Application Bulletin 271/4 e

Validation of Metrohm pH meters using Standard Operating Procedures

Of interest to
General analytical laboratories
A L 1, 2, 4, 6, 7, 8, 10, 12, 13, 1

Summary

Among other things, **GLP** (**G**ood **L**aboratory **P**ractice) 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:

691 pH Meter,
704 pH Meter,
744 pH Meter,
780 pH Meter,
781 pH/Ion Meter,
826 pH mobile,
827 pH lab.

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 voltage and temperature readings of a pH meter with the help of the 2.767.0010 Calibrated Reference is described.

Reagents

- Electrolyte solution *c*(KCl) = 3 mol/L, e.g. Metrohm no. 6.2308.020
- Buffer solution pH = 4.00, e.g. Metrohm no. 6.2307.200
- Buffer solution pH = 7.00, e.g. Metrohm no. 6.2307.210
- Buffer solution pH = 9.00, e.g. Metrohm no. 6.2307.220
- Demineralized or distilled water

Procedure

It is best to carry out the measurements or calibrations in a thermostated measuring vessel at 25 °C while stirring.

The electrode should first be checked visually (possible glass cracks; condition of the diaphragm; adequate filling level of the reference electrolyte). 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. 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 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. 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 pH = 7.00 and pH = 4.00 are used for calibration. If, on the other hand, the samples are mainly alkaline then buffer solutions pH = 7.00 and 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 ±30 mV (pH_{as} ± 0.507 or 6.493 < pH < 7.507 at 25 °C).

The test described above provides no information about the response of the pH electrode or the condition of the diaphragm. However, the 780 pH Meter and the 781 pH/Ion Meter are equipped with such a type of automatic pH electrode 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 pH = 9.00 once with and once without stirring. For a good diaphragm the potential difference should be ≤2 mV.

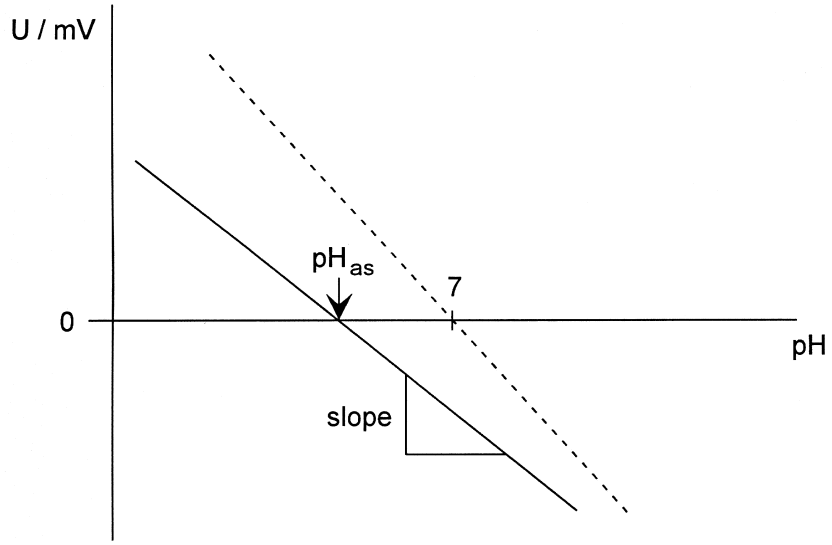
If the electrode does not fulfill the demands placed upon it then it must be regenerated or replaced by a new electrode.

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)
- Metrohm DVD: Maintenance and Care of Metrohm Electrodes

Appendix

Checking pH meters with the 2.767.0010 Calibrated Reference

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)

Attached are the protocols of measuring amplifier check for 780/781 and for 826/827. Protocols for other instruments can be found on the internet at www.metrohm.com.

Just follow the instructions written on the protocol and enter the values into the form. The checked instrument is working properly if all values are in the permitted range.

780, 781: Protocol of measuring amplifier check

Metrohm

Instrument: **1.78**... ..... **Serial / Fabr.-No.:** ..... **ID-No** (if available)**:** .....

Test agent: **2.767.0010** **Serial / Fabr.-No.:** ..... **ID-No** (if available)**:** .....

Next Cal.: ..... Cal. Master: .....

Type: ..... Certificate-No.: .....

SCS Cal. Serv. Reg. Nr.: .....

Check carried out on: ..... **Name:** ..... **Signature:** .....

Checked instrument meets requirements: ☐ yes ☐ no Decision: .....

Please read the notes on the following page first.

Checking U (mV)

	Carry out on 780/781 or on sensor	Remarks	Carry out on 767	Enter theoretical value from 767 cover	Enter value from 780/781 display[1]	Difference	Permitted difference[2]	OK ✓
1	Unscrew the cable at the plug-in head of the pH sensor. If not possible, insert cable 6.2150.040 from 767 accessory to sockets **5** 'pH/ISE'	Place sensor in sleeve	Close cover					
2	Press **<MODE>** to select Mode U (mV)		Sensor cable to socket (5)	mV value 5: 0 mV	..... mV	..... mV	± 1.0 mV	.....
3			Open cover	mV value 5: .....mV	..... mV	..... mV	± 1.5 mV	.....
4			Sensor cable to socket (4)	(actual value from step 3)	..... mV	Diff. act. value [3] step 3 and. 4 ..... mV	± 1.0 mV	.....
5			Sensor cable to socket (6)	mV value 6: .....mV	..... mV	..... mV	± 2.5 mV	.....
6			Sensor cable to socket (5)					
7			insert cable 6.2150.020 (from accessory) to socket (6).					
8	Connect grey banana plug of cable 6.2150.020 to earthing socket **13** of 780/ 781 [5]; black plug (screen) remains open	Do not touch sockets (4), (5), (6) during measure		(Actual value from step 3)	..... mV	Diff. act. value [4] step 3 and 8 ..... mV	± 1.5 mV	.....

Checking temperature (Pt1000)

	Carry out on 780/781 or on sensor	Remarks	Carry out on 767	Enter theoretical value from 767 cover	Enter value from 780/781 display[1]	Difference	Permitted difference[2]	OK ✓
1	Change to Mode T (°C) with **<MODE>**		No preference for cover.					
2	Use two banana cables (6.2150. 000) to connect temperature measuring input **8** to 767[5].	*Read the theoretical value for the sockets (1) + (3) from the white field 1 - 3 on the cover*	to sockets: (2) + (3): (1) + (3):	.....°C .....°C	.....°C .....°C	.....°C .....°C	± 1.0 °C ± 1.0 °C	....
3	Remove cables or reconnect sensors, respectively. Please put back to the case the original cables belonging to 767.							

Hints for the preparation of the measuring amplifier check

- Place Calibrated Reference on bench near sensor. Ensure that light reaches solar cell without interference (no shadows from cables or accessories). Switch on room lighting if necessary.
- The electrode cap must not necessarily be firmly screwed onto sockets (4), (5), and (6) of the 767; plugging it in is sufficient.
- Do not unplug an electrode at the measuring input 'pH/ISE'. Unplug any interconnections with other instruments or a temperature sensor that may possibly be connected.
- Switch on pH Meter.
- The decimal place in the digital display for mV (Mode U) and °C (Mode T) must be visible. If it is not, then activate it under **CONFIG / auxiliaries / last digit.**
- The bold numbers in column 2 refer to the positions of the chapter 1.2 (parts and controls) of the instructions for use 780 / 781.
- Please mind also the introduction to the measuring amplifier check that is to be found in the Metrohm home page, under <support> <validation and QM> <useful forms> (German and English) <introduction>.

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[1] *Wait until drift symbol disappears*

[2] *The given permitted difference applies for normal room temperature (20 - 30 °C) and warmed up instruments. Alternatively these values can be determinated from the technical specifications of the 767 and the 780 / 781 pH/Ion Meter*

[3] *If the variation is too large try exchanging the electrode cable*

[4] *A larger short-time change is normal*

[5] *Use adapter 6.2103.130 / 6.2103.140 from 780/781 accessories*

826, 827: Protocol of measuring amplifier check

Metrohm

Instrument: **1.82**... ..... **Serial / Fabr.-No.:** ..... **ID-No** (if available)**:** .....

Test agent: **2.767.0010** **Serial / Fabr.-No.:** ..... **ID-No** (if available)**:** .....

Next Cal.: ..... Cal. Master: .....

Type: ..... Certificate-No.: .....

SCS Cal. Serv. Reg. Nr.: .....

Check carried out on: ..... **Name:** ..... **Signature:** .....

Checked instrument meets requirements: ☐ yes ☐ no Decision: .....

Please read the notes on the following page first.

Checking U (mV)

	Carry out on 826/827 or on sensor	Remarks	Carry out on 767	Enter theoretical value from 767 cover	Enter actual value from 826/827 display[1]	Difference	Permitted difference[2]	OK ✓
1	Unscrew the cable at the plug-in head of the pH sensor. If not possible, insert cable 6.2150.040 from 767 accessory to sockets **4** 'pH/mV'	Place sensor in sleeve	Close cover					
2	In pH/ºC/mV press <OK> repeatedly until mV appears in display		Sensor cable to socket (5)	mV value 5: 0 mV	..... mV	..... mV	± 1.0 mV	.....
3			Open cover	mV value 5: .....mV	..... mV	..... mV	± 1.5 mV	.....
4			Sensor cable to socket (4)	(actual value from step 3)	..... mV	Diff. act. value [3] step 3 and. 4 ..... mV	± 1.0 mV	.....
5			Sensor cable to socket (6)	mV value 6: .....mV	..... mV	..... mV	± 2.5 mV	.....

Checking temperature (Pt1000)

	Carry out on 826/827 or on sensor	Remarks	Carry out on 767	Enter theoretical value from 767 cover	Enter actual value from 826/827 display[1]	Difference	Permitted difference[2]	OK ✓
1	In pH/ºC/mV press <OK> repeatedly until °C appears in display *Make sure Pt1000 is set in configuration*		No preference for cover.					
2	Use two banana cables (6.2150. 000) to connect temperature measuring input **6** to 767 [4].	*Read the theoretical value for the sockets (1) + (3) from the white field 1 - 3 on the cover*	to sockets: (2) + (3): (1) + (3):	.....°C .....°C	.....°C .....°C	.....°C .....°C	± 1.0 °C ± 1.0 °C	....
3	Remove cables or reconnect sensors, respectively. Please put back to the case the original cables belonging to 767.							

Hints for the preparation of the measuring amplifier check

- Place Calibrated Reference on bench near sensor. Ensure that light reaches solar cell without interference (no shadows from cables or accessories). Switch on room lighting if necessary.
- The electrode cap must not necessarily be screwed onto sockets (4), (5), and (6) of the 767; plugging it in is sufficient.
- Do not unplug an electrode at the measuring input 'pH/mV'. Unplug any interconnections with other instruments or a temperature sensor that may possibly be connected.
- Switch on pH Meter.
- The decimal place in the digital display for mV and °C must be visible.
  If it is not, then activate it under **config / auxil / last digit**.
- The bold numbers in column 2 refer to the positions of the chapter 1.2 (parts and controls) of the 826/827 Instructions for Use.
- Please mind also the introduction to the measuring amplifier check that is to be found in the Metrohm home page, under <support> <validation and QM> <useful forms> (German and English) <introduction>.

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[1] *Wait until drift symbol disappears*

[2] *The given permitted difference applies for normal room temperature (20 - 30 °C) and warmed up instruments. Alternatively these values can be determined from the technical specifications of the 767 and the 826/827 pH Meter*

[3] *If the variation is too large try exchanging the electrode cable*

[4] *Use adapters 6.2103.130 / 6.2103.140 from 826/827 accessories*