METROHM AG CH-9101 Herisau (Switzerland)

pH Meter

704

Series 01 ...

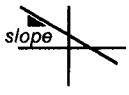
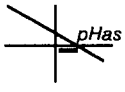
92.02 Ti/mm

8.704.1003

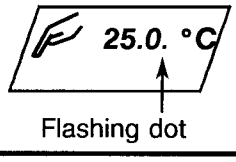
Selection of measured quantity

mode	Press <mode> key. Each keystroke changes the measured quantity from pH to °C to mV.

Meaning of the symbols in the display

Display	Meaning
	"A key must be pressed", e.g. <enter> or input of a value and <enter>.
	"Immerse electrode in buffer solution for calibration." Flashing beaker means "change buffer".
	Display of the calibration parameter "slope", relative slope of the electrode.
	Display of the calibration parameter "pHas", asymmetry pH.
	Drift display. Measured value drifts towards higher or lower value.
	The displayed temperature is measured with a Pt 1000.
hold 9	Hold buffer contains 9 values. Flashing "*hold 3*" means "the hold buffer is being viewed; the third value is displayed".
	Warning! Battery will soon be discharged. It will last for another 2-3 hours of operation.

Input of numbers

>> , ^  Flashing dot	Press <»> key several times until the dot at the bottom right of the position you wish to change flashes. Set the desired number with the <^> key. Press <enter> to store the value.

Exit

mode	Exit from – calibration (1-point calibration) – inquiries and entries – viewing the hold buffer – error messages

Configuration

config / 2nd

Call-up: <2nd> <config>.
Advance inquiries with <config> or <enter>.

Display	Meaning	Input range
d 0 hold	Drift-controlled transfer of a value to the hold buffer. 1 = yes: Value is transferred when <hold> key has been pressed and the drift criterion is met. 0 = no. 0 leads to the next inquiry:	0, 1
0.0min hold	Transfer of a value to the hold buffer after elapse of a preset time interval. Time starts when <hold> is pressed. Transfer can be stopped and restarted with <hold>. 0: Immediate transfer when <hold> is pressed.	0 ... 199.9 min
bE 1	Beeper 0 = no 1 = yes	0, 1
c 1	Display contrast	1 ... 4
t 3min	Time interval for automatic instrument shutdown after the last keystroke. 0 = no automatic shutdown.	0 ... 99 min
P 10	Display of the program version	

Parameters

param / pH cal

Call-up: <2nd> <param>.
Advance inquiries with <param> or <enter>.

Display	Meaning	Input range
25.0 °C	Temperature. If a temperature sensor is connected, the temperature is continuously updated.	–199.9 ... 199.9 °C
100.0 % slope	Calibration parameter "slope", relative slope of the electrode.	0.1 ... 199.9 %
7.00 pH pHas	Calibration parameter "pHas", asymmetry pH.	0.00 ... 14.00

Preselection of a buffer series

on/off + pH cal

Call-up: With instrument switched off, press <pH cal> and switch on instrument. Selection with <pH cal>, then <enter>.

– 1 – cal bu	1 Metrohm buffers 2 DIN/NBS buffers 3 Fisher buffers 4 Merck/Riedel deHaën buffers 5 Ciba/Geigy buffers SP Special buffers	The buffer series currently selected is marked, e.g. "- 1 -"

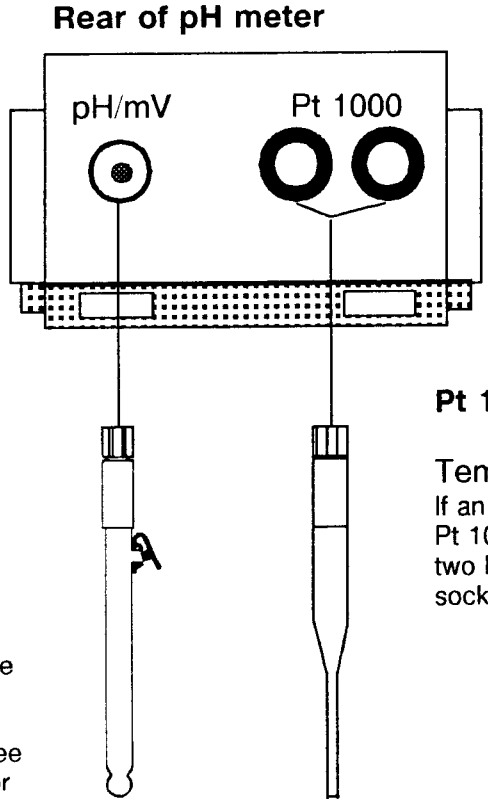
Instructions for Use for 704 pH Meter

Table of contents

1. Getting started

If you are starting operation with the 704 pH meter for the first time, it is advisable to read through section 4, pages 10 ff.

1.1 Connecting electrodes



Combined Electrode

pH or redox electrode.

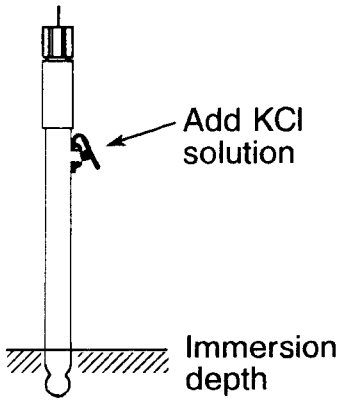
- Remove the protective cap from the electrode connector.
- Screw the cable to the electrode.
- Plug the other end of the electrode cable into the pH meter.

Please turn to page 29 to see what electrode is suitable for your measuring problem.

Pt 1000

Temperature sensor.
If an electrode with a built-in Pt 1000 is used, plug the two banana plugs into the sockets provided.

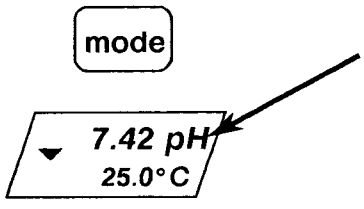
1.2 Measuring pH values



- Check whether your electrode contains sufficient KCl solution (3 mol/L). It should be filled to a depth just below the fill hole.
  During measurement, the fill hole should remain open.
  Immerse the electrode in the analysis solution until the diaphragm is covered (app. 2 cm).

- Switch on the 704 pH Meter: press the <on/off> key.

- Press the <mode> key once or more until "pH" appears in the display.
  The second line always shows the **temperature** as pH values are temperature dependent. If a Pt 1000 temperature sensor is connected, a **thermometer symbol** appears in front of the temperature which indicates that the displayed temperature has been measured. Without Pt 1000 , you should enter the current measuring temperature if it is not already correct, see page 4.
  The **triangle** in the display remains lit up until the pH value is "stable".



- Wait for the triangle in the display to disappear, i.e. your measured value is stable.

- Take the electrode out of the analysis solution and rinse it thoroughly with dist. water. If need be, carefully dry the electrode with a paper towel.

- Perform the next measurement.

For good pH measurements, a pH calibration should be performed, see following page.

After the measurement, the glass electrode must be stored in KCl solution, c = 3mol/L (in the reference electrolyte). Close the fill hole with the cap.
Never store in water: The AgCl of the reference system dissolves better in solutions containing chloride than in pure water (the chloro complex is formed). If an electrode is stored in water, AgCl can precipitate in the diaphragm (and clog it)!
Never store dry: Otherwise, the gel layer of the glass membrane will dry out.

The electrode can also be safely stored in the electrode holder after the measurement. Add KCl solution (3 mol/L) to the holder. See page 10 for instructions on how to mount the holders.

You will find details on pH measurements in Metrohm Application Bulletin 188. This is available free of charge from your Metrohm agency.

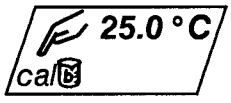
1.3 pH calibration

For pH measurements, a calibration is needed from time to time as the measuring properties of the electrodes change. Perform a calibration, e.g. daily before starting your measurements.
Two buffer solutions are required for this. If you are using Metrohm buffer solutions, you can immediately start the calibration. Other buffer solutions must first be preselected, see page 5.

- Immerse the electrode in the first buffer solution.

pH cal

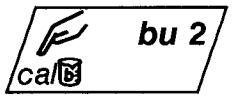
- Press the <pH cal> key.



- The display shows the temperature.
  The **finger** means that a key must be pressed.
  To **change** the **temperature**, use the <»> and <⇑> keys. Select the digit you wish to change with the <»> key. You will recognise the selected digit by the flashing dot at the bottom right. Now change the number using the <⇑> key: Press the key repeatedly until the desired digit is displayed. When the correct value is set, press <enter>.
  If you have a Pt 1000 temperature sensor connected, the temperature does not concern you, it will be measured directly.

enter

- Your first buffer solution is now measured. After the measurement, the display prompts you to immerse the electrode in the second buffer solution: The buffer beaker flashes. Carry this out and press <enter>.



- Your second buffer solution is measured.
- After the calibration, the slope and asymmetry pH (pHas) of the electrode are briefly displayed and the instrument is ready for pH measurements.
  If the pH meter comes to a stop on display of the slope or the asymmetry pH, the values are outside the limits, see page 7. If you then wish to accept the value, press <enter>. Otherwise, press <mode> to retain the old value.

enter

You have now calibrated the electrode and you are ready to start pH measurements.

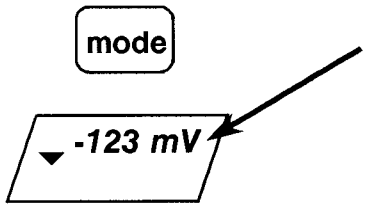
You can quit the calibration routine at any time by pressing the <mode> key.

The results of the calibration can be examined and changed with the key sequence <2nd> <param>, see supplement under "Parameters".

1.4 Measuring redox voltages and temperature

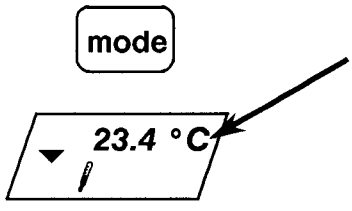
For redox voltage measurements you need a platinum or a gold electrode (see page 31) and for temperature measurements a Pt 1000 temperature sensor.

Redox voltages:



- Press the <mode> key once or more until "mV" appears in the display.
  If you have a Pt 1000 temperature sensor connected, the temperature together with the thermometer symbol will be displayed in the second line.
  The **triangle** in the display remains lit up until the measured value is "stable".

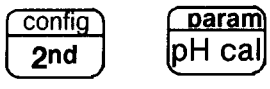
Temperature:



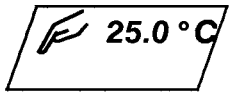
- Press the <mode> key once or more until "°C" appears in the display.
  The thermometer symbol lights up to show that the temperature has been measured.
  The **triangle** in the display remains lit up until the measured value is "stable".
  If you measure pH values or redox voltages and have a Pt 1000 temperature sensor connected, the measured temperature always appears in the second line of the display together with the thermometer symbol.

1.5 Adjusting the temperature

The measuring temperature can be set with the key sequence <2nd> <param>.



- Press <2nd> <param>.



- The temperature can now be set, see page 3.
  Measuring and calibration temperatures are identical. If you set a temperature in the calibration procedure, this is also assumed to be the measuring temperature. Conversely, any temperature set here applies to the calibration routine.

- Confirm the set value with <enter>.

- Quit the inquiry with <mode>.

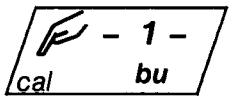
2. pH calibration

2.1 Selecting a buffer series

The instrument automatically recognises the buffers. As the pH values of different buffer series differ slightly, it is necessary to preselect the buffer series you wish to use in the subsequent calibration.
Metrohm buffers are preselected in the factory. If you wish to use a different buffer series, you have to select this.

Proceed as follows to select the buffer series:

on/off + pH cal



- Switch the instrument off.
- Press and hold the <pH cal> key while switching on the instrument (<on/off> key).
- The display for buffer selection appears.
  The number specifies the buffer series and the dashes "–" indicate which series is currently selected.
  The following buffer series can be selected:
  1 Metrohm buffers
  2 DIN/NBS buffers
  3 Fisher buffers
  4 Merck/Riedel deHaën buffers
  5 Ciba/Geigy buffers
  If you do not wish to use any of these buffers, select
  SP Special Buffers. For the calibration procedure with special buffers, see page 6.

pH cal

enter

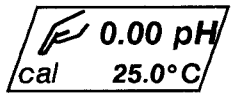
- Select the buffer series with the <pH cal> key: Press the key repeatedly until the desired buffer series is displayed. Confirm the series with <enter>.

2.2 pH calibration with special buffers

When you have selected a buffer series, turn to page 3 for the calibration procedure.

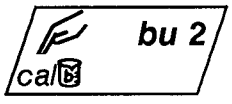
The calibration procedure with special buffers (buffer preselection SP) differs slightly from the "normal" calibration routine as the pH values of the buffers have to be entered:

- Immerse the electrode in the first buffer solution.
- Press the <pH cal> key.



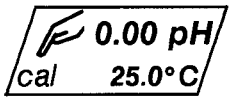
- The display shows the temperature, which you enter (keys <»>, <^> and <enter>) or which has been measured.

- Enter the pH value of your first buffer solution (keys <»> and <^>) and press <enter>. Note that the pH values of your buffer solution are temperature dependent!



- When you have entered the value, the first solution is measured.
  You are then prompted in the display to immerse the electrode in the second buffer solution. Carry this out and press the <enter> key.

- Enter the pH value of your second buffer solution and press <enter>.



- The second buffer solution is measured.
- On completion of the calibration, the slope and pHas (asymmetry pH) are briefly displayed.

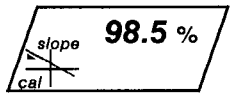
2.3 General information on pH calibration

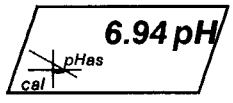
- The pH calibration remains stored even when the instrument is switched off.

- **Exit** from the calibration procedure is possible at any time with the <mode> key. If the <mode> key is pressed before measurement of the first buffer solution, the old calibration data are retained. On completion of the measurement of the first buffer solution, there is a 1-point calibration.

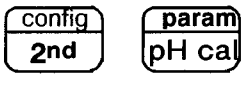
- In a **1-point calibration**, a new value of pHas is recorded, the old slope is retained.

- To **continue** the calibration procedure, the <enter> or <pH cal> key can be used. Any new values entered will be accepted only if the <enter> key has been pressed.





- If the values for the **slope** and **asymmetry pH** (pHas) are outside the limits, the calibration procedure stops and the value in the display flashes. This is intended to draw your attention to the unusual values found in your pH calibration.
  If you nevertheless wish to accept the value, press <enter>. If you press <mode>, the new value will not be accepted and the old one remains stored.
  Limits:
  Slope: 90.0 % ≤ slope ≤ 105.0 %
  Asymmetry pH: 6.40 ≤ pHas ≤ 8.00



- **Slope** and **pHas** (asymmetry pH) can be viewed and entered with the key sequence <2nd> <param>, see supplement under "Parameters".

- For good pH measurements, the two buffer solutions should be at the same **temperature**. You should also perform the calibration at or very close to the temperature at which you will subsequently measure the pH.

3. Storing measured values, hold function

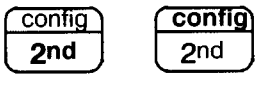
Up to 9 value pairs – measured value and corresponding temperature – can be stored with the <hold> key.

3.1 Storing measured values

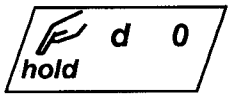
Measured values can be stored with the <hold> key. If the hold function is activated, the display shows, e.g. "hold 3", i.e. 3 pairs of measured values are stored in the hold buffer.
Depending on the setting, the measured values can be transferred to the buffer storage in several ways:

- **Immediately.**
- When the measured value is **stable**, i.e. the drift criterion is met (the triangle in the display disappears).
- **Periodically** at preset time intervals.

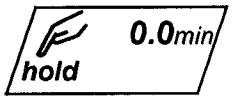
The type of measured value transfer is set with the key sequence <2nd> <config>:



- Press <2nd> <config>. The displays can be advanced with <enter>.



- Transfer **stable** measured values.
  "d" represents drift.
  1 = yes, transfer stable measured values.
  0 = no.
  The value can be changed with the <^> key.
  The entry of 0 leads to the next inquiry:



- Measured value transfer **periodically** at the preset time interval. The time interval is set with the <» > and <^> keys.
  The <hold> key is used to start the process.
  The display shows "hold 0" until the set time interval has elapsed. After this, the first measured value pair is transferred, the display changes to "hold 1" and the time interval again allowed to elapse etc.
  The measured value transfer can be interrupted with the <hold> key (display "hold") and then restarted with the same key.

- If both entries are set to 0, measured value transfer occurs **immediately** after the <hold> key has been pressed.

- Exit the entry with <mode>.

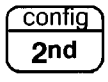
3.2 Viewing measured values

The measured values can be viewed with the <» > key from the last to the first and with the <⇗> key from the first to the last.
"hold X" flashes in the display.

Exit viewing of the measured values with <mode>.

3.3 Deleting all measured values in the hold buffer

All measured values in the buffer are deleted with the key sequence



4. Preparations

4.1 Installing the (rechargeable) batteries

You need 4 batteries, 1.5 V, type LR6, UM3 or AA, Metrohm ordering number 6.2133.000 or 4 Ni/Cd rechargeable batteries, 1.2 V and the appropriate battery charger.
Change all batteries simultaneously.

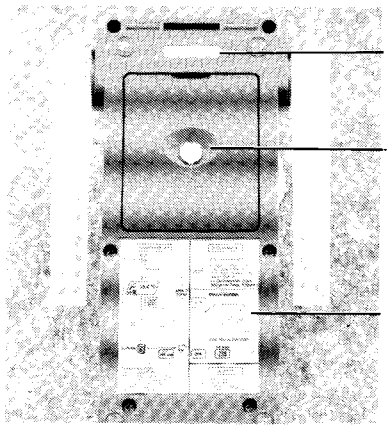
- Open the battery compartment (see illustration below). This can be done using, e.g. a coin.
- Insert the (rechargeable) batteries in accordance with the polarity directions in the battery compartment.
- Close the battery compartment. Tighten the screw firmly to ensure the housing is tight.
- When you switch on the instrument, "init" appears in the display. Confirm the display with the <enter> key.
  This operation sets the temperature to 25.0°C and the measured values of the hold buffer are deleted. All other settings as well as the pH calibration data remain stored.

If the pH Meter will not be used for a longer period of time, remove the (rechargeable) batteries and store them separately.

4.2 Affixing the short instructions for use

Stick the short instructions for use in the language you prefer on the underside of the instrument:

Underside of instrument



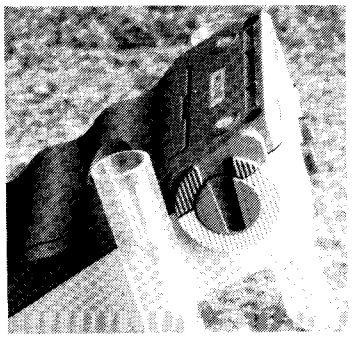
Manufacturing number, series and instrument number

Battery compartment

Short instructions for use

4.3 Mounting the electrode holders

The 6.2008.020 Electrode Holders are mounted as follows:

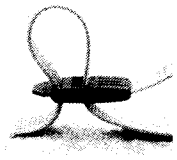


- Hold the pH meter with its underside towards you.
- Slide the holders with the opening upwards into the mount at the side. Press downwards firmly.
- Turn holders to the desired position.

Electrode holder position for bench mounting, see illustration on front cover.

4.4 Fastening the carrying strap

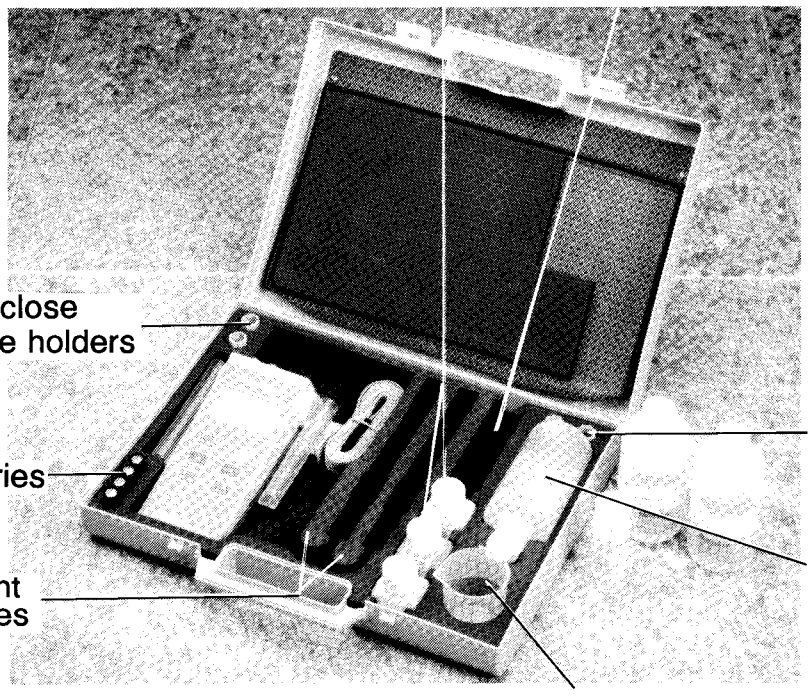
If you wish to carry the pH meter over your shoulder, you should fix the carrying strap to the bottom of the pH meter so that you can read the display properly.



- Pull the strap through the openings at the bottom end of the pH meter.
- The buckle locks the belt when you pull it through as shown in the illustration.

4.5 Working with the measuring case

The measuring case contains all accessories you need for measurements in the field.



You can store pens, pad and paper towels to wipe off the electrode in the compartment in the case lid.

4.6 Mounting in the wall holder

To have the 704 pH Meter ready to hand, it can be mounted in the 6.2051.000 Wall Holder, which can be fixed to the wall or mounted on a stand rod.

Mounting on a horizontal stand rod

- Screw the bent metal part loosely to the long part with 2 screws. Use the two outer holes at the top.
- Slide the holder onto the stand rod and fix it with the remaining two screws. Tighten all screws.
- Suspend the 704 pH Meter in the holder by means of the upper holding device.

Mounting on a vertical stand rod

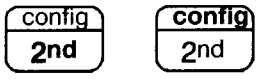
- Screw the bent metal part loosely to the long part with 2 screws. Use the two inner holes on the left.
- Slide the holder onto the stand rod and fix it with the remaining two screws. Tighten all screws.
- Suspend the 704 pH Meter in the holder by means of the upper holding device.

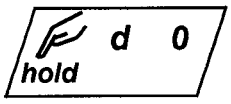
Mounting on the wall

- Fasten the long part of the holder to the wall. (The bent part is not needed.)
- Suspend the 704 pH Meter in the holder by means of the upper holding device.

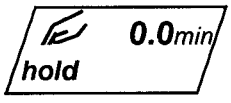
4.7 Setting the operating mode, configuration

The operating mode can be configured with the key sequence <2nd> <config> (see also supplement under "Configuration").

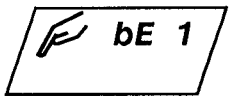




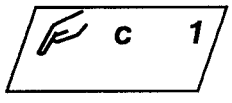
- Press <2nd> <config>. Press <enter> to move through the displays.



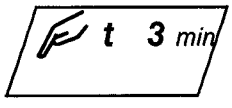
- Settings for the hold function, see page 8.



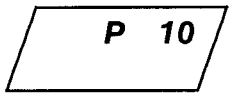
- Off/on switching of beep
  Setting 0 or 1 with the <^> key.
  1 = beep on
  0 = beep off



- Setting the display contrast
  Settings 1...4 with the <^> key.
  1 = normal setting
  4 = setting at high temperatures when the background becomes highly visible.



- Setting of the automatic shutdown time of the pH meter after the last keystroke.
  Settings 0...99 min with the keys <» > <^>.
  0 = no automatic shutdown.



- Display of the program version (display "P 10").

5. Error messages, problems and troubleshooting

5.1 Error messages

E1 In calibration, the voltage of solutions of the second buffer differs from the measured value of the first buffer solution by less than 6 mV.
Exit: <mode>
Remedy: – Change buffer solution
– Use fresh buffer solutions
– Check electrode

E2 After the error E1, the voltage difference is still less than 6 mV.
Exit: <mode>
Remedy: – Use fresh buffer solutions. Are **both** solutions OK?
– Check electrode. Is the cable connection also OK?

E3 Buffer could not be assigned.
Exit: <mode>
Remedy: – Preselect correct buffer series
– Use fresh buffer solutions
– Check electrode

E4 The temperature difference between the two buffer solutions is larger than 2°C.
Exit: <mode>

E5 The calibration temperature is lower than 0°C or higher than 99°C. The pH values for buffers are no longer defined outside these limits.
Exit: <mode>

E6 You have a Pt 100 temperature sensor connected instead of a Pt 1000, Metrohm ordering number 6.1110.100; or use the combined pH glass electrode with built-in Pt 1000, Metrohm ordering number 6.0238.000.
Exit: <mode>

 Warning! The batteries will soon be discharged. They will last for another 2 to 3 hours of operation. To change the batteries, see page 10.
The current battery tension can be checked in the diagnosis, see page 20.

5.2 Measuring problems

The following table contains a list of the most frequent malfunctions. The corresponding maintenance steps for pH glass electrodes are listed on page 16. The maintenance steps for the diaphragm are also valid for redox electrodes.

Malfunction	Possible cause	Remedial
Display of the pH Meter drifts.	– Liquid junction potential on reference electrode not constant. – Loose contact. – Electrode not plugged in or defective cable.	▸ Use 3 M KCl solution or other suitable reference electrolyte. ▸ Rectify fault.
Display of the pH Meter is "sensitive to hand capacity".	– Reference electrode is not filled. – Reference electrode filled with water by mistake. – Diaphragm clogged. – Measurement in poorly conducting solution.	▸ Top up with 3M KCl or other electrolyte solution, free from air bubbles. ▸ Empty out water and fill with 3M KCl. ▸ Clean diaphragm. ▸ Add conducting salt or use electrode with sleeve diaphragm.
Sluggish establishment of pH.	– Dirty diaphragm. – Adsorption at glass membrane.	▸ Clean diaphragm. ▸ Service glass membrane.
Slope too low	– Diaphragm contaminated – Adsorption at glass membrane. – Deswollen glass membrane after measurments in anhydrous solvents. – Old electrode. – Poor buffer solution.	▸ Clean diaphragm. ▸ Service glass membrane. ▸ Soak electrode in water between the measurements. ▸ Regenerate glass membrane. ▸ Use fresh buffer solutions.
Shows same value in pH 4 and 7 buffers.	– Buffer solutions ok? – Crack in the glass membrane. – Connector damp or dirty.	▸ Use fresh buffer solutions. ▸ Use new electrode. ▸ Dry or clean connector.

Care of pH glass electrodes

Cleaning the diaphragm

- After measurements in media with *low chloride concentration* (precipitated AgCl in the diaphragm → dark-coloured diaphragm): place electrode overnight in conc. NH_3, rinse with water and renew reference electrolyte.
- After measurement in *sulphide-containing* media (Ag_2S in the diaphragm → dark-coloured diaphragm): Place electrode in freshly prepared, slightly acidic 7% thiourea solution. Then rinse with water and renew reference electrolyte.
- With *organic contaminants*: Place electrode for app. 5 minutes in chromosulphuric acid at 80°C, then rinse thoroughly and renew reference electrolyte.
- If the above measures do not help: carefully file down diaphragm with a diamond nail file. The outflowing electrolyte should be visible as a dark ring.

Care and regeneration of glass membrane

- After measurement in *non-aqueous* media: soak electrode in water between measurements.
- After measurement in *protein-containing* media: Immerse electrode for several hours in a solution of pepsin in hydrochloric acid (5% pepsin in c(HCl) = 0.1 mol/l). Then soak thoroughly.
- Regenerating of glass membrane: Immerse glass membrane either for 1 min in a 10% solution of ammonium hydrogenfluoride (NH_4HF_2) or for a few seconds in 40% HF. After the etching rinse for app. 10 s in an HCl solution (H_2O:conc. HCl = 1:1). Rinse electrode with water and allow to stand for 24 h in the storage solution.

5.3 Diagnostic instructions (for program P 10)

The 704 pH Meter is a very precise and reliable instrument. Thanks to its rugged construction it is virtually impossible for external mechanical or electrical influences to have an adverse effect on its functions.

Although the occasional fault in the instrument cannot be ruled out completely, malfunctions are much more likely to be due to problems with the electrodes (see page 15) or to incorrect operation or use.

It is thus advisable to localise any trouble with the aid of this quick and simple diagnostic routine. The user will then need to call METROHM service only if there is really a fault in the instrument. Also, he can give the service engineer much more precise information by referring to the numbered steps of the diagnostic program.

When asking for help, always state the series number (S...., see p. 10) and program version (P XX, see p.13).

Procedure

- The steps must be carried out in sequence and compared with the reactions of the 704 pH Meter (shown indented). In the "yes" case, continue with the next instruction.

- If the instrument does not show the expected response ("no" case), the diagnostic step in question must be repeated so as to rule out any operating error. Consistently wrong responses, however, very probably indicate a defect.

- Steps marked with a double arrow (≫) allow re-entry into the test routine in the event of repetitions, provided the display shows

  d - 0 ... *d - 8* Otherwise repeat step 1 b).

- Pressing the <mode> key returns the instrument to the user program. To re-enter the diagnostic program, see preceding paragraph.

- Error indication: the display shows 'E' and a number.

Equipment needed

- Reference voltage generator, e.g. Metrohm pH Simulator 2.642.0010 (or any voltage source + accurate DVM, class 0.1 mV)
- Insulated, high impedance cable link, e.g. Metrohm 6.2108.060
- Pt 1000 simulator, or
  resistor switchbox, class 0.1 %, or
  resistor 1 kΩ/0.1 %
  and suitable short cable

≫ 1. a) **Prepare instrument for diagnostic test**

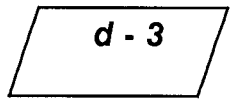
Switch off pH Meter.

Detach all external connections (cables at rear).

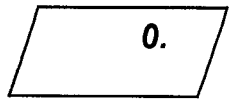
b) Before switching on, press <2nd>, switch on pH Meter; hold down <2nd> key until 'd - 1' appears.

≫ 2. **Keypad test**

Press <2nd> (as often as needed) until appears,



then press <hold/enter>



Press the keys in the order of their associated key number (see Fig. 1):

The corresponding key number will be shown
(except with 'mode' → quit).

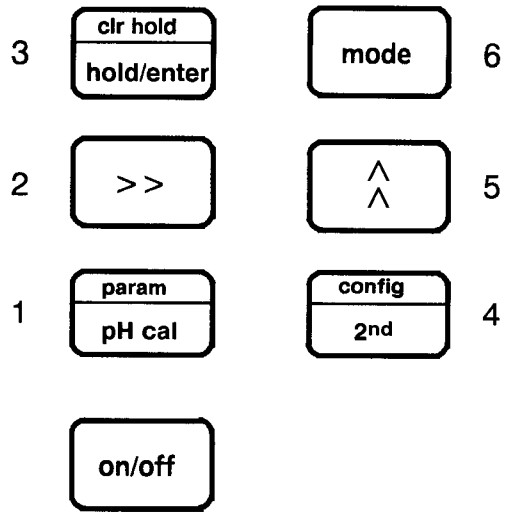


Fig. 1 Keypad with key numbers
If a wrong key number is pressed, this is displayed automatically with 'Ex' (x = number of wrong key pressed).

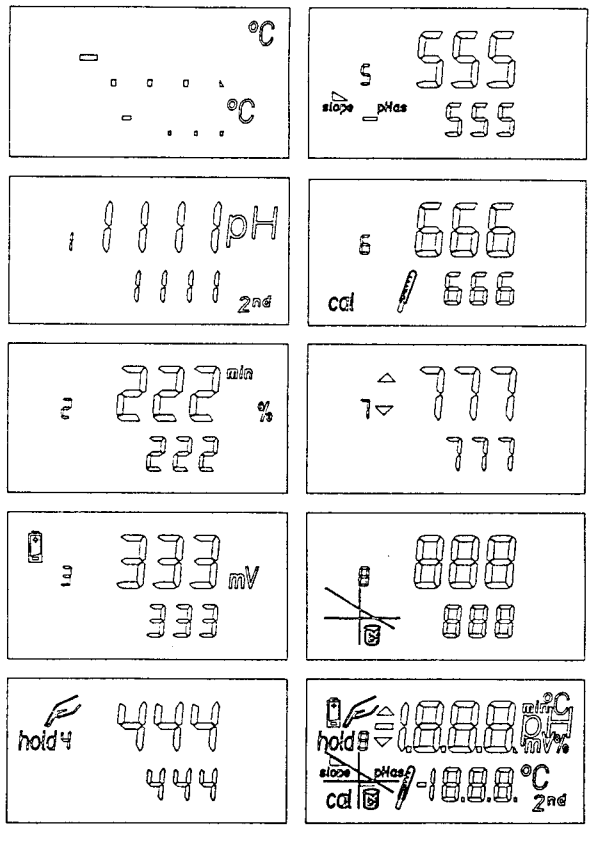
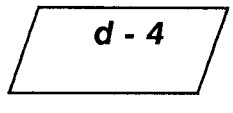


Fig. 2 Sequence of display test, see step 3

≫ 3. **Display test**

Press <2nd> (as often as needed) until appears,



then press <hold/enter>

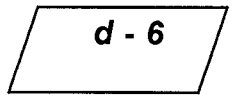
The display test runs automatically through the steps 1-10 shown in Fig. 2.

The test can be stopped at any time and started again with <hold/enter>.

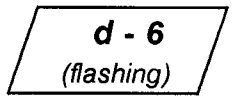
At the end of the test, the display again shows 'd - 4'.

≫ 4. EEPROM test

Press <2nd> (as often as needed) until appears,



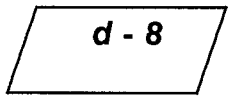
then press <hold/enter>



The entire display 'd - 6' flashes several times while the test is running. If the test is successful, 'd - 6' reappears.

≫ 5. Beep test

Press <2nd> (as often as needed) until appears,



then press <hold/enter>

A short tune is heard.

≫ 6. Check instrument calibration

<mode>

The display shows the last method selected before switching off.

6.1 Check potential measurement

Press <mode> (as often as needed) until the display shows the mV range.

Use a screened, high-impedance insulated cable to connect a voltage calibrator (mV generator, pH Simulator, etc.) of class 0.1 mV - or a less precise source connected in parallel with an accurate voltmeter (0.1 mV) - to measuring input 'pH/mV' of the 704. Set voltage to <2000 mV and compare with displayed reading (tolerance ±1 mV).

Check high impedance of input:
(if the generator allows this). Switch source to 'high impedance'
(Ri ≙ 1000 MΩ) and compare display with the value read off previously. The value must not differ by more than 1 digit.

Disconnect calibrator.

6.2 Check temperature measurement

Press <mode> (as often as needed) until the display shows '°C'.

Attach Pt 1000 simulator or resistor switchbox (or 1kΩ/0.1 %) to socket 'Pt 1000' and read off the temperature (1 kΩ gives 0 °C, tolerance ±0.1 °C).

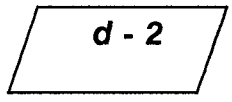
Disconnect Pt 1000 simulator (or switchbox).

End of diagnosis

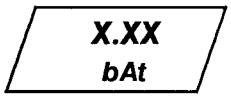
The diagnosis carried out so far, together with the tests that run automatically (battery test, RAM and ROM tests), have checked the functions of the 704 pH Meter. For more detailed investigations or more selective repeats one can also work through steps 7-10.

≫ 7. Battery voltage check

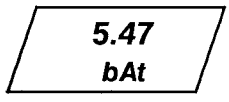
Press <2nd> (as often as needed) until appears,



then press <hold/enter>



Example

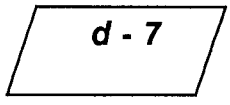


If the displayed reading is below 3.50 (and the battery symbol appears in normal operation), the batteries should be changed or accumulators recharged. If either of these warnings appears without the other, there is very probably a fault in the instrument.

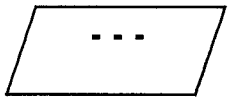
To exit, press <mode> ('d - 2' reappears)

≫ 8. ROM test

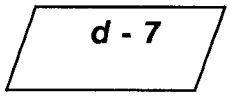
Press <2nd> (as often as needed) until appears,



then press <hold/enter>

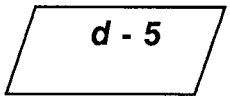


The test runs automatically. If there are no defects, three '-' appear on the display from left to right.

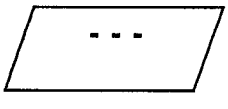


≫ 9. RAM-Test

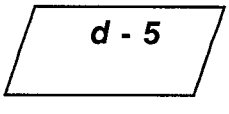
Press <2nd> (as often as needed) until appears,



then press <hold/enter>



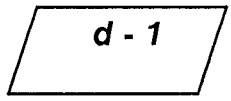
The test runs automatically. If there are no defects, three '-' appear on the display from left to right.



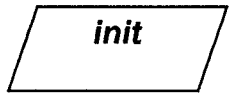
⩾ 10. Initialise RAM

It may happen on rare occasions that severe interference upsets the processor functions, causing the system to crash. After such an event the RAM area has to be intialised. Although the instrument's basic data are retained, RAM initialisation should be done only when necessary, as the stored user data (pH calibration data, selected buffers, configurations, etc.) are then erased.

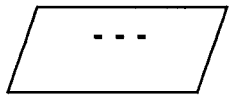
Execute step 1.



Press <hold/enter>



If initialisation cannot be avoided, press <hold/enter>



Otherwise quit with <mode>.

During initialisation three '-' appear on the display from left to right. The standard parameters are now loaded.

The data lost from the user memory then have to be entered again, see Instructions for use, Appendix.
Execute step 11.

⩾ 11. Restore the original situation

Reconnect the electrode and temperature probe detached at the start of the diagnostic routine, and carry out a brief function test with these.

Summary of key assignments in diagnostic tests

(before switching on, press <2nd>)

For repeat observations and special applications it may be an advantage to perform a particular check directly. The numbers for each test are therefore given below.

Press <2nd> as often as required.

- d - 1 RAM initialisation - only when necessary!
- d - 2 Battery check
- d - 3 Keypad test
- d - 4 Display test
- d - 5 RAM test
- d - 6 EEPROM test
- d - 7 ROM test
- d - 8 Beep test

6. Appendix

6.1 Technical specifications

Measuring range	
pH value	pH = 0.00 ... 14.00
Voltage	U = −1990 ... +1990 mV
Temperature	t = −130.0 ... +199.9 °C
Resolution	
pH value	ΔpH = 0.01
Voltage	ΔU = 1 mV
Temperature	Δt = 0.1 °C
Errors	
pH value	± 0.01
over operational voltage range	± 0.14% of (meas.value−pH7)
over temperature of use range	± 0.20% of (meas.value−pH7)
Voltage	± 1 mV
over operational voltage range	± 0.05% of meas.value
over temperature of use range	± 0.18% of meas.value
Temperature	± 0.1 °C
over operational voltage range	± 0.1 °C
over temperature of use range	± 0.4% of final value
Measuring rate	
pH value with alternating temperature measurement	1.9 measurements/s each
Voltage with alternating temperature measurement	1.9 measurements/s each
Temperature	3.8 measurements/s
pH measurement	
Temperature compensation of the slope in the temperature range	0.0...100.0 °C
pH calibration	
Type	1- or 2-point-calibration
Buffer solutions which can be used for the automatic buffer recognition, temperature dependence of the pH values considered automatically	Metrohm, DIN/NBS, Fisher, Merck/Riedel deHaën, Ciba/Geigy
Special buffers without automatic recognition	
Signal amplifier	
Input resistance	> 10^{13} Ω
Offset current	< $3 \cdot 10^{-13}$ A

Display

Type	LCD
Digit height	10 mm for measured value 6.9 mm for temperature
Dialog	with pictograms

Housing

waterjet-proof, dust-tight, according to DIN 40050, IP65

Materials	
Housing	Polybutylenterephthalate (PBTP)
Keypad membrane	Polyester (PETP)
Protection against static discharges	inner walls of housing coated with aluminum, IEC 801-2, class III

Ambient temperature, humidity

Operational temperature	–10...55 °C
Storage, transport	–40...70 °C
Humidity	5...85 % rel. humidity

Reference conditions

Adjusting interval	annually
Temperature	23 ± 2 °C
Operational voltage	5.0 ±0.1 V

Error influence quantities

Operational voltage range	3.6...6 V
Temperature of use range	0...55 °C

Safety specifications

Designed and tested in accorance to IEC publication 348, safety class I. This manual contains some information and warnings which have to be followed by the user to ensure safe operation and to retain the apparatus in safe condition.

Power supply

4 batteries or rechargeable batteries	1.2...1.5 V, type LR6, UM3, AA or Mignon
Power consumption	max. 0.06 W with Pt 1000

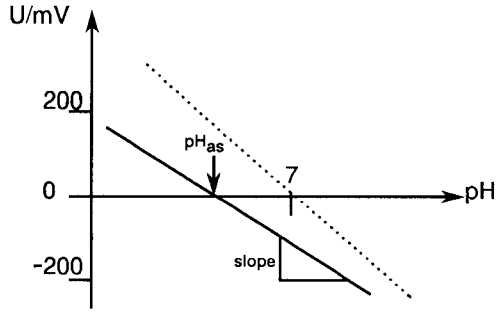
Dimensions

Width	
without electrode holder	90 mm
with electrode holder	125 mm
Length	194 mm
Height	48 mm

Weight

incl. 4 batteries	390 g

6.2 Explanation of technical terms

Asymmetry pH	See pH calibration.
Buffer solutions	Buffer solutions have an exactly known pH value at a specified temperature. They are used for the pH calibration.
Calibration	See pH calibration
Diaphragm	Part of the electrode which forms a conductive connection between the analysis solution and the reference electrolyte solution. pH electrodes have either a round ceramic diaphragm directly above the glass bulb or a sleeve diaphragm.
Drift	Measured values are usually not immediately *stable* when an electrode is immersed in the analysis solution. The measured value changes somewhat over a period of time. This change is called drift. In the 704 pH Meter, such drifting values are marked in the display with a triangle. The triangle fades as soon as the measured value is more stable than a preset drift threshold. Drift threshold: pH: 0.028 pH/min U/mV: 1.875 mV/min t/°C: 0.974 °C/min
pHas	See pH calibration
pH calibration	 In the pH calibration, the measured voltage is plotted against the specified pH value of the buffer solution. This results in a straight line (at least in the middle pH range). The intersection point of this straight line with the pH axis gives the *asymmetry pH, pHas*. The *slope* of the line at 25°C is theoretically 59.16 mV per pH unit. This slope is specified as a relative slope 1 = 100%. Real pH calibrations usually result in a somewhat lower slope.

pH value	The pH value specifies the acidity or alkalinity of a solution. At pH = 7, the solution is neutral. Solutions with pH values less than 7 are acidic, those with pH values greater than 7 alkaline.
Redox measurements	Voltage measurement with a platinum or a gold electrode. The ratio of a **red**uced to an **ox**idised substance is measured.
Reference electrolyte	The reference electrolyte solution is an essential part of the reference electrode. In most cases, KCl solution, 3 mol/L is used.
Slope	See pH calibration

You will find additional information in the Metrohm monograph "Electrodes in potentiometry" and in Metrohm Application Bulletin 188. Both these publications can be obtained free of charge from your Metrohm agency.

6.3 pH values of buffer solutions

Metrohm buffers

Buffer / t/°C	pH 4.00 ±0.02	pH 7.00 ±0.02	pH 9.00 ±0.02
0	3.99	7.11	9.23
5	3.99	7.08	9.18
10	3.99	7.06	9.13
15	3.99	7.04	9.08
20	3.99	7.02	9.04
25	**4.00**	**7.00**	**9.00**
30	4.00	6.99	8.96
35	4.01	6.98	8.93
38	4.02	6.98	8.91
40	4.02	6.98	8.90
45	4.03	6.97	8.87
50	4.04	6.97	8.84
55	4.06	6.97	8.81
60	4.07	6.97	8.79
65	4.09	6.98	8.76
70	4.11	6.98	8.74
75	4.13	6.99	8.73
80	4.15	7.00	8.71
85	4.18	7.00	8.70
90	4.20	7.01	8.68
95	4.23	7.02	8.67

pH 4: potassium hydrogen phthalate
pH 7: potassium/sodium hydrogen phosphate
pH 9: borax

DIN/NBS buffers

Buffer / t/°C	C	D	F
0	4.01	6.98	9.46
5	4.00	6.95	9.40
10	4.00	6.92	9.33
15	4.00	6.90	9.28
20	4.00	6.88	9.23
25	**4.01**	**6.87**	**9.18**
30	4.01	6.85	9.14
35	4.02	6.84	9.10
38	4.03	6.84	9.08
40	4.03	6.84	9.07
45	4.04	6.83	9.04
50	4.06	6.83	9.01
55	4.07	6.83	8.99
60	4.09	6.84	8.96
65	4.11*	6.84*	8.94*
70	4.13	6.85	8.92
75	4.14*	6.85*	8.90*
80	4.16	6.86	8.89
85	4.18*	6.87*	8.87*
90	4.21	6.88	8.85
95	4.23	6.89	8.83

C: potassium hydrogen phthalate
D: phosphate
F: borax
according to DIN 19266 (1979)

Fisher buffers

Buffer / t/°C	pH 4.00 rot	pH 7.00 gelb	pH 10.00 blau
0	4.01	7.13	10.34
5	3.99	7.10	10.26
10	4.00	7.07	10.19
15	3.99	7.05	10.12
20	4.00	7.02	10.06
25	**4.00**	**7.00**	**10.00**
30	4.01	6.99	9.94
35	4.02	6.98	9.90
38	4.02*	6.98*	9.87*
40	4.03	6.97	9.85
45	4.04*	6.97*	9.81*
50	4.06	6.97	9.78
55	4.07*	6.97*	9.74*
60	4.09	6.98	9.70
65	4.11*	6.99*	9.68*
70	4.13*	7.00*	9.65*
75	4.14*	7.02*	9.63*
80	4.16*	7.03*	9.62*
85	4.18*	7.06*	9.61*
90	4.21*	7.08*	9.60*
95	4.23*	7.11*	9.60*

pH 4: potassium hydrogen phthalate (SB 101)
pH 7: potassium dihydrogen phosphate/NaOH (SB 107)
pH 10: potassium borate/carbonate/KOH (SB

Merck/(Riedel-deHaën[1]) buffers

Puffer / t/°C	pH 4.00	pH 7.00	pH 9.00
0	4.05	7.13	9.24
5	4.04	7.07	9.16
10	4.02	7.05	9.11
15	4.01	7.02	9.05
20	**4.00**	**7.00**	**9.00**
25	4.01	6.98	8.95
30	4.01	6.98	8.91
35	4.01	6.96	8.88
38	4.01*	6.96*	8.86*
40	4.01	6.95	8.85
45	4.00*	6.95*	8.82*
50	4.00	6.95	8.79
55	4.00*	6.95*	8.76*
60	4.00	6.96	8.73
65	4.00*	6.96*	8.71*
70	4.00	6.96	8.70
75	4.00*	6.96*	8.68*
80	4.00	6.97	8.66
85	4.00*	6.98*	8.65*
90	4.00	7.00	8.64
95	4.00*	7.02*	8.63*

pH 4: sodium citrate/sodium chloride
pH 7: potassium/sodium dihydrogen phosphate
pH 9: boric acid/KCl/NaOH

[1]: The values indicated by Riedel deHaën may vary until up to ΔpH 0.02.

Ciba/Geigy buffers

Puffer / t/°C	pH 4.00 (P01)	pH 7.00 (P10)	pH 9.00 (P12)
0	4.01	7.11	9.20*
5	4.00	7.08	9.15
10	4.00	7.05	9.10
15	4.00	7.02	9.05
20	**4.00**	**7.00**	**9.00**
25	4.01	6.98	8.96
30	4.01	6.97	8.91
35	4.02	6.96	8.88
38	4.03	6.95*	8.85
40	4.03	6.95	8.84
45	4.04	6.94	8.80
50	4.06	6.94	8.77
55	4.07	6.93	8.74
60	4.09	6.93	8.71
65	4.11*	6.93*	8.69
70	4.13	6.94	8.67
75	4.14*	6.94*	8.65
80	4.16	6.95	8.63
85	4.18*	6.96*	8.61
90	4.21	6.97	8.60
95	4.23	6.98*	8.59

pH 4: potassium hydrogen phthalate
pH 7: potassium/sodium hydrogen phosphate
pH 9: borax/potassium dihydrogen phosphate

* : interpolated or extrapolated values

The values without * correspond to the manufacturer's specifications.

6.4 Warranty

The warranty regarding our products is limited to rectification free of charge in our workshops of defects that can be proved to be due to material, design or manufacturing faults which appear within 12 months from the day of delivery. Transport costs are chargeable to the orderer.

For day and night operation, the warranty is valid for 6 months.

Glass breakage in the case of electrodes or other glass parts is not covered by the warranty. Checks which are not a result of material or manufacturing faults are also charged during the warranty period. For parts of outside manufacture insofar as these constitute an appreciable part of our instrument, the warranty stipulations of the manufacturer in question apply.

With regard to the guarantee of accuracy, the technical specifications in the Instructions for Use are authoritative.

Concerning defects in material, construction or design as well as the absence of guaranteed features, the orderer has no rights or claims except those mentioned above.

If damage of the packaging is evident on receipt of a consignment or if the goods show signs of transport damage after unpacking, the carrier must be informed immediately and a written damage report demanded. Lack of an official damage report releases METROHM from any liability to pay compensation.

If any instruments and parts have to be returned, the original packaging should be used if at all possible. This applies above all to instruments, electrodes, burette cylinders and PTFE pistons. Before embedment in wood shavings or similar material, the parts must be packed in a dustproof package (for instruments, use of a plastic bag is imperative). If open assemblies are enclosed in the scope of delivery that are sensitive to electromagnetic voltages (e.g. data interfaces etc.) these must be returned in the associated original protective packaging (e.g. conductive protective bag). (Exception: assemblies with built-in voltage source belong in a non-conductive protective packaging). For damage which arises as a result of non-compliance with these instructions, no warranty responsibility whatsoever will be accepted by METROHM.

6.5 Scope of delivery and ordering designations

704 pH Meter **2.704.0010**
including the following accessories:

2 Electrode holders 6.2008.020
1 Carrying strap 6.2050.000
1 Set of batteries, 1.5 V LR6, 4 pcs. 6.2133.000
1 Set short Instructions for Use for sticking on 6.2825.000
1 Instructions for Use for 704 pH Meter 8.704.1003

704 pH Meter with measuring case **2.704.0020**
including the following accessories:

2 SGJ sleeves for electrodes 6.1236.040
2 Plastic stoppers 6.1446.000
1 Bottle 25 ml 6.1613.010
1 Bottle 25 ml for buffer pH 7 ..... 6.1613.020
1 Bottle 25 ml for buffer pH 4 ..... 6.1613.030
1 Wash bottle 6.1614.000
1 Bottle 250 ml for buffer pH 4 ..... 6.1614.010
1 Bottle 250 ml for buffer pH 7 ..... 6.1614.020
2 Electrode holders 6.2008.020
1 Carrying strap 6.2050.000
1 Set of batteries, 1.5 V LR6, 4 pcs. 6.2133.000
1 Set buffer concentrate, buffer pH 4 and pH 7 and 3M KCl solution 6.2302.010
1 Case 6.2716.010
1 Beaker 100 ml, PP 6.2717.000
2 Sets short Instructions for Use for sticking on 6.2825.000
1 Instructions for Use for 704 pH Meter 8.704.1003

6.6 Accessories

6.6.1 General

Pt 1000 temperature sensor 6.1110.100
Cable for Pt 1000 temperature sensor, length 1 m 6.2104.080
length 2 m 6.2104.110
Wall holder 6.2051.000

6.6.2 For pH measurements

Solutions:
Ready-to-use solutions, 1000 ml
Buffer pH 4 ..... 6.2307.000
Buffer pH 7 ..... 6.2307.010
Buffer pH 9 ..... 6.2307.020
Sets buffer concentrate 50 ml each, total 250 ml buffer solution
Buffer pH 4 and pH 7 and 3M KCl solution 6.2302.010
Buffer pH 4, pH 7 and pH 9 ..... 6.2304.000

Which electrode do you use for your measuring problem?

The list below gives a recommendation of electrodes for different measuring tasks. If you need more information, you will find it in the Metrohm electrode catalog. Together with the electrodes, you need a separate electrode cable:

Length 1 m	6.2104.020
Length 2 m	6.2104.030
Length 3 m	6.2104.040

Boiler feed water	6.0219.100, 6.0233.100
Cheese	6.0236.100, 6.0214.100
Creams	6.0219.100
Emulsions	6.0219.100
Fruit juices	6.0202.100[1)]
Fruits	6.0236.100, 6.0214.100
General applications	6.0202.100[1)]
Honey	6.0219.100
Jam	6.0219.100
Lacquer	6.0219.100
Lotions	6.0219.100
Marmelade	6.0219.100
Meat	6.0236.100, 6.0214.100
Milk and milk products	6.0219.100
Non-aqueous solutions	6.0219.100, 6.0233.100
Ointments	6.0219.100
Paint	6.0219.100
Paper	6.0217.000[2)]
Paste	6.0219.100
Protein containing solutions	6.0219.100
Puncture measurements	6.0236.100, 6.0214.100
Rain water	6.0219.100, 6.0233.100
Salt-"free" media	6.0219.100, 6.0233.100
Semisolid substances	6.0236.100, 6.0214.100
Small samples	6.0236.100, 6.0214.100
Soils	6.0233.100, 6.0219.100
Surfaces	6.0217.000[2)]
Suspensions	6.0219.100
Textiles	6.0217.000[2)]
Vegetable juices	6.0202.100[1)]
Vinegar	6.0202.100[1)]
Waste water	6.0219.100, 6.0233.100
Water	6.0219.100, 6.0233.100
Wine	6.0202.100[1)]

[1)] Instead of the 6.0202.100 electrode you may also use the 6.0233.100 or 6.0238.000 electrodes. The 6.0238.000 electrode has a built-in Pt 1000 temperature sensor and the electrode cable is included.

[2)] Electrode cable included, an additional 6.2104.000 adaptor is necessary.

6.0202.100

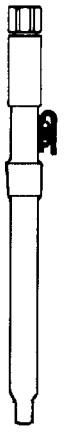
General applicability.

6.0217.000

With fixed electrode cable.
For measurements on surfaces.

6.0219.100

Electrode with sleeve diaphragm and bridge electrolyte.
For sample solutions that lead to precipitations in the diaphragm or when a special bridge electrolyte is needed.

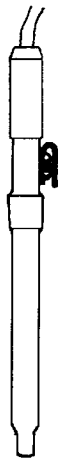


6.0233.100

Electrode with SGJ 14/15.
General applicability.
Specially suitable for water samples. (Contains only little AgCl in the reference electrolyte.)

6.0236.100

For puncture measurements in semisolid substances or for measurements in small vessels.



6.0238.000

Electrode with SGJ 14/15 and built-in Pt 1000 temperature sensor. Fixed electrode cable.
General applicability.

6.6.3 For redox measurement

Solutions:

Redox standard solution, 250 ml	6.2306.020
3M KCl solution, 250 ml	6.2308.020

Electrodes:

A separate electrode cable forms part of the electrode:

Length 1 m	6.2104.020
Length 2 m	6.2104.030
Length 3 m	6.2104.040

Platinum electrode	6.0415.100
Gold electrode	6.0413.100

Declaration of Conformity

Metrohm Ltd.
CH-9101 Herisau
Switzerland
Tel. +41 71 353 85 85
Fax +41 71 353 89 01
www.metrohm.com

for the instrument
704 pH Meter

Description
Pocket pH meter for field, plant and lab use.

The above instrument was developed and manufactured in accordance with the requirements demanded by the ISO 9001 quality system regarding the design, manufacture and servicing of Metrohm instruments.

The instrument was manufactured and tested according to the following standards:

Electromagnetic compatibility: emission

EN50081-1, EN50081-2, EN55011 class B, EN55022 class B	Generic emission

Electromagnetic compatibility: immunity

EN50082-1	Immunity
IEC801-2, IEC1000-4-2 (class 2)	Static discharge
IEC801-3, IEC1000-4-3, ENV50140+ENV50204 (class 2)	Radiated rf electromagn. field immunity
IEC801-4, IEC1000-4-4 (class 2)	Electrical fast transient requirements

Safety specifications

EN61010, IEC1010, UL3101

The instrument meets the requirements of the CE mark as contained in the EU directives 89/336/EWG and 73/23/EWG and fulfils the following specifications:

EN50081-1	Electromagnetic compatibility, basic specification «Emitted Interference»
EN50082-1	Electromagnetic compatibility, basic specification «Interference Immunity»
EN61010	Safety requirements for electrical laboratory measurement and control equipment

The technical specifications are documented in the instruction manual.

The instrument was validated with respect to functionality, analytical performance and accuracy of results. The instrument functions are documented in the instruction manual.

Herisau, 12th December 1997

Dr. J. Frank
Development Manager

Ch. Buchmann
Production and
Quality Assurance Manager

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Texts which appear in the display are *printed in italics*. Keys are marked with < >.

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