Titel der Präsentation

Untertitel
pH-measurement an easy thing?

• asymmetry and slope are determined by the calibration and, thus the slope and axial intercept of the calibration function.
• values are relevant for quality of the measurement
• examples Calibration 1 ideal slope (Nernst Equation) pH value changes by one unit (green) voltage electrode 1 changes 59mV(red)
• curve 2, voltage changes only approx. 25mV (blue marking) with pH change of one unit, this electrode is less sensitive.
PH-measurement an easy thing?

- avoiding basic buffer- frequ. underestimated problem; carbon dioxide from ambient air can change the value of basic buffers!
- available measurement range between pH 2 - pH 10
- temperatures of the calibration/measurement solutions should differ less than 2 K.

<table>
<thead>
<tr>
<th>Ideal values:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope:</td>
<td>-57 to -60.5 mV/pH at 25°C</td>
</tr>
<tr>
<td>Offset voltage:</td>
<td>±15 mV</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Acceptable values:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope:</td>
<td>-56 to -61 mV/pH at 25°C</td>
</tr>
<tr>
<td>Offset voltage:</td>
<td>±20 mV</td>
</tr>
</tbody>
</table>
pH-measurement an easy thing?

- QS requirements of asymmetry and slope in calibration standard buffers must be fulfilled.
- Example evaluation of calibration by a WTW pH meter.
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Calibration interval

• daily fresh calibration should be used
• If slope and asymmetry of the electrode lie within the tolerances this is enough, during series in intervals of 2h measuring of cal.-buffer as sample between analysis samples
• If buffer results lie outside the tolerances (+/-0,02pH) renew calibration; check temperature, filllevel, outflow of reference electrolytes and diaphragm/electrode-surface
• calibration procedure should document status of system (buffer, electrode+pH meter) and not adjust interfering influences
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**Buffer solutions 1**

- primary reference material (powder form) is produced by NIST 9 buffer solutions whose pH values at 25 °C are plotted in diagram

- We use standard DIN buffer solutions (Merck p. E.) corresponding in composition to the primary reference material with a conservation additive. The accuracy of these solutions is ± 0.02 pH units.
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**Buffer solutions 2**

- diagram shows real pH values of an opened technical buffer solution (pH 10) and a standard buffer solution (pH 9) over 12 hours, the value of the buffer pH 10 changes by 0.22 and buffer pH 9 by 0.02 pH units. carbon dioxide effect!
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Electrode

• cleaner and less electrolyte charged sample ⇒ sensitivity to pH changes through "external influences“, e.g. temperature, carbon dioxide from air, outflow of the ref.-electrolyte (as constant and high as possible) to minimize potential fluctuations (diffusion potentials)
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Practising measurement 1

• Measuring range: pH 3 – pH 9
• Measuring equipment pH meter:
  - minimum resolution of the pH value display: 0.01
  - minimum resolution of the temperature display: 0.1 K
  - calibration procedure selected for DIN buffersolutions
• pH combination electrode:
  – Membrane: Cylindrical membrane;
  – Diaphragm: ceramic (outflow speed > 0.1 ml/d)
• Accessories: Magnetic stirrer with stirring rod;
  Electrode stand; Temperature probe; UPS
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**Practical measurement Rainwater 1**

- Using of 2 or 3-Point calibration
- Voltage Buff. $4,006 = 175\text{mV} \pm 20$, Slope -56 to -61 mV/pH
- measuring under Drift(Autoread)control
  \[ \sigma \leq 0,02 : 0,1\text{mV} / 30\text{sec} \]
pH-measurement an easy thing?

Practical measurement Rainwater 2

• Starting 2-Point calibration 4,006-6,86
gentle stirring is recommended during all measurements to ensure solutions remains homogenized and stable state will faster reached (approximately 5 minutes)
making sure that magnetic field of the stirrer does not influence the electrode!

• Using the automatic drift control of the measuring instrument.

• Repeating of the measure till two following results of one samples do not differ $\geq 0,01$ pH unit
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Practical measurement electrode validation

• Making a 3-Point calibration pH: 4,006-6,86-9,18
• Reading slope1 for acidic range and slope2 for basic range separately
• Setting slope1 and slope2 in relation, the relative slope is a good quality criteria for the yielded calibration;
• relative slope of 1 means both slopes (1+2) are identically, the electrode is working total linear in the range pH 4,006-9,18 (deviations $>\pm 5\%$ are else valid)
• Routine acc.: to WTW Appl.-Report pH 492009
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Practical measurement electrode protocolation

30.09.09 14:00:22

AutoCal DIN/NBS  Tauto
  Buffer 1          4,006
  Buffer 2          6,865
  Buffer 3          9,180

C1  -134,4mV  24,3 °C
C2   3,7mV     24,3 °C
C3   170,2mV   24,4 °C

S1   -58,3mV/pH
S2   -59,7mV/pH
S REL 0,98
ASY-POT -4mV
pH-measurement an easy thing?
The heaven of thermodynamics
Physical-Technical-Bundesanstalt (PTB) Hannover

National Metrology Referencelab

primary pH-Measuring equipment

Primary buffer solution
$U(k=2) = 0.002$
The primary method for pH:
Harned cell: Pt | H2 | buffer, Cl- | AgCl | Ag

- Cl- are added to stabilize the potential of the Ag/AgCl electrode
- The potential difference $E$:

$$E = E_0 - k \lg(aH_mCl \chi Cl)$$

$a$ activity
$m$ molality
$\chi$ activity coefficient
$E_0$ standard potential of the Ag/AgCl electrode

- Rearranged to give the acidity function $p_a$:

$$p_a = -\lg(aH_+ \chi Cl-) = E - E_0 / k + \lg(mCl-)$$

- $p_a$ is extrapolated to zero chloride molality.

$$p_a0 = -\lg(aH_+ \chi Cl-)mCl \to 0$$

- $\chi$ is obtained by the Bates-Guggenheim convention:

The ion size parameter of the Debye-Hückel theory at low ionic strength ($I < 0.1 \text{ mol kg}^{-1}$) is set equal to 1.5

- $pH = p_a0 + \chi Cl$
pH-measurement an easy thing?

Our Equipment Deposition+Soilsolution

- complete Level-II water analysis includes ELC, pH value, alkalinity; ELC, pH measurement and the pH titration
- response time can be several minutes long, stirring rate can influence measured pH value
- Aquatrode Plus with special glass membrane guarantees rapid, correct very precise pH measurements and titrations in low ionic strength solutions
Aquatrode Plus specifications

Temperature sensor: Pt 1000
Diaphragm: Fixed ground joint

Characteristics
- Combined pH-glass electrode ground-joint diaphragm insensitive to contaminations
- Variable outer electrolyte for special applications
- Special pH glass membrane: short response time, excellent long-term stability, stirring robust

pH-measurement an easy thing?

Our Equipment Deposition + Soilsolution

\[ \text{measured pH-value solution } c(\text{Na}_2\text{CO}_3) = 0.14 \text{ mmol/L different stirringspeed (x-Coordinate } \rightarrow \text{ Start-pH-Value of titration). Aquatrode Plus lies closer to the with an präzisionselectrode measured pH-value von 9.98 than the pH-elektrode with ceramicdiaphragma. Strong stirring effects only decreasing of ca. 0.05 pH-values (according ca. 3 mV) in an unistirred aliquote of the same solution} \]
pH-measurement an easy thing?

Our Equipment ELC, pH, Alcalinity