

# ISE Info

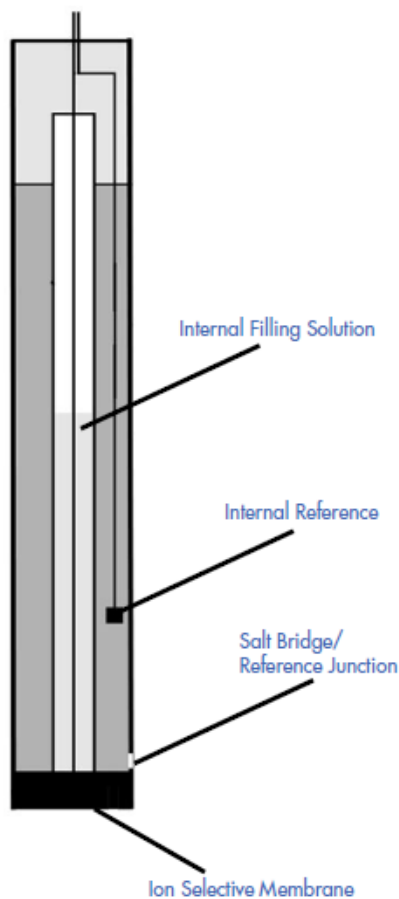
## Basic Theory

Ion-selective electrodes (ISEs) utilize an ionophore-impregnated membrane that makes the electrode selective for a particular ion.

ASI manufactures four different types of ISEs using the following membrane technologies:

- Glass membrane (such as Na<sup>+</sup> or pH)
- Solid state membrane (such as Pb<sup>2+</sup>)
- Polymer membrane (such as K<sup>+</sup>)
- Gas permeable membrane (such as NH<sub>3</sub>)

An electrical potential develops across the membrane when the electrode is placed in solution. This potential is compared to a reference potential (from an internal or external reference electrode) and the difference is measured by the meter, and equated to the ion activity.

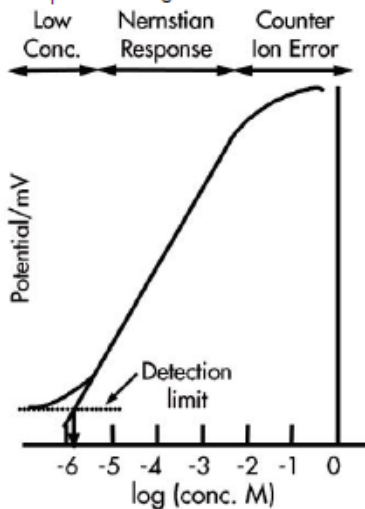


The relationship between the measured potential,  $E$ , and the ion activity in the sample,  $a_i$ , is mathematically described by the Nernst equation:

$$E = E_0 + \text{slope} \log a_i$$

The slope term is equal to  $2.3RT/z_iF$ , where

- R is the gas constant,  $8.314 \text{ JK}^{-1}\text{mol}^{-1}$
- T is the absolute temperature, K
- F is the Faraday equivalent,  $9.6487 \cdot 10^4 \text{ Cmol}^{-1}$
- $z_i$  is the charge of the measured ion



The slope is equal to  $59.16 \text{ mV}/z_i$  at  $25^\circ\text{C}$ . If the measured ion is a monovalent ion such as potassium ( $z_i = +1$ ), a potential change of  $59.16 \text{ mV}$  would be observed at  $25^\circ\text{C}$  for a ten-fold change in the concentration. Similarly, the potential change for a 10 fold change in concentration for a divalent ion such as calcium ( $z_i = +2$ ) would be half, or  $29.58 \text{ mV}$ , also at  $25^\circ\text{C}$ .

$E_0$  is an electrode constant potential, which is typical of every ISE/reference electrode combination. The term  $a_i$  is the activity of the ion, which is proportional to the concentration. The activity of the ion depends on the ionic strength of the sample, which is determined by its ionic content.

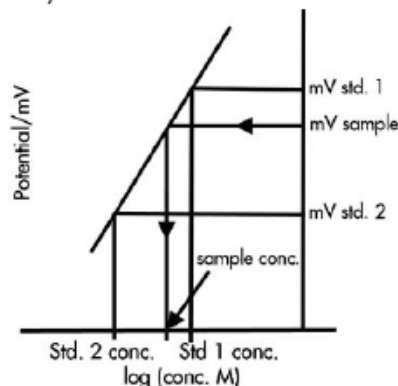
Deviation from linearity occurs both at low and high concentrations of the measured ion, and determines the lower and higher limits of detection. Accurate determinations can be done for samples with concentrations as low as  $10^{-6} \text{ M}$ . At high concentrations (usually higher than  $0.1 \text{ M}$ ) the deviation from linearity is due to the effect of the counter-ion.

## Calibration and ISA/Buffers

In order to ensure the same ionic strength in standards and samples, it is strongly recommended to use an Ionic Strength Adjustor (ISA), usually in a 50:1 sample to ISA ratio.

Moreover, some ISEs (such as ammonia) can be used only in a limited pH range. The addition of a buffer to some of the ISAs will adjust standards and samples to the desired pH value. More complex ISA formulations can include additives (like chelation agents) that complex possible interferences. The ISA can also contain preservatives such as antioxidant agents.

In order to make accurate determinations, it is strongly recommended to use at least two solutions of known concentration (standards) to calibrate the electrode. The standards are usually prepared by dilution with deionized water a 1000 ppm stock solution of the ion to be measured. The expected concentration of the sample should be included in the range of concentrations covered by the standards. Ideally, the electrode should be calibrated as often as possible, or at least once a week. Every electrode needs its own calibration.



A response curve of the ISE can be defined by plotting the potential readings from the two standards (mV std 1 and mV std 2), versus the logarithm of the standard concentrations (Std 1 conc and Std 2 conc). Graphically, the concentration of the ion in the sample (sample conc) can be determined by measuring the sample potential (mV sample) and interpolating that value in the response curve defined by the two standards. Mathematically, from the Nernst equation:

$$\text{mV sample} = E_0 + \text{slope} \log (\text{sample conc})$$

$$\text{or}$$

$$\text{sample conc} = 10^{[(\text{mV sample}) - E_0] / \text{slope}}$$

where the  $E_0$  and the slope terms can be calculated from the standard concentrations and mV readings.

# ISE Quick Reference Information

## How do they work or what is an Ion-Selective Electrode?

An Ion Selective Electrode measures the potential of a specific ion in solution. This potential is measured against a stable reference electrode of constant potential. The potential difference between the two electrodes will depend upon the activity of the specific ion in solution. This activity is related to the concentration of that specific ion, therefore allowing the end-user to make an analytical measurement of that specific ion.

**How Does the mV Reading Correspond to the Concentration?** Standard solutions of known concentrations must be accurately prepared. These solutions are then measured with the pH/mV meter. The mV reading of each solution is noted and a graph log of concentration vs. mV reading must be plotted. Now the unknown solution can be measured. The mV value of the unknown solution is then located on the graph and the corresponding solution concentration is determined. This is also done in the calibration program of most mV/ISE meters.

**Several types of sensing electrodes are commercially available.** They are classified by the nature of the membrane material used to construct the electrode. It is this difference in membrane construction that makes an electrode selective for a particular ion.

- 1. Polymer Membrane Electrodes (Organic Ion Exchangers and Chelating Agents)** -- Polymer membrane electrodes consist of various ion-exchange materials incorporated into an inert matrix such as PVC, polyethylene, polyurethane or silicone rubber. After the membrane is formed, it is sealed onto the end of a PVC tube. The potential developed at the membrane surface is related to the concentration of the species of interest. Electrodes of this type include potassium, calcium, fluoroborate, nitrate and perchlorate.
- 2. Solid State Electrodes** -- Solid state electrodes utilize relatively insoluble inorganic salts within a membrane. Solid state electrodes exist in homogeneous or heterogeneous forms. In both types, potentials are developed at the membrane surface due to the ion-exchange process. Examples include silver/sulfide, lead, cupric, cyanide, thiocyanate, chloride and fluoride.
- 3. Gas Sensing Electrodes** -- Gas sensing electrodes are available for the measurement of dissolved gas such as ammonia, carbon dioxide, dissolved oxygen, nitrogen oxide and sulfur dioxide. These electrodes have a gas permeable membrane and an internal buffer solution. Due to their construction, gas sensing electrodes do not require an external reference electrode.
- 4. Glass Membrane Electrodes** -- Glass membrane electrodes are formed by doping the silicon dioxide glass matrix with various chemicals. The most common of the glass membrane electrodes is the pH electrode. Glass membrane electrodes are also available for the measurement of sodium ions.

The response of an ISE can be affected by the presence of other ions in the sample. The effect of these interfering ions can be quantified for every particular ISE and if the concentration of the interference is known, it can be corrected for. In other cases it is possible to analyze the sample by other methods, such as the Standard Addition method. This method in particular is very accurate when the sample matrix is complex or contains a high level of interfering ions. Contact ASI for more information on this methodology.

## Cleaning

A good working ISE response stabilizes in typical samples within three minutes depending on activity. However the ISE can become sluggish if the membrane becomes dirty from grease or particles in the sample. The tip of a glass electrode can be cleaned with alcohol or a mild detergent, such as the one used to clean lab glassware (see pH cleaning procedure on page 8). Polishing strips with very fine particles (e.g. 3 micron aluminum oxide) can be used to restore the surface of solid state ISEs. A PVC ISE should just be rinsed with water only. After thoroughly rinsing with deionized water, the electrodes should be reconditioned by soaking for 2-4 hours in the lowest concentration standard used for calibration. If the slope or the response time of the electrode is out of specification, longer soaking times (e.g. overnight) may be required before a new calibration is attempted with solid state styles.

## Storage

Regarding storage, glass ISEs should be stored in the provided storage solution. Solid state, PVC and gas ISEs can be kept in a low concentrated standard between samples, otherwise, these electrodes should be stored dry if not in use for several hours for solid state and PVC and several days for gas ISEs. Please refer to the Instruction Manual for particular recommendations for each ISE.



# ISE Applications

## Species used by Industry

Agriculture:	Nitrate, calcium, sodium, potassium, bromide, chloride, ammonia & fluoride
Plant Tissue:	Nitrate, chloride, fluoride, iodide, cyanide, calcium, sodium and potassium
Fertilizer:	Nitrate using the ammonia electrode, potassium and fluoride
Aquaculture:	Ammonia, nitrate, calcium and dissolved oxygen
Biomedical Research:	Calcium, carbon dioxide and ammonia
Education:	Various ISEs electrodes are used in most colleges and universities
Food Processing:	Chlorides, nitrate, sodium and fluoride
Milk and Dairy Products:	Chloride, calcium, fluoride, sodium and iodide
Soft Drinks:	Chloride, fluoride, carbon dioxide and residual chlorine
Alcohol:	Potassium, sodium, CO <sub>2</sub> , fluoride, bromide, calcium, and residual chlorine
Vegetables:	Nitrate, chloride and sodium
Geology and Mining:	Fluoride, calcium and cyanide
Metallurgy and Metal Plating:	Fluoride, cupric, cyanide, fluoroborate and nitrate
Plating Baths:	Chloride, residual chlorine and ammonia
Pulp and Paper:	Sodium, chloride, calcium and sulfate
Petroleum Refining:	Ammonia and chloride
Pharmaceuticals:	Fluoride and sodium
Sewage Treatment:	Nitrate, ammonia, residual chlorine and dissolved oxygen (BOD)
Steam and Power Generation:	Chloride, sodium, residual chlorine, fluoroborate and dissolved oxygen
Drinking Water:	Total, free & residual chlorine, nitrate, calcium, chloride, and fluoride
Natural Water:	Bromide, calcium, chloride, fluoride, nitrate, potassium, silver, sodium & cupric
Sea Water:	Sodium, chloride, fluoride, nitrate and ammonia

## Standard Methods & Applications

SPECIES	ASTM	EPA	APHA	AOAC	USGS
ALKALINITY	D1067-88	310.1	2320B	973.43	I-1030
AMMONIA	D1426-89	350.3	4500-NH <sub>3</sub> (F), (G)	- - -	I-1524
BROMIDE	D1246-88	60 FR 37974 (6)	- - -	- - -	- - -
CARBON DIOXIDE	D513-88A	- - -	- - -	- - -	- - -
CHLORIDE	D512-89	60FR 37974 (6)	4500-CL (D)	971.27, 980.25	- - -
CHLORIDE BY TITRATION	- - -	- - -	- - -	962.05, 962.07, 963.05, 966.10, 969.10	- - -
CHLORINE RESIDUAL	- - -	59 FR 62456	4500-CL (I)	- - -	- - -
CYANATE	- - -	- - -	4500-CN (L)	- - -	- - -
CYANIDE	D2036-89A	60 FR 37974 (6)	4500-CN (E) (F)	- - -	- - -
DISSOLVED OXYGEN	- - -	- - -	4500-O	- - -	- - -
FLUORIDE	D3868-79, D1179-88B, D1179-88A	59 FR 62456, 60 FR 37974 (6)	4500-F (C)	984.37, 975.08, 973.10	I-1327, I-2327
IODIDE	D3869	- - -	- - -	- - -	- - -
KJELDAHL NITROGEN	D3590-89A	.351.4	4500-NORG (A) (B)	- - -	- - -
NITRATE	- - -	59 FR 62456 60 FR 37974 (6)	4500-NO <sub>3</sub> (D) (G)	- - -	- - -
POTASSIUM	- - -	- - -	3500-K (E)	- - -	- - -
SODIUM	D2791	- - -	- - -	976.25	- - -
SULFIDE	D4658	60 FR 37974 (6)	- - -	- - -	- - -