

ionode pH and redox instruction sheet

DESCRIPTION AND USE

pH is a measure of acidity and alkalinity and is defined as:

$$\text{pH} = -\log \text{hydrogen ion activity}$$

and covers a scale from 0 (acid) to 14 (alkaline) for almost all aqueous solutions. A pH of 7 is termed "neutral". The pH electrode consists of a pH sensitive glass membrane attached to a sealed insulating tube containing a solution of fixed pH in contact with a silver-silver chloride half cell. The potential developed across the membrane is compared to a stable reference potential e.g. a silver-silver chloride half cell in contact with an electrolyte containing chloride. Completion of the circuit is accomplished by means of a porous constriction (the salt bridge) which allows the reference electrolyte to slowly flow into the sample, continuously flushing the ceramic constriction (Flow types). Gel electrodes have a sealed reference which is not self cleaning and can only be used in clean samples free of oils, fats, proteins and in samples of high ionic strength.

pH glass is attacked by alkaline solutions with high sodium ion levels, causing a "sodium error" i.e. the observed value is lower than the true value. The magnitude of the error depends on the age and history of the membrane and the type of pH glass ($B < C \ll A$). Hydrofluoric acid also attacks pH glass, reducing electrode life. Silver and mercuric ions react with the reference electrolyte and require the use of a double junction reference.

The redox electrode with inert platinum tip measures the oxidizing or reducing power of a solution in millivolts and will only give a stable reading in the presence of a reversible redox couple with a well defined concentration of both oxidized species. pH and redox electrodes may be "single", requiring a separate reference, or "combination".

ELECTRODE PREPARATION

1. Remove wetting cap from the membrane and replace with the membrane protector if desired.
2. Expose reference filling hole (Flow Types) and fill with electrolyte if necessary:
 - (a) Saturated (4M) or 3.5M potassium chloride for all pH reference systems
 - (b) 1M potassium chloride for redox/silver-silver chloride systems or saturated potassium chloride for redox/calomel reference systems.

The filling hole must be left open during measurement to allow electrolyte to flow into the sample. The electrolyte level should be kept within 2cm of the filling hole during measurement. Reference electrodes may take several hours to stabilize if refilled from a dry state.

3. Screw the electrode into the cap of the cable-connector to finger tightness (types X). Make sure the washer seals correctly. DO NOT OVERTIGHTEN. Replace washer if deteriorated.
4. Flick the electrode to remove any bubble within the membrane cavity. Store in buffer pH 4.0 before use.

CALIBRATION

pH ELECTRODES

1. Consult meter instruction manual. Remove electrode(s) from soaking buffer. Switch on the meter then connect the electrode(s) and place in a buffer as close as possible to pH 7.0 e.g. phosphate buffer 6.86. The membrane and salt bridge must be immersed. Rotate slope control to 100% if using for the first time, or leave at the previous value and then adjust the asymmetry control until the indication shows the value of the buffer. Allow the electrode(s) to stand in the buffer for several minutes to check for excessive drift. Reset if necessary.
2. Remove the electrode(s) from the buffer and wash the membrane and salt bridge with distilled water. Blot dry with a tissue. DO NOT WIPE.
3. Lower the electrode(s) into a second buffer (at the same temperature as the first) which has a value several pH units from 7.0 e.g. the phthalate buffer pH 4.00. Allow indication to stabilize and then use slope control to move the indication to the value of the second buffer. DO NOT move the asymmetry control with the second buffer calibration.
4. Recheck in the first buffer. If the electrode(s) is being used for the first time, or has not been used for some time, several restandardizations should be made before use on samples. The frequency of calibration depends on the stability of the system and is best determined by experience. For highest accuracy use a third buffer with a pH value close to that of the sample, or the expected mean of samples. Use asymmetry control only after preliminary two buffer calibration.

REDOX ELECTRODES

1. ZoBell solution (see appendix) is used as standard. The potential of platinum against a calomel reference should be +186mV at 25°C and 186 ± 10 mV against 1M potassium chloride/silver-silver chloride. Use the asymmetry control to set the indication to +186mV for either reference. With some meters the asymmetry control does not function on the mV mode. In this case between the actual value in ZoBell solution and +186mV must be added or subtracted to all readings.
2. Some redox measurements in literature refer to the Standard Hydrogen Electrode (S.H.E.). The formal potential of platinum against the S.H.E. is +430mV in ZoBell solution. To relate measurements against calomel or 1M potassium chloride/silver-silver chloride to the S.H.E., add +244mV.

NOTE: If the electrode is hand-held during measurement, hold the electrode by the cap above the washer, otherwise a small capacitive effect may be produced when transferring from one solution to another.

MAINTENANCE, CLEANING AND REJUVENATION

1. After measurement, remove electrode(s) from sample, wash and blot dry. Disconnect electrode(s), then switch off meter with electrode(s) in upright position. Store pH and redox in tap water or pH 4.00 buffer. Top up reference electrolyte regularly. For long term storage, drain electrolyte and wash reference chamber several times with distilled water. Stand electrode(s) in distilled water for at least 12hrs. to remove potassium chloride from the salt bridge. Dry and store in container, with wetting cap replaced.

2. Both the membrane (or platinum tip) and the salt bridge **MUST** be clean at all times. **DO NOT** allow fats, oils, proteins etc. to dry on the membrane or salt bridge.
The membrane or platinum tip may be cleaned with solvents, detergents or acid. Place a small amount of acetone, ethanol etc on cotton wool and gently wipe the membrane. **ABRASIVE MATERIALS MUST BE ABSENT.** For acid cleaning use sulphuric or chromosulphuric acid. After cleaning, wash well with tap water and soak before use. To clean the salt bridge, gently abrade the surface of the ceramic and immerse in hot (60°C) water for several minutes.
3. Some improvement in the response of aged pH electrodes may be obtained by the following treatment:
- Alternate between 0.1M hydrochloric acid and 0.1M ammonia, or
 - Immerse for 2 minutes in a 20% solution of ammonium bifluoride. Rinse well in tap water.
 - Immerse for 10 seconds (**NO LONGER**) in 10% hydrofluoric acid and immediately wash well in tap water. This treatment should be used sparingly.

TROUBLE SHOOTING

A fault may develop in either meter or electrode. If a number of electrodes and/or meters are available, interchange to isolate the fault. Note that the fault conditions described below are for **ELECTRODES ONLY**.

SYMPTOM	POSSIBLE CAUSES	REMEDY
Drift	salt bridge blocked Membrane not clean Membrane aged	see CLEANING . Test for flowing electrolyte by clamping electrode upright in air. Crystals of potassium chloride should form around the ceramic. see CLEANING see REJUVENATION , or replace
Low Slope (<94%)	Membrane not clean Membrane aged connectors damp buffers inaccurate	as above as above dry in warm place replace buffers
Large Assymm. Potential (>0.7pH)	salt bridge blocked reference electrolyte contaminated	as above flush with distilled water and replace electrolyte
Noisy	salt bridge blocked bubble in membrane bad connection to meter salt bridge not immersed potassium chloride crystallized around ceramic	as above see PREPARATION check connection see CALIBRATION wash reference chamber with distilled water until dissolved Replace electrolyte
Displays pH 7.0 for all buffers	electrical short	check connector
Displays pH 4-5 for all buffers	membrane or stem cracked	replace
Off Scale (Open Circuit)	See NOISY	see NOISY
Non Linear (over three buffers)	buffers inaccurate sodium error salt bridge contaminated	replace buffers. Note alkaline buffers absorb carbon dioxide and become inaccurate when exposed to air replace as above

APPENDIX

Preparation of phthalate buffer

Weigh 10.21gm of dry potassium hydrogen phthalate and dissolve in 1 litre of distilled water at 25°C. Discard if mould appears.

Preparation of phosphate buffer

Weigh 3.38gm of dry anhydrous potassium dihydrogen phosphate and 3.53gm of dry anhydrous disodium hydrogen phosphate in 1 litre of distilled water at 25°C.

Preparation of borate buffer

Dissolve 3.81gm of sodium tetraborate decahydrate in 1 litre of distilled water at 25°C. The solution must be stoppered as it absorbs carbon dioxide.

T°C	Phthalate	Phosphate	Borate
0	4.01	6.98	9.46
5	4.00	6.95	9.40
10	4.00	6.92	9.33
15	4.00	6.90	9.28
20	4.00	6.88	9.23
25	4.01	6.87	9.18
30	4.02	6.85	9.14
35	4.02	6.84	9.10

Preparation of ZoBell Solution

Solutions of 1/300M potassium ferricyanide in 0.1M potassium chloride and 1/300M potassium ferrocyanide in 0.1M potassium chloride are made up separately and then mixed in equal volumes before calibration. Discard the mixture after calibration.