White Paper

pH Electrode Troubleshooting

Diagnosis and Treatment

The electrode is the key to successful analysis. Since the electrode is the only part of the analytical instrument that is in direct contact with the sample, its selection and maintenance (and therefore sensitivity) has the strongest influence on precise and accurate measurements. However, an electrode that has been correctly selected and that has been working properly may nevertheless suddenly start performing badly. In this article we will help you to identify possible reasons for this and suggest a number of procedures for restoring the electrode to its original performance.

1. Before beginning the diagnostic procedure

Before testing an electrode, make sure that the electrode cable and the instrument are working properly. Then examine the sensor closely. Visual inspection can very often provide important clues about the cause of the problem, e.g. a clogged diaphragm or an air bubble in the tip of the electrode.

In general, three procedures can be followed to restore an electrode to its normal working state. First of all, the glass membrane can be regenerated, secondly, the reference diaphragm may have to be cleaned and thirdly, it may be necessary to replace the electrolyte. This latter point will not be discussed in this article because it forms part of the normal electrode maintenance procedure.

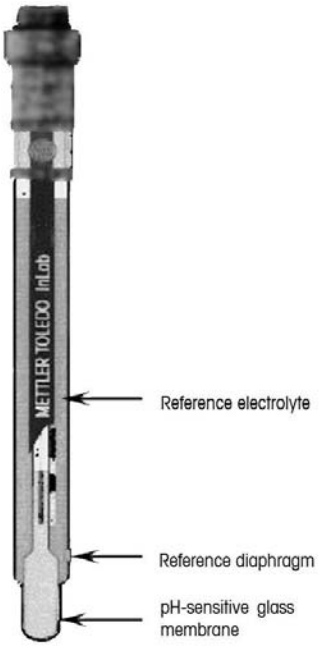

Fig. 1 What can be fixed?

2. Glass membrane

a) Diagnosis

One symptom may very often have various causes. The following table will help you to find out what caused your electrode to fail with regard to the pH-sensitive glass membrane:

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Cause Symptom	Ageing of glass	Scratches on membrane	Broken membrane or shaft	Gel layer destroyed or dehydrated	Dry storage of electrode	Calcium on glass membrane (whitish film)	Oil, fat or tar residues (visible?)	Deposits of unknown substances (visible?)
Reduced slope (>80% - <90%)								
Very small slope (<80%)								
Slow response								
Fluctuation of reading								
Zero point shift								
Reading jumps up and down								
Due to	High temperature, age of sensor	Abrasion, solid particles, incorrect cleaning	Mechanical or temperature shock	Ion deficient media, non-aqueous applications	Wrong storage	Measure-ment media	Measure-ment media	Measure-ment media, no cleaning
Procedures for restoring the electrode	Regeneration (see next page)	Sensor cannot be repaired	Sensor cannot be repaired	Rehydration with electrolyte or tap water	Rehydration with electrolyte or tap water	Dip sensor in conc. acetic acid until deposits are dissolved. Afterwards regeneration	Clean sensor with degreasing agent, then rinse with water. If necessary, regeneration. .	Clean sensor with suitable cleaning agent. If necessary, regeneration.

Explanations:  Highly probable  Probable  Possible

Table 1: pH-Sensitive Glass Membrane: Symptoms, Causes and Procedures

b) Regeneration procedure

A reduced calibration slope as a result of changes in the gel-layer on the glass membrane can very often be observed with older electrodes or electrodes that have been stored dry. Similar effects are noticeable when an electrode is used for non-aqueous applications because the gel-layer is dehydrated. The pH-sensitive glass membrane is reactivated using a regeneration solution. This solution is a mixture of hydrochloric (HCl) and hydrofluoric acids (HF).

Since these acids are extremely aggressive, make sure that you observe all the necessary safety precautions, e.g. wear protective goggles, a laboratory coat and chemical-resistant gloves!

Keep the volume of solution to a minimum by using a small acid-resistant vessel. Dip the tip of the electrode into the regeneration solution for 5 to 15 minutes. The maximum immersion point is level with the upper shoulder of the pH-sensitive glass (see Fig. 2). Never dip the sensor shaft into the solution because the hydrofluoric acid will damage it.

Then rinse the electrode thoroughly with water and condition it for approximately an hour in a buffer solution of pH7. Finally, place the sensor overnight in the reference electrolyte specific to that sensor.

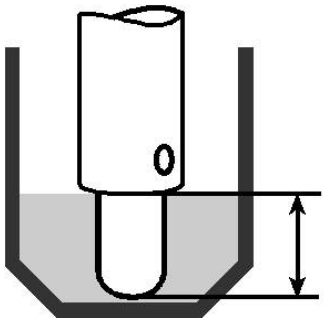

Fig. 2 Regeneration Procedure

3. Reference diaphragm

a) Diagnosis

Faulty electrodes often have a clogged diaphragm. In most cases, the diaphragm is visibly discolored. Some are black, others are gray or just an off-white color. Sometimes the discoloration is so faint that it is only visible when the ceramic tube is viewed from the side through the glass. A gradual change from white on the inside to off-white or gray on the outside can be seen. Silver sulfide makes the diaphragm appear black. Proteins can cause a whitish discoloration that is hardly visible. This form of contamination rarely occurs just on the surface. It usually penetrates into the pores of the diaphragm. Lipophilic substances, such as fats and oils, can create a thin, non-permeable layer over the diaphragm that is often invisible.

b) Cleaning procedures

The following table gives tips and hints on how to clean ceramic diaphragms. Some of these measures can be used on the outside as well as on the inside of the electrode. The same applies of course to Redox or separate reference electrodes which have a contaminated ceramic diaphragm.

Type of contamination	Cleaning agent	Reaction time	Remarks
Silver sulfide	Thiourea	5 –60 mins.	Leave until discoloration disappears.
All possible types of contamination. First recommendation for removing unknown substances.	HCl 0.1 mol/L	Approx. 12 hrs.	Can also be used for internal cleaning.
All possible types of contamination. Second recommendation for removing unknown substances.	Chromic-sulfuric acid mixture	Approx. 30 mins.	Also cleans deposits on the membrane very well. Sensor must be regenerated after this procedure.
Proteins	Pepsin / HCl cleaning solution	> 1 hr.	Can also be used for internal cleaning.
Proteins	NaOH 2%	Approx. 20 mins.	
Lipophilic substances	Ethanol, acetone	Approx. 30 mins.	Highly suitable for edible oils. Possibly with support of a soft brush.
Calcium, scale	Acetic acid	Approx. 30 mins.	Sensor must be regenerated after this procedure.
Soaps, tensides	Hot water (80° C)	Approx. 12 hrs.	Rinse sensor well with hot water. Afterwards, immerse in hot water and leave to cool, approximately 12 hours. Only use tap water, not distilled or de-ionised water.

Table 2: Clogged Reference Diaphragm: Causes and Cleaning Procedures

Despite all the corrective procedures mentioned above, it is not always possible to repair a faulty electrode. Damage that has occurred to the wiring or casing of an electrode during use, is irreparable. In such cases the electrode must be replaced.