

Calibration of electrodes - yes or no?

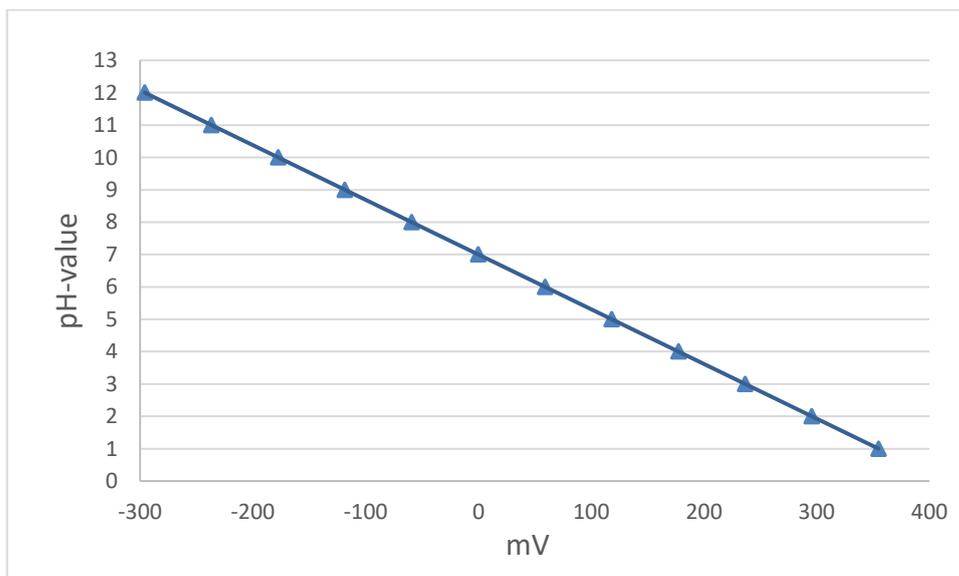
Again and again the question arises how an electrode can be tested correctly or how electrodes are calibrated.

In short: Only pH electrodes are calibrated, (almost) all others are not!

An electrode (or an electrode system consisting of indicator and reference electrode) always only provides a potential in mV, even if the measuring device to which the electrode is connected indicates something else, e.g. a pH value. This potential depends on the concentration (better: the activity) of the ions that interact with the electrode. The dependence of potential and ion activity is described by Nernst's equation:

$$E = E^{\circ} + \frac{RT}{z_e F} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

The pH value, the negative, decadic logarithm of the H⁺ ion concentration, is nothing other than a concentration indication. When calibrating a pH electrode with at least 2 different buffers, the slope and the zero point of the calibration curve are determined. Using this calibration curve, the meter or titrator calculates the pH value from the potential of the electrode in the solution to be measured. The calibration is therefore only needed to calculate a concentration (or pH value) from the electrode potential.



Calibration curve

Due to the large influence of the smallest potential changes on the result, a direct measurement of the acidity via the pH value is very inaccurate. The acidity can only be determined quickly and accurately by titration.

Calibration of an electrode

For a calibration, several solutions (min. 2) of exactly known concentration of the ions to which the electrode responds are required. The difference in concentration should be at least one factor of ten! Such solutions are (almost) only available for pH calibrations (pH buffers).

For electrodes other than pH electrodes, pH buffers are not suitable. So it is nonsense to try to "calibrate" e.g. a silver electrode with a pH buffer - nothing sensible can come out of this!

With a pH electrode, the calibration gives a good indication of the condition of the electrode: If the slope is above 95% of the theoretical slope (at 25°C 59.16 mV/pH, Nernst equation), the electrode is still OK for titrations. If the slope is below 95%, the electrode should be replaced.

Checking pH electrodes for non-aqueous titration

With pH electrodes with non-aqueous electrolytes (e.g. N 6480 eth with LiCl in ethanol) the zero point of the electrode is shifted so far that the electrode may be recognised by the titrator as not calibratable. In this case, the slope is determined manually by measuring the electrode potential in 2 buffers - the slope results as a potential change in mV per pH.

Potentialänderung in mV pro pH:

- Set titrator to a mV method.
- Open the refill opening of the electrode
- Rinse electrode with water
- Immerse in pH buffer 4.00
- Read off measured value after 45 seconds
- Repeat measurement with buffer 7.00
- $\Delta mV / \Delta pH$ (in the example with buffers pH 4 and pH 7: $\Delta pH = 3$)

59.16 mV/pH = 100 % Slope (at 25°C)

$\Delta mV / \Delta pH$ = slope of the Electrode in mV/pH

Except for pH measurements, only ISE measurements calculate a concentration directly from the electrode potential - but this requires a special sample matrix, and the adjustment time of the electrode is often 10 minutes or longer until a stable potential is reached.

Checking electrodes where calibration is not possible

For titrations which work directly with the electrode potential in mV as the measured value, a calibration is not required, nor is it possible - the potential is not converted into a concentration or similar.

But how to test an electrode if calibration is not possible? No matter which electrode it is, whether Ag, Pt (redox), Copper or Calcium electrode, the best way to check the electrode is by regular titration of a suitable standard material.

Titre determination is a good way to do this: If a titre determination is carried out regularly, the current titration curves can be compared with those obtained with a fresh electrode. This is particularly easy if the titration results are automatically stored or printed - this way all titration curves are available.

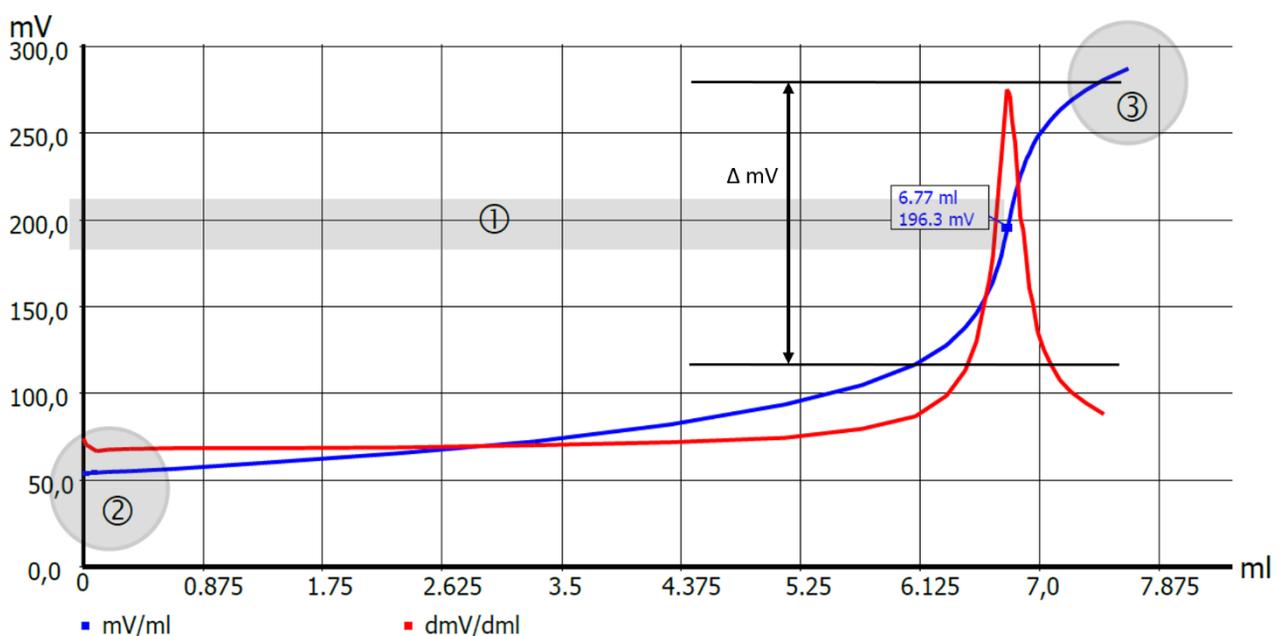
Clearly flatter, noisier titration curves with a smaller potential jump indicate an aged electrode.

The criteria are there:

- Is the content recovered? Recovery rate should be $100 \pm 2 \%$ of the specified content.
- Is the EQ in expected potential range? (1)
- Does the titration take longer than normal?
- Are the start and stop potentials and the potential jump ΔmV in the expected range? (2 and 3)
- Does the first derivative have the usual height or value at the maximum?
- Is the titration curve free of noise?

When titrating a standard with a 0.1 mol/l titrant, the potential jump ΔmV in the steep part of the curve should be above 80 mV.

Usually the potential jump is much larger, with some redox titrations (e.g. Potassium dichromate with Fe^{2+}) the ΔmV can be well above 500 mV!



Suitable applications for testing electrodes are, for example:

Ag-Electrode	Ag 62 AgCl 62 AgCl 62 RG AgCl 6280 Ag 1100	Titre determination of AgNO ₃
Pt-Electrode	Pt 62 Pt 62 RG Pt 61 Pt 6280 Pt 5901	Titre determination of Sodium thiosulfat
Cu - Electrode	Cu 1100 Cu 60	Titre determination of EDTA
Ca - Electrode	Ca 1100 Ca 60	Titre determination of EDTA

The applications mentioned (and many more) can be found on our website.

Any questions? Please contact the application team:

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