battery is loaded with the poles reversed.	Re-insert the battery with the poles correctly oriented.
The battery voltage is low.	Remove the old battery and correctly insert a 6F22 dry-cell battery. If an extended unit is being used, connect the optional AC adapter.
There is a problem with the battery snap connection.	Tighten the battery snap plus terminal using a plier, etc.

• The indicated value fluctuates

When there is a problem with the electrode...

Cause	How to solve problem
The responsive membrane is dry or dirty.	Wash the responsive membrane.
The responsive membrane is damaged or worn out.	Replace the electrode.
There are air bubbles on the electrode.	Shake the electrode to remove the air bubbles.
There is no reference solution remaining.	Fill the electrode with new reference solution, as noted in the electrode operation manual.
The wrong reference solution is being used.	Use the correct reference solution.

● The indicated value fluctuates

When there is a problem with the main unit of the pH meter...

Cause	How to solve problem
There is a motor or other device causing electrical interference.	Move the meter to a place where it is not subject to dielectric effects. Devices that use commercial electricity must always use a meter that has a ground (earth) terminal.
The electrode is not connected correctly.	Connect the electrode correctly.

● The indicated value fluctuates

When there is a problem with the standard solution...

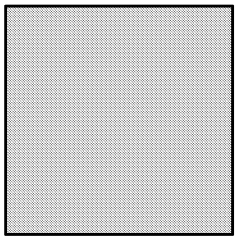
Cause	How to solve problem
The liquid junction is not immersed in the sample solution.	Immerse the electrode in the sample solution up until the liquid junction.
This is caused by the effects of the sample.	Judge by measuring with a stable standard solution.

● The response is slow

Cause	How to solve problem
This is caused by the effects of the sample.	Response time may slow down, depending on the properties of the sample solution.
The electrode is dry or dirty.	Wash the responsive membrane.
The electrode is cracked.	Replace the electrode.
There is a problem with the reference solution.	Fill the electrode with new reference solution, as noted in the electrode operation manual.

- **The indicated value does not change/There is absolutely no response**

Cause	How to solve problem
The key–lock function is ON.	Turn the power OFF, then turn it back ON again.
The system is locked.	Turn the power OFF, then turn it back ON again.
The electrode connector is not attached correctly.	Attach the electrode connector correctly.
The electrode is defective. (The responsive membrane is cracked.)	Replace the electrode.



● The measured value is flashing

The pH value exceeds the measurement range (when pH value is displayed).

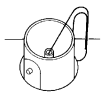
Measurement range: pH 0.00 – pH 14.00

The mV value exceeds the measurement parameters (when mV value is displayed).

Display range: ± 1999

Cause	How to solve problem
The sample solution is inappropriate.	Change to a sample solution with properties within the measurement range.
The liquid junction is not immersed in the sample solution.	Immerse the electrode in the sample solution all the way until the liquid junction.
The electrode cable has been severed.	Replace the electrode.
The main body of the pH meter is defective.	Check the point described below.
The meter has not been calibrated or it has been calibrated incorrectly.	Calibrate the meter correctly.

Check this point



Short the pin at the center of the electrode connector with the metal part. If the flashing measured value disappears when this is done, the meter is normal.

- **The temperature display is flashing.**
  The temperature display does not change from 25°C.

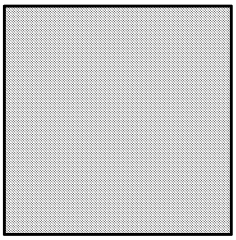
  The temperature measurement exceeds the measurement range.

  Measurement range: –10 – 100.0°C

Cause	How to solve problem
The temperature of the sample solution exceed the measurement range.	Check the temperature of the sample solution and change to a sample solution that has a temperature within the measurement range.
The thermistor connection within the electrode is severed or shorted.	Measure the resistance of the temperature sensor connector. If it is 50 kΩ or more at room temperature, replace the electrode.
The electrode connector is not attached properly.	Attach the electrode connector properly, such that the O–ring on the temperature connector disappears from sight.
The main unit of the pH meter may be defective.	In temperature display calibration mode (See p. 53.) check whether or not the ”minus” display appears, regardless of whether or not there is a temperature connector.
There is a problem with the setting for the temperature display calibration mode (See p. 53.).	Initialize the settings (See p. 55.).

● Measurements are not repeatable

Cause	How to solve problem
The effects of the sample solution.	The pH or other properties of the sample solution may have changed over time, making reproducibility poor.
The responsive membrane is dry or dirty.	Wash the responsive membrane.
There is not enough reference solution or it is dirty.	Replace the reference solution with a new solution.
The responsive membrane is cracked or worn out.	Replace the electrode.



This chapter provides a simple compilation of information for people who would like to know more details about the functions of the main unit of the pH meter and other measurement principles.

5 Reference

5. Reference

5.1 pH measurement

• pH measurement and temperature

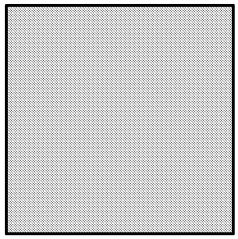
The temperature of the solution being inspected is an important parameter in the accurate measurement of pH. There are many possible sources of errors during measurement, such as the state of the solution junction potential, asymmetric potential, and reference solution pH concentration, but all of these items contain factors that change with the temperature. The best way to minimize these potential causes of errors is to keep the temperature of the pH standard solution uniform at the time of calibration.

• Liquid junction potential

“Liquid junction potential” is the electric potential that occurs to a greater or lesser degree at the liquid junction. The size of the electric potential differs depending on the type of solution, temperature of the solution, and the structure of the liquid junction.

When solutions of different compositions come in contact, ion diffusion occurs on the contact surface between the two solutions. The ions are of various sizes, so a difference occurs in the diffusion transfer speed.

As diffusion proceeds, a difference in charges occurs on the contact surface of the two solutions, giving rise to a difference in potential. This potential works to reduce the transfer speed of fast ions and increase the speed of slow ions, ultimately achieving a state of equilibrium when the transfer speed of the positive and negative ions on the contact surface of the two solutions is equal. In this state of equilibrium, the potential at the contact surface between the two solutions is called the “liquid junction potential.” A large liquid junction potential means very inaccurate measurement.



- **Asymmetric potential**

  The glass electrode is immersed in a pH 7 reference solution. When the electrode is immersed in the pH 7 solution, both the internal and external sides of the electrode membrane are supposed to take on a pH of 7, making the potential 0. In actuality, however, a potential does occur. This potential is called an “asymmetric potential.” The size of an asymmetric potential differs depending on any stress that may have occurred during the processing of the glass and the shape and compositions of the glass. Asymmetric potential also changes depending on the degree of contamination of the reference solution and the state of the glass membrane. Also, if the electrode membrane dries out, a large asymmetric potential will occur, giving rise to measurement errors.

- **Temperature compensation**

  The electromotive force generated by the glass electrode changes depending on the temperature of the solution. “Temperature compensation” is what is used to compensate for the change in electromotive forces caused by temperature. There is absolutely no relation between the change in pH caused by the temperature of the solution and temperature compensation. This is often misunderstood. When pH is to be measured, the temperature of the solution when the pH is measured must be recorded along with that pH value, even if a meter that has automatic temperature compensation is used. If the solution temperature is not recorded, the results of the pH measurement are relatively meaningless.

5.2 pH standard solution

• Types of standard solutions

When measuring pH, the pH meter must be calibrated using a standard solution. There are several kinds of standard solutions." For normal measurement, three standard solutions –– with a pH of 4, 7, and 9 –– are sufficient to accurately calibrate the meter.

pH 1.68 standard solution: **Oxalate**	0.05 mol/L tetra–potassium oxalate aqueous solution
pH 4.00 standard solution: **Phthalate**	0.05 mol/L potassium hydrogen phthalate aqueous solution
pH 6.86 standard solution: **Neutral phosphate**	0.025 mol/L potassium dihydrogen phosphate, 0.025 mol/L sodium dihydrogenphosphate aqueous solution
pH 9.18 standard solution: **Borate**	0.01 mol/L tetra–sodium boric acid (boric sand) aqueous solution
pH 12.45 standard solution: **Saturated calcium hydroxide solution**	Saturated hydrogenated calcium solution

pH values of pH standard solutions at various temperatures (NIST(former NBS) settings)

Temp. (°C)	pH 1.68 standard solution Oxalate	pH 4.00 standard solution Phthalate	pH 6.86 standard solution Neutral phosphate	pH 9.18 standard solution Borate	pH 12.45 standard solution Saturated calcium hydroxide solution
0	1.666	4.003	6.984	9.464	13.423
5	1.668	3.999	6.951	9.395	13.207
10	1.670	3.998	6.923	9.332	13.003
15	1.672	3.999	6.900	9.276	12.810
20	1.675	4.002	6.881	9.225	12.627
25	1.679	4.008	6.865	9.180	12.454
30	1.683	4.015	6.853	9.139	12.289
35	1.688	4.024	6.844	9.102	12.133
38	1.691	4.030	6.840	9.081	12.043
40	1.694	4.035	6.833	9.068	11.984
45	1.700	4.047	6.834	9.038	11.841

Ref.▶▶▶ When the standard solutions use U.S. settings, pH 7 is a shown in the below table and pH 9 becomes pH 10.

Temp. (°C)	pH 7 standard solution Neutral phosphate	pH 10 standard solution Carbonate
0	7.119	10.318
5	7.086	10.245
10	7.058	10.178
15	7.035	10.117
20	7.015	10.061
25	7.000	10.011
30	6.988	9.965
35	6.979	9.925
40	6.973	9.888
45	6.969	9.856

Note▶▶▶ Calibration is performed using Nernst's equation with the above values.

● Using standard solutions

Standard solutions are used to calibrate the scale of the pH meter employed to measure the unknown pH of a solution. Standard solutions of pH 4, 7, and 9 are used in combination according to the particular conditions of the solution that is to be inspected.

When the approximate pH value is desired (1−point calibration)

Use the pH 7 standard solution or a standard solution that approximates the pH value of the solution that is to be inspected.

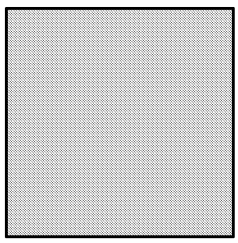
When it is known beforehand whether the test solution is acidic or alkaline (2−point calibration)

Acidic: Use the pH 4 and 7 standard solution.
Alkaline: Use the pH 7 and 9 standard solution.

When an unknown solution is to be inspected (3−point calibration)

Use the pH 4, 7, and 9 standard solution.

When finding the pH of other solutions, perform 2−point or 3−point calibration using pH 2, 4, 7, 9, or 12 standard solutions randomly, then measure the test solution.



5.3 Measuring mV (oxidation–reduction potential [ORP])

• ORP principles

ORP (or “redox potential”) is an abbreviation for oxidation–reduction potential. ORP is the energy level (potential) determined according to the state of equilibrium between the oxidants (M^{z+}) and reductants ($M^{(z-n)+}$) that coexist within a solution.

One type of equilibrium in a solution

$$M^{z+} + ne^- \Leftrightarrow M^{(z-n)+} \quad \cdots\cdots\cdots ①$$

If only ① exists within a solution, a metal electrode (platinum, gold, etc.) and a reference electrode are inserted into the solution, forming the ORP measuring system shown in Fig. 5–1. Measuring the potential (ORP) that exists between the two electrodes enables the potential to generally be expressed by the following equation.

$$E = E_0 - \frac{RT}{nF} \ln \frac{aM^{(z-n)+}}{aM^{z+}} \quad \cdots\cdots\cdots ②$$

E: Electric potential E_0: Coefficient R: Gas coefficient
T: Absolute temperature n: Electron count
F: Faraday constant a: Activity

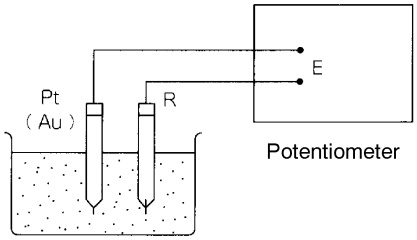


Fig.5–1 ORP measuring system

For example, for a solution in which trivalent iron ions coexist with bivalent iron ions, equations ① and ② would be as follows.

$$Fe^{3+} + e^{-} \Leftrightarrow Fe^{2+} \quad \cdots\cdots\cdots\cdots \text{①'}$$

$$E = E_0 - \frac{RT}{F} \ln \frac{aFe^{2+}}{aFe^{3+}} \quad \cdots\cdots\cdots \text{②'}$$

When only one type of state of equilibrium ① exists in the solution, the ORP of the solution can only be determined by equation ②. What is important here is that ORP is determined by the ratio of activity between the oxidant (Fe^{3+}) and the reductant (Fe^{2+}) (using the equation a $Fe^{2+}/a\,Fe^{3+}$). In actuality, however many kinds of states of equilibrium exist simultaneously between various kinds of ions, in most solutions. This means that under actual circumstances, ORP cannot be expressed using the simple equation shown above and that the physical and chemical significance with respect to the solution is not very clear.
In this respect, the value of ORP must be understood to be only one indicator of the property of a solution.
The measurement of ORP is widely used, however, as an important index in the analysis of solutions (potentiometric titration) and in the disposal and treatment of solutions. Recently, there have appeared various claims regarding this matter, such as that a high degree of ORP is effective in sterilization or that drinking water that has a low ORP reduces the chance of illness by reacting with the activated oxygen in the cells of the body. ORP is used as an index for alkaline drinking water.

• Standard electrode (reference electrode) types and ORP

The ORP of a solution that is obtained through measurement is a value that corresponds to the reference electrode employed. If different kinds of reference electrodes are used for measurement, the ORP value of the same solution may appear to be different. HORIBA uses Ag/AgCl

with 3.33 mol/L KCl as the reference solution for reference electrodes. According to general technical literature, standard hydrogen electrodes (N.H.E.) are often used as the standard electrode. The relationship between N.H.E. and the ORP that is measured using an Ag/AgCl with 3.33 mol/L KCl electrode is expressed by the following equation.

$E_{N.H.E.} = E + 206 - 0.7\,(t - 25) mV \quad t = 0 - 60\,℃$

$E_{N.H.E.}$: Measured ORP value using N.H.E. as the reference electrode

E: Measured ORP value using Ag/AgCl with 3.33 mol/L KCl as the reference electrode

- **Potential sign**

Standard ORP is expressed in the following way, in literature related to electrochemistry and analytical chemistry.

$A \qquad Li^{+} + e^{-} \rightarrow Li$

$E_0 = -3.024V \quad VS \ N.H.E.$

However, in some literature, the "+" and "–" signs are reversed.

$B \qquad Li \rightarrow Li^{+} + e^{-}$

$E_0 = +3.024V \quad VS \ N.H.E.$

In expressions like B, above, the reaction is just reversed and there is no essential difference. But this kind of expression does invite confusion. The majority of the world, today, is consistent in its use of the signs as they are used in A, above. For this reason, HORIBA, too, uses signs concerning ORP that are consistent with A, above.

● ORP standard solution

There are two kinds of standards substances. Under normal circumstances, it is sufficient to use only the one type of substance that is closest to the measured value.

Table 1. Indicated value of ORP standard solution at various temperatures

Standard solution C°	160 – 22 Phthalic–acid chloride + quinhydrone	160 – 51 Neutral phosphate + quinhydrone
5	+274.2	+111.9
10	+270.9	+106.9
15	+266.8	+101.0
20	+262.5	+95.0
25	+257.6	+89.0
30	+253.5	+82.7
35	+248.6	+76.2
40	+243.6	+69.0

● Operation check using standard solution

Note▶▶▶ Standard solution is not used only for calibration of the meter, but to confirm whether or not the condition of electrodes is good.

1. Add 250 mL pure (ion exchange) water to one packet of any of the above listed standard solutions and mix well. (When mixing, the excess quinhydrone [a black powder] will float to the surface of the solution.)
2. Immerse a washed and dried ORP electrode in the ORP standard solution and measure the mV value.
3. If the electrode and the meter, itself, are working correctly, numerical values within 15 mV or less of those listed in Table 1 should be obtained.

4. If measurements that fall within 15 mV of the values listed above are not obtained using this method, measure the solution again after replacing the reference electrode internal solution and removing the dirt from the surface of the metal electrode by moistening a cotton swab with alcohol or a neutral cleaning agent and lightly rubbing the electrode or by soaking the electrode in diluted nitric acid (1:1 nitric acid).
5. If measurements within 15 mV of the values listed above are still not obtained after re−measuring, the reference electrode or the meter may be faulty. Either replace the electrode or have the meter inspected.

Note▶▶▶ If the prepared ORP standard solution is allowed to stand in open air for one hour or more, it may undergo transformation. For this reasons ORP standard solution that has finished being prepared cannot be stored.
When measuring a solution that has low concentrations of oxidants and reductants after conducting an operational check using a standard substance, the measured values may not stabilize or the results of measurement might not be repeatable. If this is the case, use the meter after immersing the electrodes in the solution again and mixing it thoroughly.

● Precautions when measuring actual samples

- Note that when measuring the ORP of solution that has extremely low concentrations of oxidants and reductants, such as tap water, well water, or water treated with purifying equipment, there may be less responsiveness, repeatability, and stability, in general.
- When alkaline water is allowed to stand, its ORP undergoes big changes. Always measure alkaline ion water promptly.

5.4 Default settings

Category	Item	Default values
Common	MEASUREMENT mode	pH
	DATA IN	No. 1
	DATA OUT	No. 1
	Temperature compensation	Automatic temperature compensation
	Manual temperature compensation	25℃
	Automatic power–OFF	Approx. 30 min (ON)
	Electrode ID	000
	Calibration cycle	0
	Clock settings	1997, 1, 1, 12:00
pH	Standard calibration solution	NIST (former NBS)
	Calibration settings	Asymmetry potential: 0 mV Sensitivity: 100%

Note▶▶▶ The calibration settings for the pH category are the default values before calibration. The values are automatically updated when calibration is performed.

Note▶▶▶ The clock function uses the initial (default) settings from when the extended unit is newly connected.

5.5 Specifications

Note ○: Applicable –: Unapplicable

Item		D-21	D-22	D-23	D-24	D-25
pH		○	○	○	○	○
	Measuring principle	Glass electrode				
	Display range	pH –2.00 to 16.00				
	Resolution	0.01 pH				
	Repeatability	±0.01 pH ±1digit				
Temp.		○	○	○	○	○
	Measuring principle	Thermistor				
	Display range	–10.0 to 100.0℃				
	Resolution	0.1℃				
	Repeatability	±0.1℃ ±1digit				
mV		–	○	○	○	○
	Display range	–1999 to 1999 mV (input range ±1600 mV)				
	Resolution	1 mV				
	Repeatability	±1 mV ±1digit				
Ion		–	–	○	–	–
	Measuring principle	Ion electrode				
	Display range	0.00 μg/L to 99.9 g/L(mol/L)				
	Resolution	Valid numbers 3 digits				
	Repeatability	±0.5% of full scale				
Conductivity		–	–	–	○	–
	Measuring principle	2 AC electrode				
	Display range SI units (Former units)	 0.0 μS/m to 199.9 S/m (0.0 μS/cm to 1.999 S/cm)				
	Resolution	0.05% of full scale				
	Repeatability	±0.5% of full scale				
Dissolved Oxygen		–	–	–	–	○
	Measuring principle	Membrane galvanic cell				
	Display range	0.00 to 19.99 mg/L				
	Temperature compensation	0 to 40℃				
	Resolution	0.01 mg/L				
	Repeatability	±0.5% of full scale				

Item	D-21	D-22	D-23	D-24	D-25
Data memory capacity	Max.: 30 pieces of data				
Power	6F22 (S-006P) or 6LR61 dry cell with automatic power-off function AC adapter can be connected when extended unit is attached (sold separately)				
Acceptable ambient temperature	0 to 45 ℃				
Dimensions (with extended unit connected)	180(H) ×79(W) ×40(D) unit: mm [180(H) ×79(W) ×82(D)]				
Mass of main unit (incl. battery) (with extended unit connected)	Approx. 325 g (Approx. 425 g)	Approx. 325 g (Approx. 425 g)	Approx. 355 g (Approx. 455 g)	Approx. 350 g (Approx. 450 g)	Approx. 350 g (Approx. 450 g)

5.6 Accessories and options

❑Accessories

• Electrodes

Part name	Model	Accessory no.	Notes
pH electrode	9620–10D	9096–0001–00	Water–resistant plastic Combination pH electrode
pH electrode	9610–10D	9096–0002–00	Water–resistant thick membrane glass Combination pH electrode
ORP electrode (platinum)	9300–10D	9096–0004–00	Water–resistant Platinum combination electrode

Note▶▶▶ Information on ion, conductivity, and dissolved oxygen electrodes is contained in the operation manual entitled, “Operation Manual: Measuring ions, conductivity and dissolved oxygen.”

● Standard solution & reference solution

pH standard solution (500 mL) Accuracy: ±pH 0.02			
Part name	**Model**	**Accessory no.**	**Notes**
pH2	100–2	9003–0015–00	
pH4	100–4	9003–0016–00	
pH7	100–7	9003–0017–00	
pH9	100–9	9003–0018–00	

pH standard powder (for making 500 mL x 10 packets) Accuracy: ±pH 0.05			
Part name	**Model**	**Accessory no.**	**Notes**
pH2	150–2	9003–0026–00	
pH4	150–4	9003–0027–00	
pH7	150–7	9003–0028–00	
pH9	150–9	9003–0029–00	

Standard solution for ORP check			
Part name	**Model**	**Accessory no.**	**Notes**
ORP value: 95 mV	160–51	9003–0031–00	Electrode for Silver/Silver chloride at 20°C
ORP value: 262 mV	160–22	9003–0030–00	Electrode for Silver/Silver chloride at 20°C

Reference solution			
Part name	**Model**	**Accessory no.**	**Notes**
Reference solution	300	9003–0032–00	250 mL

❑Consumable items

Part name	Model	Accessory no.	Notes
Battery cover packing	–	9096–0013–00	–
EXT cover O–ring	–	9096–0014–00	S32

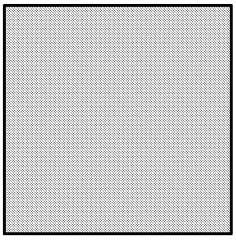
❑Options

Part name	Model	Accessory no.	Notes
Sensor adaptor	–	9096–0011–00	To hold 2 electrodes
Carrying case	–	9096–0012–00	–
Attache case	–	9096–0015–00	–
Extended unit	EX–20	–	–
Electrode stand	DP–20S	9096–0016–00	–
Analogue output cable	–	9078–0002–00	For use together with extended unit
AC adapter (Output: 9 V DC, 1 A)	AC–10 (100V)	9078–0001–00	100 V AC 50/60 Hz
	AC–10 (220V)*	–	220 V AC 50 Hz, 22 W For use together with extended unit

*AC–10(220V): Double insulation construction, CE Marking

Accessories, consumable items and options are available at HORIBA authorized dealers. Place orders by providing the name of the part, model and accessory number.

Notes



For technical questions regarding this pH meter, contact the following HORIBA representative.

HORIBA Customer Support Center
Toll-free tel. no. (within Japan):
0120-37-6045

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