STAATSBETRIEB SACHSENFORST

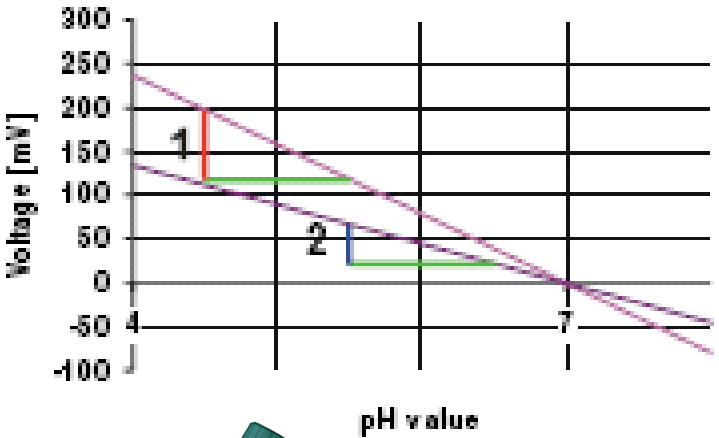
Freistaat SACHSEN

Titel der Präsentation

Untertitel

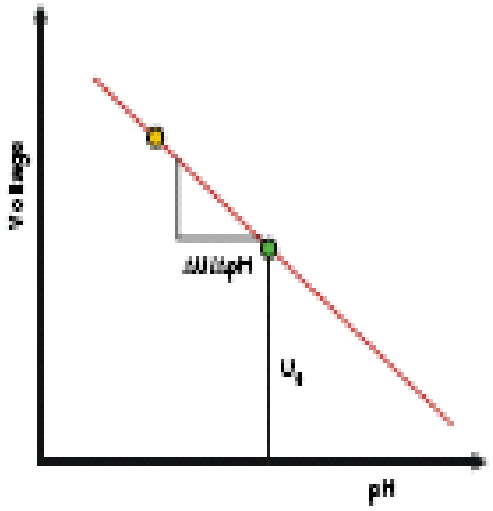
pH-measurement an easy thing?

- 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?

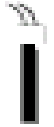
- avoiding basic buffer- frequ. underestimated problem; carbon dioxide from ambient air can change the value of basic buffers!
- available measurement range between pH 2 - pH 10
- temperatures of the calibration/measurement solutions should differ less than 2 K.



Ideal values:	
Slope:	-57 to –60.5 mV/pH at 25°C
Offset voltage:	±15 mV
Acceptable values:	
Slope:	-56 to –61 mV/pH at 25°C
Offset voltage:	±20 mV

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

Display	Quality of calibration
	S = –58 ... –60.5 mV/pH UASY = –15 ... +15 mV Very good
	S = –57 ... –58 mV/pH UASY = –15 ... +15 mV Good
	S = –56 ... –57 mV/pH or S = –60.5 ... –61 mV/pH UASY = –20 ... +20 mV Satisfactory
	S = –56 ... –50 mV/pH or S = –61 ... –62 mV/pH UASY = –30 ... –20 mV or UASY = +20 ... +30 mV Poor
E3	Calibration error/

pH-measurement an easy thing?

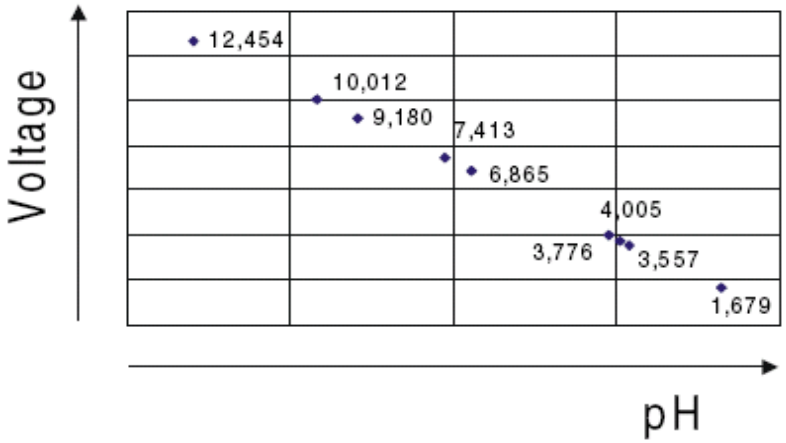
Calibration interval

- 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

pH-measurement an easy thing?

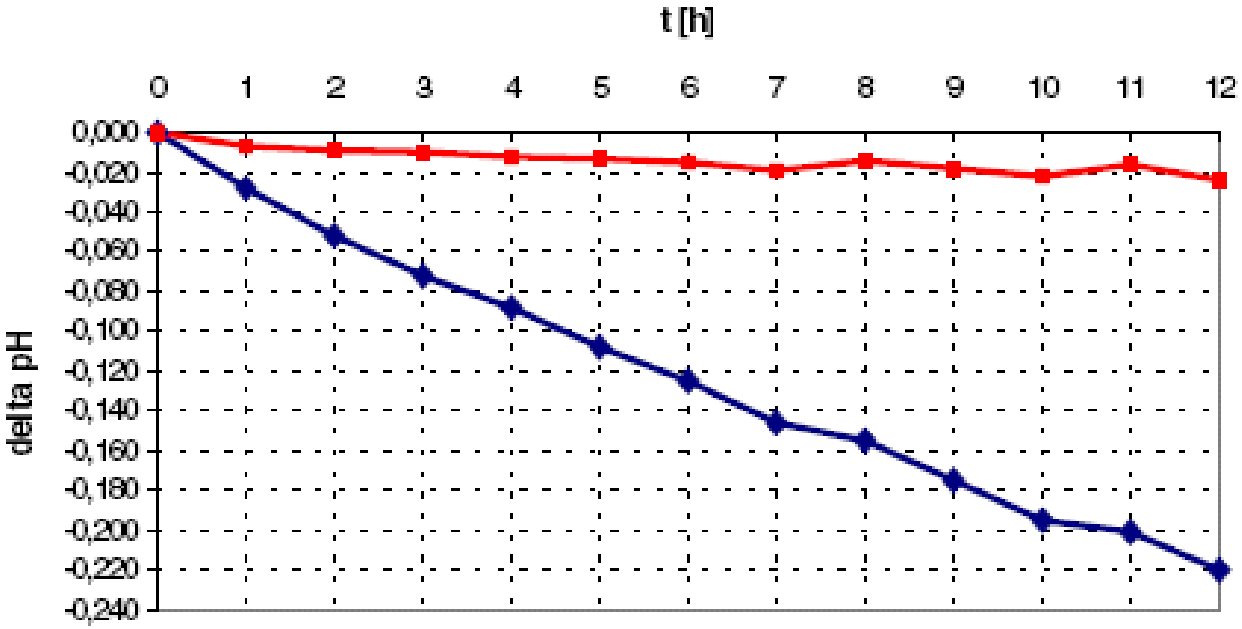
Buffer solutions 1

- 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.



pH-measurement an easy thing?
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. carbondioxide effect !



pH-measurement an easy thing?

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)

Electrode equipment	Diffusion of the ref
Electrode with ceramic ⇒ direct position in soil solution	High and even bec through ground-join
Electrode with ground ⇒ hauptmuasg, mso	High and extremely provided by adjusta

pH-measurement an easy thing?
Practising measurement 1

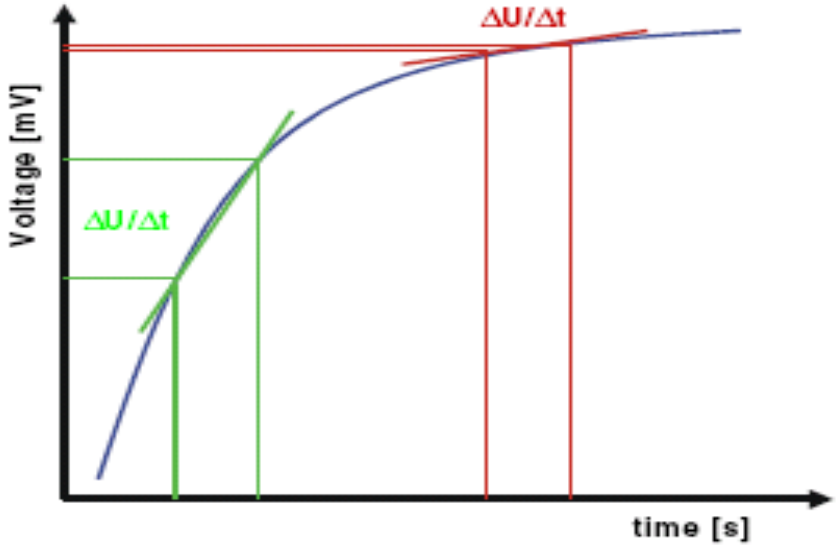
- Measuring range: pH 3 – pH 9
- Measuring equipment pH meter:
  - minimum resolution of the pH value display: 0.01
  - minimum resolution of the temperature display: 0.1 K
  - calibration procedure selected for DIN buffersolutions
- pH combination electrode:
  - Membrane: Cylindrical membrane;
  - Diaphragm: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

pH-measurement an easy thing?

Practical measurement Rainwater 1

- Using of 2 or 3-Point calibration
- Voltage Buff. 4,006 = 175mV **+/-** 20,
  Slope -56 to –61 mV/pH
- measuring under Drift(Autoread)control

  $\sigma \leq$ **0,02 : 0,1mV / 30sec**



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 follwing results of one samples do not differ ≥ 0,01 pH unit

pH-measurement an easy thing?

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 identicaly, the electrode is working total linear in the range pH 4,006-9,18 (deviations >± 5% are else valid)
- Routine acc.: to WTW Appl.-Report pH 492009

pH-measurement an easy thing?

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

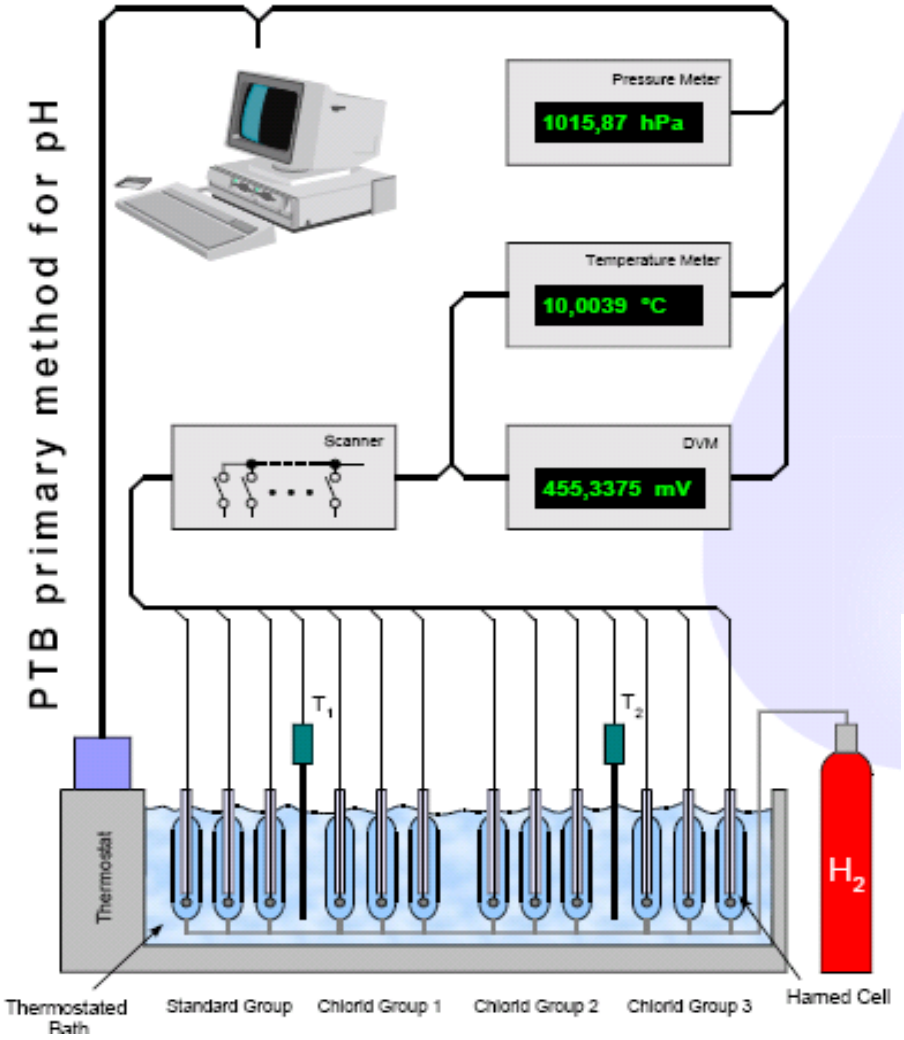
C1	-134,4mV	24,3 °C
C2	3,7mV	24,3 °C
C3	170,2mV	24,4 °C
S1	-58,3mV/pH	
S2	-59,7mV/pH	
S REL	0,98	
ASY-POT	-4mV	

pH-measurement an easy thing?

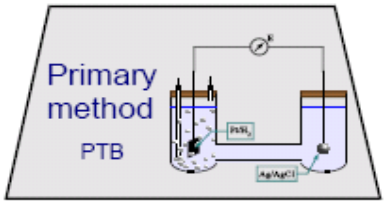
The heaven of thermodynamics

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:

$E = E0 - k \lg(aH\ mCl\ \chi Cl)\ k = R\ T \ln 10 / F$

a activity

m molality

χactivity coefficient

*E*0 standard potential of the Ag/AgCl electrode

- Rearranged to give the acidity function p*a*:

p*a* is measured as a function of *m*Cl.

$pa = -\lg(aH+\ \chi Cl-) = E - E\ 0 / k + \lg(mCl-)$,

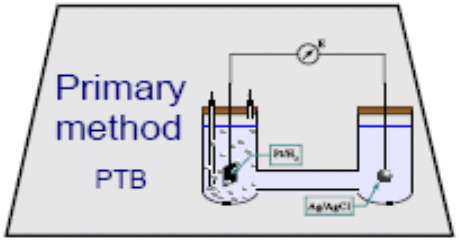
- p*a* is extrapolated to zero chloride molality.

$pa0 = -\lg(aH+\ \chi Cl-)mCl \rightarrow 0$

- χC is obtained by the Bates-Guggenheim convention:

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

- pH = p*a*0 + χCl-



Primary buffer solution
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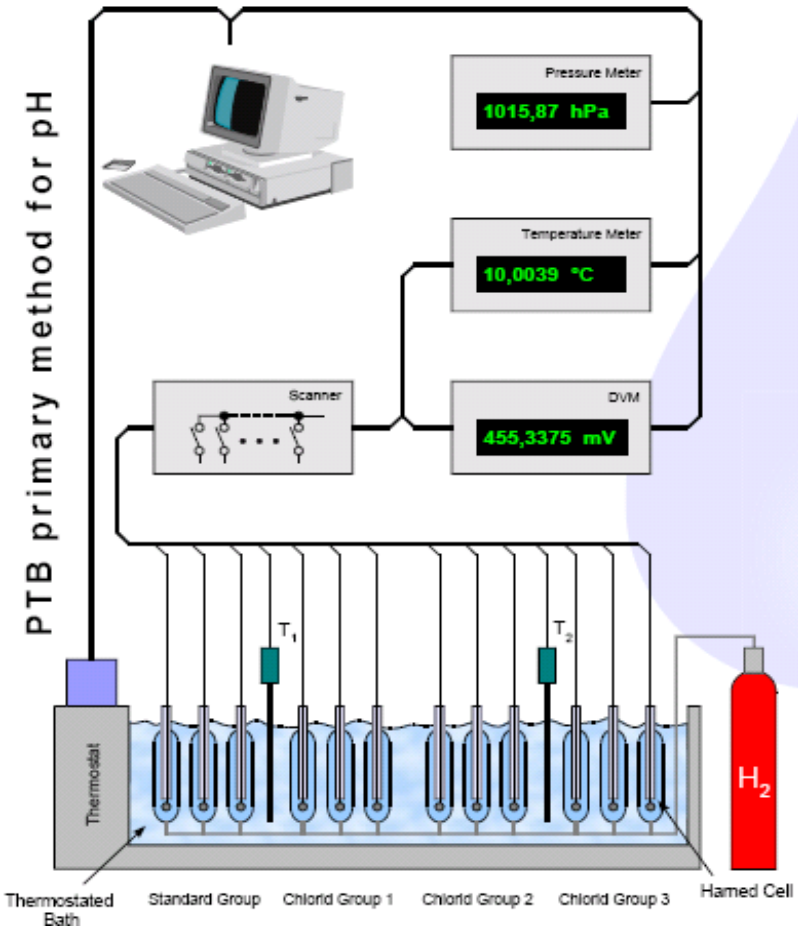


pH-measurement an easy thing?

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 measure-ments and titrations in low ionic strength solutions

pH-measurement an easy thing?

Our Equipment Deposition+Soilsolution pH

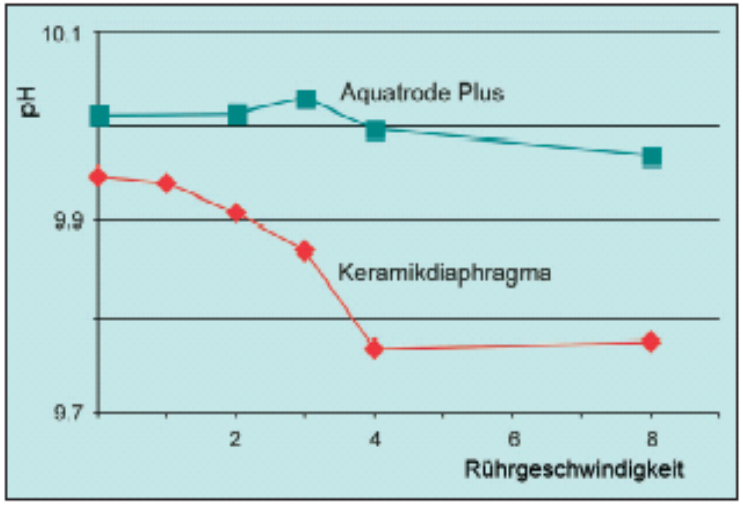
Aquatrode Plus specifications

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 roboust



measured pH-value solution c(Na2CO3) = 0,14 mmol/L different stirringspeed (x-Coordinate → 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 unstirred aliquote of the same solution

pH-measurement an easy thing?

Our Equipment ELC, pH, Alcalinity