Aqueous Glass/pH Electrodes: Performance Check and Cleaning

Electrode Calibration:

The values of relative slope, asymmetry voltage, $\mathbf{U_{as}}$, or asymmetry pH, $\mathbf{pH_{as}}$, reflect the working conditions of a glass/pH electrode. Cleaning becomes necessary whenever one of the conditions below is observed:

- Relative slope falls outside of 1.03 and 0.95
- $\mathbf{U_{as}}$ is greater than ± 30 mV (vs. Ag/AgCl - 3M KCl)
- $\mathbf{PH_{as}}$ falls outside of 6.50 and 7.50 (vs. Ag/AgCl - 3M KCl)
- Amount of time required to measure buffer

Potentials of standard buffered solutions are listed in Table 1. Deviations of greater than ±30 mV signify the need of thorough cleaning of the electrodes.

Table 1: pH - mV Relationship

°C	20.0	21.0	22.0	23.0	24.0	25.0
mV/pH	58.2	58.4	58.6	58.8	59.0	59.2
pH	U/mV					
1.00	349.0	350.2	351.4	352.6	353.8	355.0
2.00	290.8	291.8	292.8	293.8	294.8	295.8
3.00	232.7	233.5	234.3	235.1	235.8	236.6
4.00	174.5	175.1	175.7	176.3	176.9	177.5
5.00	116.3	116.7	117.1	117.5	117.9	118.3
6.00	58.2	58.4	58.6	58.8	59.0	59.2
7.00	0	0	0	0	0	0
8.00	-58.2	-58.4	-58.6	-58.8	-59.0	-59.2
9.00	-116.3	-116.7	-117.1	-117.5	-117.9	-118.3
10.00	-174.5	-175.1	-175.7	-176.3	-176.9	-177.5
11.00	-232.7	-233.5	-234.3	-235.1	-235.8	-236.6
12.00	-290.8	-291.8	-292.8	-293.8	-294.8	-295.8
13.00	-349.0	-350.2	-351.4	-352.6	-353.8	-355.0

- Besides the slope and pH(AS), the time it takes for that electrode to read is also very important. Below is a table that shows the slope and response time for a range of electrode status

Status of Electrode	Slope Range	Response Time
excellent	0.98 – 1.01	< 30s
good	0.96 – 1.02	< 45s
passing	0.95 – 1.03	< 60s
bad	< 0.95 or > 1.03	> 60s

- Cracks and deep scratches in the glass pH bulb nullify their response! It cannot be salvaged!

- Use the correct filling solution for your electrode and make sure that the level of the fill solution is higher than the level of solution in the sample vessel and check for build up of crystals in the reference compartment.

- Check the diaphragm (frit) for blockage (dark color build up). Clean by submerging the diaphragm area in a test tube containing ammonim hydroxide until the area is clear. Rinse well with de-ionized water, replace the filling solution and soak in pH 4 buffer for at least one hour.

- During titrations be sure the fill hole is open! The flow of electrolyte through the diaphragm is the only electrical contact between the reference and the sample!

Cleaning and Conditioning

• *Reagents*

1. Alcohol: methyl, ethyl or isopropyl
2. Ammonium hydroxide, NH4OH, 25% or higher concentration
3. Mixed acid cleaner: 50% nitric acid solution

• *Procedure*

pH Measuring Electrodes (for non-combination or combination with sleeve diaphraghm)	**pH Combination Electrodes (with ceramic diaphragm only)**
• Gently wipe the glass membrane (bulb portion) with alcohol. • Submerge the lower 2-cm portion (only the glass bulb) in the nitric acid for 10 to 15 minutes. • Remove the electrode and rinse thoroughly with de-ionized H2O. • Store all glass/pH electrodes in de-ionized H2O or other recommended aqueous media (e.g., 3M, 4M, and sat'd. KCl, sat'd KNO3 for at least 30 minutes before use.	• Gently wipe the glass membrane (bulb portion) with alcohol. • Soak the lower 2-cm portion in concentrated NH4OH for 15 minutes (longer if the slope falls below 0.950). • Submerge the lower 2-cm portion (only the glass bulb) in the nitric acid for 10 to 15 minutes. • Remove electrode and rinse thoroughly with de-ionized H2O. • Store all glass/pH electrodes in de-ionized H2O or other recommended aqueous media (e.g., 3M, 4M, and sat'd. KCl, sat'd KNO3 for at least 30 minutes before use.

Asymmetry Voltage and pH

Asymmetry voltage, U_{as}, of a glass/pH electrode is the potential difference between the inner and outer surfaces, or hydrated gel layers, of the glass membrane. It is caused by the differences in their absorptive power for water and Ion-exchange capacity for hydrogen ions. These differences are the results of :

1. Unequal strains in the two surfaces of the glass bulb due to non-uniform heating when the electrode is fabricated;
2. Chemical etching and mechanical abrasion during use;
3. Coating of the outer surface with grease film and adsorbable matters; and
4. Dehydration of the gel layers.

U_{as} of a glass/pH electrode in good working condition is of the magnitude of ±30 mV.

$\mathbf{U_{as}}$ is sometimes expressed as an absolute pH value, known as asymmetry pH, $\mathbf{pH_{as}}$. The relationship between the parameters can be described by the equation:

$$\mathbf{U_{as} = (pH_{as} - pH_{7.00}) * m * U_m}$$

where :
- $\mathbf{pH_{7.0}}$ = 7.00 (pH buffer value)
- $\mathbf{m}$ = relative slope, from calibration
- $\mathbf{U_m}$ = theoretical slope, in mV.

$\mathbf{U_m}$, the theoretical slope, varies with temperature and may be calculated with the equation below:

$$\mathbf{Um = 0.19835\ mV/^oC * T + 54.20\ mV}$$

where:
- $\mathbf{T}$ = Temperature in ^oC.

and
- $\mathbf{U_m}$ = 58.17 mV at 20 ^oC
- = 58.76 mV at 23 ^oC
- = 59.16 mV at 23 ^oC

Conversion of pHas to Uas on Titrino (all models except 701)

Asymetry voltage, Uas = (C46 – C01) * C47 * (C02 * C03 + C04)

Where :
- C01 = pH value of buffer 7.00= 7.00
- C02 = Temperature coefficient = 0.19835 mV/^oC
- C03 = Measurement temperature, in ^oC
- C04 = Theoretical electrode slope value at 0.00 ^oC
- = 54.20 mV
- C46 = Asymmetry pH, pHas, transferred automatically from calibration.
- C47 = Relative slope, m, transferred automatically from calibration

Remark : C03 can be substituted by C44 if a PT 1000 Temperature Probe is used in electrode calibration.

2. The effect of different references and salt-bridge electrolytes on the potentials of pH buffers, as measured with a glass indicator electrode at 25°C, is shown Table 3:

pH	4.00	7.00	10.00	pHas
Electrolytes / References	**Potential (U/mV, vs Ag/AgCl)**			
3M KCl	176.4	**0**	-176.4	**7.00**
Sat'd KCl	165.4	**-14.0**	-184.4	**6.76**
Sat'd LiCl in EtOH	133.2	**-43.2**	-219.6	**6.27**
TEABr	131.4	**-45.0**	-221.4	**6.24**
Sat'd KNO3	-39.4	**-215.8**	-392.2	**3.35**
***SCE**	214.4	**38.0**	-138.4	**7.64**
****Ag Titrode**	138.4	**-28.0**	-204.4	**6.53**

Sat'd LiCl in EtOH = saturated LiCl in ethanol, reference electrolyte for Solvotrode 6.0229.100
TEABr = Tetraethylammonium bromide, alternative electrolyte for Solvotrode 6.0229.100
*SCE = Standard Calomel Electrode = Hg/Hg2Cl2 . saturated KCl
**Ag Titrode 6.0430.100 uses a silver ring as reference when functions as a combination pH electrode.