Introduction to checking measuring inputs with the 767 Calibrated Reference

The 767 Calibrated Reference is a diagnostic tool which enables the customer to check the functions of the measuring amplifier (pH/mV, Ipol, conductivity, temperature) himself/herself. This instrument can be used for periodic checks within the framework of a quality assurance system or for a quick check if instabilities or difficulties occur.

Quality assurance requirements often demand that all activities involving the instrument or the unit are documented. This also affects the above-mentioned measuring input checks. You will therefore find **..Link..** instrument-specific forms which will considerably facilitate your work. Apart from a table for entering the measuring results these also contain the exact working procedure. These forms are available in PDF-format. You can simply print them out and fill them in by hand, but you can also enter the numbers and values given on the cover of your 767 (which always remain the same) in the form and then photocopy it to obtain sub-originals. In this way these checks can be carried out in a short time and with less writing being required.

Information worth knowing about the checks

In all measurements, particularly with the pH amplifier, it is very important that the sensor cable or cables are included in the check. Please read the remarks given in section 1: 'The important basic term 'high impedance'.

The reference point for the measuring amplifier is either earthed or floating. Both types of circuit have their specific advantages, see section 2.

The 'internal' calibration of the instrument is important. However, it should be remembered that pH and conductivity measurements are not absolute measurements and that therefore the accuracy of the result does not depend directly on this internal calibration, see section 3.

Checks with the 767 Calibrated Reference should be carried out as simply and rapidly as possible. With pH meters and titrators the checks should be carried out in the mV range if possible, see section 4.

Validation, continuous monitoring and maintenance of the instruments are other important terms, see section 5. Naturally the demands placed on the instrument and its requirement profile can differ greatly and must be determined individually. However, these additional checks should not be too excessive. It is best to observe the basic rule that every investment in quality assurance must pay for itself in the long term via an improvement in the product.

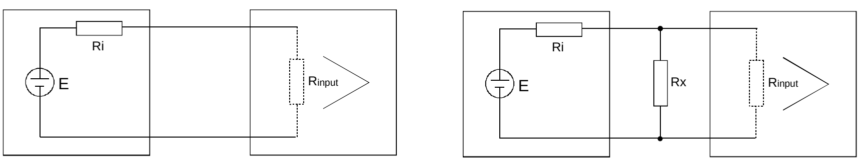
1. The important basic term 'high impedance'

pH electrodes are voltage sources with a very high internal resistance. To prevent falsification of the measuring voltage, no current should flow from the source if possible. This means that the whole measuring circuit, from the electrode via cable, plug, socket, switching element up to the measuring amplifier itself must be very well insulated. Only high-quality insulation material such as PTFE (teflon), polyethylene, glass, siliconized ceramics, etc. are acceptable. The target is an insulation resistance of up to 10^{14} ohms. This is a really extreme requirement. In the following example this resistance can be regarded as being infinite. From diagram a) it can be seen that the potential E in the amplifier is always effective, even if Ri changes greatly with the temperature (this is normal for electrodes).

The smallest contamination by atmospheric deposits or from spilt liquids can influence the insulation values.

What happens in such a case?

R_x in the diagram b) corresponds to the contamination. The current flowing through this resistance generates a voltage drop at R_i and thus falsifies the potential measured at the amplifier input.



a) unloaded potential source b) loaded potential source

If the electrode is now calibrated, i.e. the electrode parameters are determined, then the instrument is adapted to the electrode. This means that the previously determined error is also compensated. The measurements are again correct.

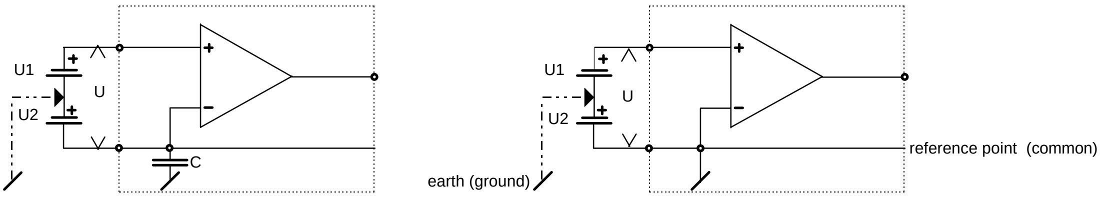
If this is the case then why get so excited?

It is important to know that such a contamination represents a highly unstable resistance whose value can change with the atmospheric humidity, temperature and many random factors. The resistance can therefore vary to a very large extent. Together with Ri, which is strongly temperature-dependent, this results in a very unstable potential divider. This is no longer compensated, or only at the next electrode calibration (and therefore again at random). However, because this fault is again concealed at each calibration it often goes unnoticed for a long time, during which incorrect (and above all unstable) results are obtained.

From this it can be seen that constant additional monitoring of the high impedance of pH meters and titrators must be a basic concern of quality assurance. However, this only makes sense when the most exposed element, the sensor cable, is included in the monitoring process.

2. Fixed and floating reference points of the measuring amplifier

We are going to present the facts in a very simplified manner so that you will be able to avoid possible problems. We simply represent the electrodes as being potential sources with the partial potentials U1 and U2 (corresponding to the reference and measuring potentials). Figure a) shows the measuring amplifier circuit separated from the earth (ground), figure b) shows it connected to the earth.



a) Measuring amplifier with floating reference point b) Measuring amplifier with fixed reference point

For measurements on unearthed potential sources, e.g. an electrode in a beaker, both circuits behave exactly the same. However, for measurements on an earthed solution, e.g. when the solution to be measured is contained in an earthed steel container or an earthed stirrer is immersed in the solution (symbolized by the broken line to earth), then in case a) the resulting total potential does not alter. In case b) the partial potential U2 is short-circuited and the total potential U is therefore falsified. In this case a correct measurement can only be made with separate electrodes.

Earth connections (earth loops) are often not readily visible. For example, the connection of an earthed printer to an instrument with a type a) circuit can mean that the amplifier itself is again earthed.

This makes it clear that with an instrument with a type a) circuit it is necessary to check the separation at regular intervals as it may be negatively affected by, for example, dirt on the insulation. This check can be carried out with the 767. If the pH Meter is included in an assembly it may even be possible to find an earth connection which is not immediately visible.

3. Internal calibration and accuracy of the pH meter

The output potential of the pH electrode must be corrected. In such a case the asymmetry potential is compensated and the change of the slope caused by aging must be balanced by adjusting the sensitivity of the measuring circuit. These electrode parameters must be determined by a calibration process. From this it can be seen that the accuracy of the subsequent measurement only depends on the accuracy of the calibration buffers and the calibration procedure.

The internal calibration of the measuring amplifier therefore has only an indirect influence. Even an instrument with a large calibration error will display the correct pH value; only the asymmetry potential and the slope will be slightly incorrect. However, the parameters asymmtry potential and slope (together with the speed of response) are only used for monitoring the electrodes in order to assess (with a large measure of discretion) whether the electrodes can still be used for further measurements.

Nevertheless stability, resolution, linearity, etc. are of course important properties which influence the accuracy and reproducibility of the measurements.

4. Checking the instrument calibration for pH

Microprocessor-controlled pH meters (e.g. 691) and titrators monitor the quantities mV and pH via the same analog measuring channel as a mV value and use it, with the help of the temperature and the electrode parameters, to calculate the pH value. The processor system is automatically checked each time the instrument is switched on and it is therefore safe to assume that this conversion is correct. This means that for such instruments a check of the mV value is sufficient; a check of the pH value is unnecessary.

This means that a very simple check of the pH/mV amplifiers is possible without resetting the electrode parameters; this considerably reduces the time and effort needed.

This is not the case for analog pH meters (e.g. 620) and digital pH meters with logic circuits (e.g. 632). In these instruments the mV value is converted into the pH value in an analog process. Checking the internal calibration of such instruments must therefore include both pH and mV.

5. Validation, continuous monitoring and maintenance of Metrohm instruments

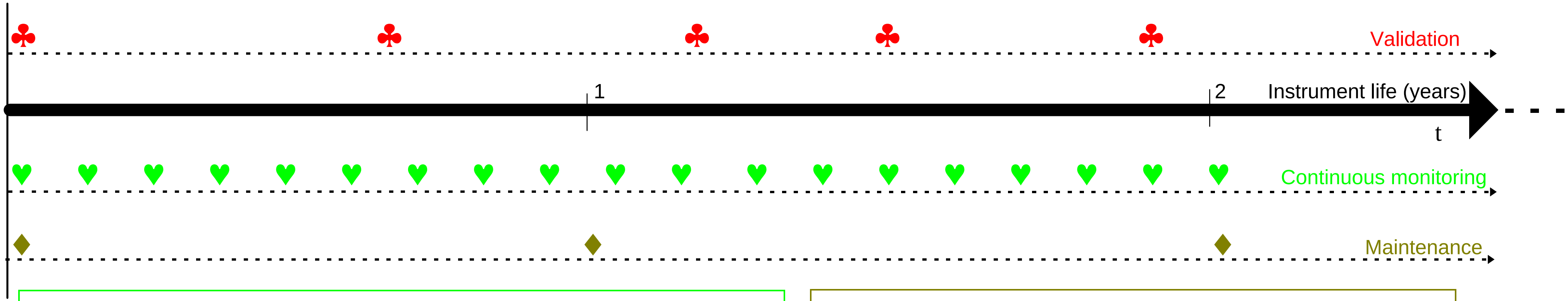
In this diagram you find the definitions of the important Quality Assurance terms „Validation“, „Maintenance“ and „Continuous Monitoring“, whose interrelationships over the instrument’s lifetime are also shown.

Validation:

Validation includes checking the complete installation of an instrument or system including sensors, samples, measuring methods and measuring procedure.

The interval for the validation is individually determined by the operator according to his/her particular requirements. The following occurrences may justify a validation:

- new start-up
- repeated start-up (e.g. after a long interruption)
- alteration of a method
- after a defined interval



Continuous monitoring (instrument or system):

Instrument, sensors and accessories should be monitored continuously. Contamination or small defects must be remedied immediately. Parameters which are less visible, such as instrument calibration or the high impedance of the measuring cables and sockets, should be checked by the operator at reasonable intervals by suitable means. The following occurrences could mean that a detailed check with the 767 Calibrated Reference for mV, pH, Ω, µS, °C would be a good idea (this check does not replace the normal maintenance work!):

- each recalibration of the electrode
- exchange of sensor
- each validation (see above)
- repeated start-up after a long interruption
- change in the application
- before the start of a series of measurements
- when instabilities or difficulties occur

It is also possible to imagine checks at fixed intervals (e.g. once per month)

Maintenance:

During maintenance the instrument is subjected to a detailed inspection by a specialist. All functions (both electronic and mechanical) are checked according to the instructions given in the Service Manual. This should provide a guarantee that the instrument will survive the next maintenance interval without a fault. Worn or corroded parts are replaced as a preventative measure.

The maintenance interval is normally 1 year. For extensively used instruments (24 h operation or very corrosive surroundings) the interval must be reduced accordingly (e.g. to six months).

Care must be taken that the maintenance is actually carried out at the stipulated time. For instruments which are subject to a quality assurance system (ISO 9000, GLP, etc.) a corresponding maintenance interval monitoring system must be verifiable.

We therefore recommend that you enter into a maintenance contract with Metrohm or your local Metrohm supplier. In this case, monitoring the maintenance time which has been agreed upon becomes the responsibility of Metrohm or your local supplier.

For further information concerning maintenance contracts