White Paper

The Right Electrolyte

For Every Application

The characteristics of an electrode are determined largely by the electrolyte. In the following article we will describe the options available to the user and summarize the different factors influencing the choice of the right electrode.

1. Liquid electrolytes

The traditional electrode uses liquid reference electrolyte which is in direct contact with the sample via a ceramic junction. For viscous samples or samples containing small particles sleeve junctions are applicable. Liquid electrolytes provide good electrolyte flow and thus good response time of the electrode. Furthermore refilling of electrolyte is normally not a problem.

a) KCl/water – the universal electrolyte

A 3M solution of potassium chloride (KCL) is nowadays used as electrolyte for almost all electrodes. Why KCl in particular? One reason is that the silver/silver chloride (Ag/AgCl) reference system requires the presence of chloride in the electrolyte. The other reason is that the mobility of the anions and cations in the electrolyte must be comparable in order to prevent the formation of diffusion potentials. KCl provides an optimum solution to these requirements. With samples of low ionic strength, a double chamber-reference electrode and 1M KCl as bridge electrolyte should be used.

When is KCl alone used, and when KCl saturated with AgCl? In principle, only 3M KCl solution is used for electrodes equipped with ARGENTHAL™ or Ag/AgCl cartridge reference systems. For electrodes with an ARGENTHAL™ reference system (see Figur 1), the electrolytically deposited AgCl layer is surrounded by silver granules so that the silver reserves are maximized. Since a small amount of silver is constantly consumed, the reference volume is made as large as possible. In addition, the cartridge surrounding the reference element creates a stable microenvironment, which enables a constant reference potential to be maintained. An additional silver ion trap prevents the silver ions entering the electrolyte and thereby coming into contact with the measurement solution.

METTLER TOLEDO

For electrodes with a conventional Ag/AgCl reference system, a solution of AgCl-saturated 3M KCl must be used. The purpose of the AgCl-saturated electrolyte is to compensate the consumption of silver at the lead-off element. A disadvantage is that the free silver ions can react with sulfides or proteins in the sample.

b) LiCl/ethanol or glacial acetic acid – for non-aqueous solutions

Aqueous electrolytes should not be used for the measurement of non-aqueous solvents or solvent/water mixtures because leakage from the electrode can lead to the formation of two phases. KCl is however only slightly soluble in ethanol and glacial acetic acid. LiCl is therefore normally used instead of KCl. Because of the higher diaphragm resistance of LiCl electrolytes, electrodes with ground glass joint diaphragms or multiple diaphragms are usually recommended. In addition, it is better if the electrodes have an ARGENTHAL™ or Ag/AgCl cartridge reference system because LiCl electrolytes are not saturated with AgCl.

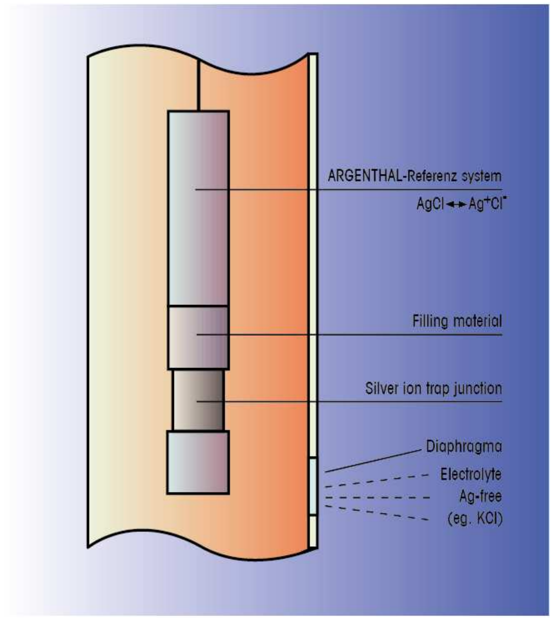

Fig. 1 The ARGENTHAL™ principle

c) FRISCOLYT-B® – for high and low temperatures

FRISCOLYT-B® electrolyte has a particularly wide temperature range from –30 °C to 130 °C. The electrolyte is a 2:1 mixture of glycerin (2 parts) and 3M KCl solution (1 part). The electrical resistance of the electrolyte is high because of the high concentration of glycerin. The measuring range should be limited to pH 2 to 12, or maximum 13 because of the deprotonation of the glycerin.

Table 1 summarizes the various electrolytes according to the different types of electrode.

Type of sample	**Type of electrode**	**Recommended electrolyte**
Aqueous samples that might also contain sulfides or proteins	All electrodes with ARGENTHAL™ or Ag/AgCl cartridge	KCl 3M
Aqueous samples that do not contain any sulfides or proteins.	All electrodes with no ARGENTHAL™ or Ag/AgCl cartridge (must not be used in electrodes with ARGENTHAL™ or Ag/AgCl cartridge)	KCl 3M, saturated with AgCl
Nonaqueous samples	In principle all electrodes, but preferably electrodes with ground glass joint diaphragms or multiple diaphragms and ARGENTHAL™ or Ag/AgCl cartridge	LiCl in ethanol
At low temperatures and for media containing proteins and solvents or for nonpolar, lipophilic media	All electrodes with ARGENTHAL™ or Ag/AgCl cartridge	FRISCOLYT-B®

Table 1: Criteria for the right electrode and electrolyte

Fig. 2 A combination pH electrode

2. Solid electrolytes

Electrodes with solid electrolyte are more robust and easier to handle. They need less maintenance and no electrolyte refilling. However, the response time of electrodes with solid electrolyte is somewhat slower and as soon as all electrolyte is used the electrode needs to be replaced with a new one. There are two different types of solid electrolytes: gel electrolytes and polymer electrolytes.

a) Gel electrolytes

The gel is composed of KCl, ethylene glycol and cellulose. It is in addition saturated with silver nitrate ($AgNO_3$). Since $AgNO_3$ and KCl react to form AgCl, there is sufficient AgCl present in the gel electrolyte to compensate for silver consumption.

b) Polymer electrolytes

The solid electrolyte XEROLYT® does not require the use of a diaphragm so that there is an open connection between the electrolyte and the sample. This has the great advantage that the electrodes can be used for samples containing proteins, fats and sulfides, i.e. for applications where clogging of the diaphragm can occur when other electrodes are used. XEROLYT® is a cross-linked polyacrylamide. If measurements are performed over a long period of time below pH 2, the polymer undergoes hydrolysis. It can however be used successfully for short periods at pH values down to pH 0. The response times can be longer than for electrodes with ceramic diaphragms because XEROLYT® polymer material tends to swell like a sponge. In addition, large temperature fluctuations should be avoided because otherwise the accompanying temperature-dependent expansion and contraction would cause the diffusion potential to change.