
Application Bulletin

Of interest to: General analytical laboratories

A 1, 2, 4, 6, 7, 8, 10, 12, 13, 16

Validation of Metrohm pH meters using Standard Operating Procedures

Summary

Among other things, **GLP (Good Laboratory Practice)** requires that the accuracy and precision of analytical instruments are checked at regular intervals using **Standard Operating Procedures (SOPs)**.

The user is advised to validate the pH meter as a whole integrated measuring system, i.e. including the electrode(s) and any stirrer that may be used.

The checking of the electronic and mechanical components can and should be carried out by qualified personnel from the manufacturing company as part of regular servicing. All newer Metrohm pH meters are provided with start-up test routines, which check that the instrument is functioning perfectly when it is switched on. If no error message is displayed it can be assumed that the instrument is functioning correctly. Metrohm also supplies its instruments with integrated diagnostic programs, which enable the user to check the functioning of certain components in the event of malfunctions or erratic behavior and to localize the fault. These diagnostic programs can also be included in a validation procedure.

The procedure described below is meant as a guideline for setting up a Standard Operating Procedure to check your pH meter (with electrode connected). The limits specified should be regarded as examples. Depending on the requirements placed on the accuracy of the measuring system these limits may have to be redefined in the Standard Operating Procedure.

Application range

These test specifications can be used with the following Metrohm instruments:

704 pH Meter,
713 pH Meter,
744 pH Meter,
780 pH Meter and
781 pH/Ion Meter.

Of course, older pH meters can also be checked in a similar way.

Under «Appendix» at the end of this bulletin the checking of the pH, voltage and temperature readings of a pH meter with the help of the 2.767.0010 Calibrated Reference is described.

Reagents

- Electrolyte solution $c(\text{KCl}) = 3 \text{ mol/L}$, e.g. Metrohm no. 6.2308.020
- Buffer solution $\text{pH} = 4.00$, e.g. Metrohm no. 6.2307.100
- Buffer solution $\text{pH} = 7.00$, e.g. Metrohm no. 6.2307.110
- Buffer solution $\text{pH} = 9.00$, e.g. Metrohm no. 6.2307.120
- Demineralized or distilled water

Procedure

It is best to carry out the measurements or calibrations in a thermostatted measuring vessel at $25 \text{ }^\circ\text{C}$ with stirring.

The electrode should first be checked visually (possible glass cracks; condition of the diaphragm; adequate filling level of the reference electrolyte; no air bubbles in the inner compartment). With electrodes equipped with a ground sleeve diaphragm the ground sleeve is loosened slightly and then returned to its original position. This causes a small amount of electrolyte to flow out.

If necessary, the electrode is fitted with the corresponding electrode cable and connected to the pH meter. It is rinsed well with distilled water and then dried by touching it lightly with a soft paper tissue (do not rub). Afterwards, the electrode is immersed in the first buffer solution. The stirrer is switched on and the temperature is allowed to become constant. If no temperature sensor is connected the user must enter the measuring temperature or, with older pH meters, set the correct temperature value. The automatic pH calibration is now started. (For those pH meters mentioned under «Application range» it does not matter in which order the buffers are used; for older pH meters buffer solution $\text{pH} = 7.00$ must always be used first.)

When the instrument has accepted the first buffer value the measuring vessel and electrode(s) are rinsed well with distilled water and the electrode(s) dried again with a soft paper tissue. The second buffer solution is filled into the measuring vessel and the procedure described above is repeated. Modern pH meters then automatically conclude the two-point calibration.

If in everyday work mainly acidic samples are measured then buffer solutions $\text{pH} = 7.00$ and $\text{pH} = 4.00$ are used for calibration. If, on the other hand, the samples are mainly alkaline then buffer solutions $\text{pH} = 7.00$ and $\text{pH} = 9.00$ are used.

The slope and asymmetry pH of the investigated electrode are given as the result of the pH calibration.

The electrode can be used for measurements if the slope is ≥ 0.95 and the asymmetry potential lies in the range $\pm 30 \text{ mV}$ ($\text{pH}_{\text{as}} \pm 0.507$ or $6.493 < \text{pH} < 7.507$ at $25 \text{ }^\circ\text{C}$).

The test described above provides no information about the response of the pH electrode or the condition of the diaphragm. However, the 780 and 713 pH Meters as well as the 781 pH/Ion Meter are equipped with such a type of automatic pH electrode and diaphragm test. With other models a printer or analogue recorder must be connected to the pH meter in order to plot the potential curve and evaluate it manually. The electrode potential is measured in buffer solution $\text{pH} = 9.00$ once with and once without stirring. For a good diaphragm the potential difference should be $\leq 2 \text{ mV}$.

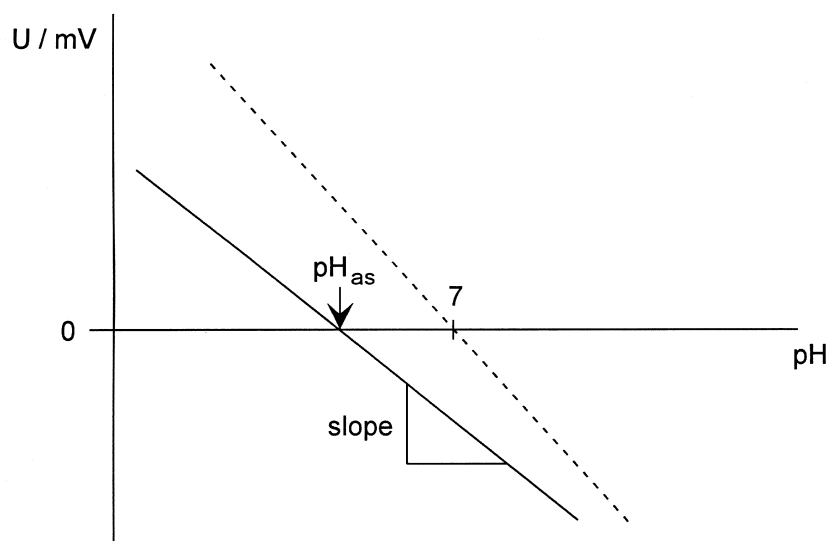
If the electrode does not fulfil the demands placed upon it then it must be regenerated (or sent away for regeneration) or replaced by a new electrode.

Testing intervals

It is advisable to repeat the validation of the pH meter each year. Depending on the frequency of use and the type of measuring media the electrode check should be carried out at least once per month. Under «rough» conditions of use and with critical measuring solutions it may be necessary to check the electrode at weekly intervals.

Explanations concerning the pH calibration

In pH calibration the measured voltage in mV is plotted against the specified pH value of the buffer solution. A straight line is obtained (except at extreme pH values). The intersection point of this straight line with the pH axis yields **pH_{as} (asymmetry pH)**. The **slope** of the straight line at 25 °C is theoretically 59.16 mV per pH unit (at 20 °C the theoretical slope is 58.16 mV/pH). This value corresponds to a relative slope of 1 or 100%. The straight lines resulting from actual pH calibrations usually have slightly lower slopes.



Literature

Further information about the use, maintenance and regeneration of pH glass electrodes can be found in:

- Application Bulletin No. 188 «pH measurement technique»
- Sales brochure «Electrodes for pH Measurement»
- Special electrode leaflets (in the electrode boxes)

Appendix

Checking pH meters with the 2.767.0010 Calibrated Reference using the 744 pH Meter as an example

As the Calibrated Reference is equipped with a solar cell for power supply it should be placed in as bright a location as possible near the pH meter to be checked (switch on the room lighting if necessary).

Electrode cables can also be a source of trouble. It is therefore recommended to include the original sensor cables in the testing process (only possible with plug-in cables).

If, on the other hand, only the pH meter is to be checked, then you need the following tested standard cables, which form part of the accessories of the 2.767.0010 Calibrated Reference:

- 6.2150.040 Electrode cable for Metrohm plug-in head G, with instrument plug F (corresponds to 6.2104.020 electrode cable)
- 2 x 6.2150.000 Cable with plug B on both ends (corresponds to 6.2106.020 cable)

1. pH value

For these tests it is necessary that on the pH meter to be checked the reference temperature is set to 25 °C, the electrode slope to 1.00 (100%) and the pH_{as} to 7.00!

Plug the electrode cable into socket 6 of the 2.767.0010 and measure the pH value once with the lid closed and once with the lid open (over the solar cell). (The values given below are examples only.)

	Value read off	Theoretical value	ΔpH	Error tolerance 744*
Lid closed	6.99	7.00	-0.01	± 0.01
Lid open	12.87	12.87	0	± 0.01

2. Voltage

Plug the electrode cable into socket 5 or into socket 6 of the Calibrated Reference and measure the voltage in both cases once with the lid closed and once with the lid open.

	Value read off / mV	Theoretical value / mV	ΔU / mV	Error tolerance 744* / mV
Socket 5, lid closed	0	0	0	± 1
Socket 5, lid open	1200	1200	0	± 1
Socket 6, lid closed	0	0	0	± 1
Socket 6, lid open	-341	-341	0	± 1

3. Temperature

With the 744 pH Meter only a Pt 1000 resistance thermometer can be used for temperature measurement. To check the temperature reading the two red input sockets of the 744 are connected with the sockets 2 and 3 of the 2.767.0010 Calibrated Reference using two cables with plug B on both ends. (In this case the measured value does not depend on the lid's position.)

Value read off / °C	Theoretical value / °C	ΔT / °C	Error tolerance 744* / °C
0.1	0.17	-0.07	± 0.1

*) According to the technical specifications given in the Instructions for use of the 744 pH Meter.

Assessment: *The checked pH meter is OK.*