

TrupH

TrupH™ Electrode Storage, Cleaning, and Aging

TrupH measurement systems require proper handling during storage, cleaning, and calibration. Good care of the pH electrode is important, and will optimize the performance of the pH measurement system. Incorrect handling can shorten the life of the electrode, or even result in an unreliable measurement. This application note reviews storage and cleaning procedures for TrupH electrodes. It also explains how TrupH electrodes age, so that the operational lifetime of these electrodes can be maximized. For calibration procedures, please refer to the application note entitled “TrupH Calibration”.

Storage

The duration of the storage period will determine how the pH electrode is stored, i.e. long-term (weeks or months) storage methods will differ from short storage intervals between consecutive process runs. The type of electrode (measurement, reference, or combination) must also be taken into account.

TrupH electrodes are gel-filled, combination electrodes. A combination electrode consists of a measuring electrode and a reference electrode combined into one, single-rod electrode. The storage conditions for TrupH electrodes must therefore be simultaneously suitable for a measuring and for a reference electrode. The general storage conditions for measuring and reference electrodes will first be reviewed.

Measuring Electrodes

Measuring electrodes can be stored dry for long periods. However before using a measuring electrode, it must be hydrated for at least 48 hours in normal tap water or a slightly acidic aqueous solution, in order to establish an outer gel layer at the pH sensitive membrane.

Most manufacturers supply measuring electrodes hydrated, i.e. a plastic or rubber cap filled with a liquid solution is placed over the membrane, so that they are available for immediate use. Do not discard the plastic caps as they can be re-used for short-term storage.

For short-term storage between measurements, a measuring electrode should be immersed in a container filled with storage solution, or be fitted with a watertight plastic cap filled with storage solution.

Reference Electrodes

Reference electrodes should always be stored wet, i.e. the diaphragm must be immersed in the same reference electrolyte as the one with which the reference electrode is filled. Wet storage applies for both short- and long-term storage. The refill aperture should be closed with a suitable stopper.

Reference electrodes should not be stored dry because the reference electrolyte will slowly penetrate through the diaphragm and crystallize across the bottom of the electrode. If the reference electrode dries out completely, the diaphragm resistance will increase substantially. Even when the reference electrode is refilled with electrolyte, the high diaphragm resistance may persist and produce significant measurement error. Similarly, storage in tap or distilled water should be avoided as well. Penetration of the diaphragm by water will substantially increase the diaphragm voltage potential and thereby adversely affect any subsequent pH measurement.

Storage methods for TrupH electrodes

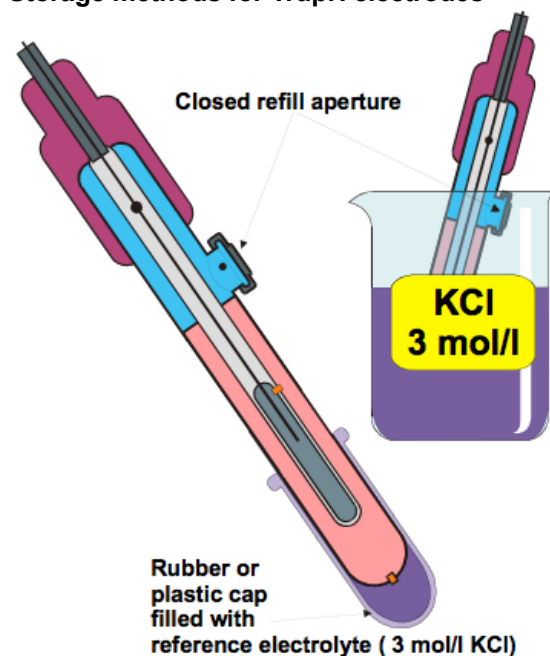


Figure 1 Proper storage of TrupH electrodes. These electrodes are gel-filled and must always be stored wet in 3 molar KCl solution, with the refill aperture closed.



TrupH Gel-Filled, Combination Electrodes

Normally, the storage method of a reference electrode applies equally to the storage of a combination electrode, namely that the optimum storage liquid for a combination electrode is the respective reference electrolyte of the electrode itself. The refill aperture has to be closed during storage time.

However, gel-filled combination electrodes such as the TrupH electrode are an exception to the rule. These electrodes have no refill aperture and the drying-out of their diaphragm must always be avoided. Therefore, TrupH electrodes must always be stored wet in a 3 mol/l KCl solution with the refill aperture closed (see figure 1). This storage solution (PHS-STO) is readily available from Finesse.

Cleaning

The immersion of pH electrodes in bioprocess media can lead to the contamination of the measurement membrane or the reference electrode diaphragm, or both. As result, the pH electrode performance can change in one or more of the following ways:

- a zero point shift
- b reduced slope
- c longer response time

Cleaning the pH electrode will mitigate this performance degradation. We recommend cleaning pH electrodes prior to sterilization (i.e., autoclave, steam in place, or clean in place) for a new growth run. Depending on the bioprocess application, the cleaning interval can vary from hours to weeks.

The cleaning procedure will depend on the type and quantity of contamination. The following general guidelines have been found practical and effective in cleaning pH electrodes:

- Initially remove any deposits from the membrane or from the diaphragm by rinsing the electrode with a mild detergent.
- Calcium deposits may be removed by soaking the electrode for several minutes in a 0.1 molar solution of HCl.
- To remove proteins from the membrane and diaphragm, soak the electrode for several hours in a solution of 1% pepsin and 0.1 molar HCl.
- Inorganic coatings can be removed using commercially available glass cleaning solutions (e.g., Windex).

- Measuring solutions containing sulphides will react with the silver chloride present in most reference electrolytes, resulting in contamination of the diaphragm with silver sulphide deposits (i.e., the diaphragm will appear black). To remove the silver sulphide deposit, soak the electrode in a 0.1 molar thiourea/HCl solution until the diaphragm is totally bleached.
- Highly resistant deposits can be removed with hydrogen peroxide or sodium hypo-chlorit.
- Any other acid or alkaline soluble deposits may be removed by either rinsing the electrodes in 0.1 molar HCl or in 0.1 molar NaOH for a few minutes (only).

Note that after any cleaning process, the TrupH electrode must be soaked in storage solution (PHS-STO or 3 molar KCl) for at least 12 hours, and preferably 24 hours. As the cleaning solution may penetrate the diaphragm (and thereby change the diffusion potential), it is absolutely necessary to calibrate the pH measurement loop after the hydration process of the cleaned pH electrode is complete.

During the cleaning process the electrode should only be rinsed or soaked. Under no circumstances should a pH electrode be cleaned mechanically (i.e. with a knife, screwdriver or any other sharp tool), as the electrode can be destroyed. Rubbing the electrode with a cloth must also be avoided as rubbing will produce a static charge on the glass shaft of the electrode, and thereby considerably prolong the response time.

Refilling or Replacing the Reference Electrolyte

Typically, the electrolyte level in a reference electrode or a combination electrode must be checked regularly. The electrolyte must be replenished when the internal reference system is no longer fully covered by the electrolyte. Additional reference electrolyte is injected through the refill aperture using a pipette or syringe.

TrupH electrodes are gel-filled, combination electrodes. They do not require refilling or replacing the reference electrolyte. Do not attempt to refill the gel, as this may destroy the electrode.

Aging

Every TrupH electrode will undergo an aging process, even if it is not in use. The aging process is continuous and starts immediately after the electrode is manufactured. TrupH electrodes are combination electrodes, and contain both the measuring and reference electrodes. These two types of electrodes undergo different aging processes, both of which affect the performance of the TrupH electrode.

Measuring Electrode Aging

Primary reasons for measuring electrode aging are:

- 1 Changes in the chemical composition of the membrane glass
- 2 Steady growth of the internal membrane gel layer
- 3 Chemically and mechanically induced degradation of the outer gel layer of the membrane during measurement and cleaning

Aging is significantly accelerated by:

- 1 Operation of the pH electrode in process media or solutions that have elevated temperature ($> 60\text{ }^{\circ}\text{C}$),
- 2 Operation of the pH electrode in process media or solutions that have either high acidity or alkalinity,
- 3 Incorrect handling of the pH electrode when not in use, e.g. incorrect cleaning and storage procedures

Typical symptoms of an “aged” measuring electrode are:

- a an increased response time
- b an increased membrane resistance
- c a declining slope, especially in the alkaline region
- d a shift of the asymmetry potential

Predicting the exact lifetime of a TrupH electrode is unfortunately impossible, because the lifetime depends on the operating and handling conditions. A TrupH electrode has a maximum potential operating life of 18 months if handled correctly at all times and used continuously in aqueous solutions at ambient temperature having a pH range from 4 to 8. The same TrupH electrode might only last only 2 months if operated under the same conditions but at temperatures exceeding $90\text{ }^{\circ}\text{C}$. The same electrode can stop working after only 2 weeks if it is exposed to solutions having high alkalinity ($\text{pH} > 13$) pH and high temperature ($> 90\text{ }^{\circ}\text{C}$).

Under benign operating conditions, such as those found in most bioprocesses, pH electrodes will age very gradually. The aging will manifest itself as an increasing membrane resistance, a declining slope and a zero point drift (shift of the asymmetry potential), which may all be mitigated, within limits, by calibration of the pH measurement loop.

A deteriorating (longer) response time is a direct indication of aging. If the response time becomes unacceptable for process control, then the only alternative is to replace the pH electrode with a new one.

Reference Electrode Aging

In theory, reference electrodes do not age, although their lifetime may be considerably shortened by incorrect handling, during either use or storage.

The diaphragm is the most critical part of the reference electrode system, and must be kept clean at all times. No measuring solution must enter the electrolyte vessel through the diaphragm and chemical reactions at the diaphragm must be avoided.

TrupH reference electrodes use a gel-electrolyte, so that they do not need to be refilled (or “topped-up”), thus reducing maintenance costs. Although they are pressure resistant to a certain degree (up to 200 kPa), bi-directional diffusion across the diaphragm will still occur, so that

contaminants can gradually reach and poison the reference electrode. Furthermore, the KCl concentration in the gel-electrolyte will be diluted over time by the media being measured. Therefore, even gel-filled reference electrodes will have a limited operating lifetime. As is also the case with measuring electrodes, high temperatures, large temperature gradients, or rapid temperature changes will also shorten the life of a gel-filled reference electrode. We recommend that for optimal performance, TrupH electrodes should never be operated at process temperatures exceeding 60°C. A reasonable life span of a TrupH reference electrode is approximately 6 months if used under normal operating conditions: specifically, in a pH range of 2 to 12, and at process temperatures of 25°C to 40°C.