Orion pH, ORP and ISE Theory

Recommended Measuring Techniques
Within Linear Response Range Direct measurement, known addition, titration
Within Non-Linear Response Range Low level measurement
Increased Precision Titration
Occasional Sampling Known addition, analate subtraction
Small Sample Volume Direct measurement, analate subtraction
Large Number of Samples Direct measurement, low level measurement, known addition, analate subtraction
Reduce Chemical Usage Known addition, analate subtraction
Field Measurement Direct measurement, low level measurement
Ionic Strength > 0.1 M Known addition, analate subtraction
Non-specific Ion Measurement Indicator titration

ISEasy™ Measurement Techniques

In an ion selective electrode (ISE), the potential difference developed between the sensing and reference electrodes is a measure of the activity of the reactive species. As the activity of the species reacting at the sensing electrode varies, so does the potential measured between the two electrodes. As first shown by Nernst, electrode response may be described by a linear equation:

$E = E_o + S \log a$

where "E" is the measured voltage, "E_o" is a combination of several constants within the system including reference potentials, "S" is the slope of the electrode, and "a" is the activity of the measured species. By measuring the electrode's potential in both a standardizing solution and in a sample solution, it is possible to calculate the unknown solution's concentration by using the following form of the previous equation:

$C_x = C_i \times 10^{\Delta E/S}$

where "C_x" is the concentration of the unknown solution, "C_i" is the concentration of the standardizing solution, "ΔE" is the difference between the observed potentials in the standardizing and sample solutions, and "S" is the electrode slope, the change in electrode potential per ten-fold change in concentration. All measurement techniques are based upon some form of this concentration equation. A meter with microprocessor capability is recommended for all the measurement methods using ion selective electrodes. Meters with a millivolt readability to ± 0.1 mV may also be used.

Choosing the Right Measuring Technique

A variety of analytical techniques are available to the analyst. Direct measurement is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. Orion ISE meters calculate and store the calibration curves, saving you time in analysis and ensuring an accurate result. Ionic strength adjustor is added to all solutions to ensure that samples and standards have similar ionic strength, proper pH, and to reduce the effect of interfering ions. Low level measurement is a similar method to direct measurement. This method is recommended when the expected sample concentration is within the non-linear response range of the electrode. A minimum 3 point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. Calibration is performed in one beaker, reducing the chance of cross contamination of the solutions. Known addition is a useful method for measuring samples, since calibration is not required. This method is recommended when measuring only a few samples, or when samples have a high (› 0.1 M) ionic strength, or a complicated background matrix. The electrodes are immersed in the sample solution and an aliquot of standard solution, containing the measured species, is added to the sample. The original sample concentration is determined from the change in potential before and after the addition. As in direct calibration, any convenient concentration unit can be used. Many Orion ISE meters automate this measurement, by performing the additions and automatically calculating the result. Analate subtraction is also a useful method for measuring samples, since calibration is not required. The electrodes are immersed in a reagent solution that contains a species that the electrode senses, and that reacts with the sample. It is useful when sample size is small, for samples for which a stable standard is difficult to prepare, and for viscous or very concentrated samples. The method is not suited for very dilute samples. It is also necessary to know the stoichiometric ratio between standard and sample. Titrations are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time consuming. Orion titration systems automate the titration process, through exclusive programming and automatic titrant addition. Indicator titration methods are useful for measuring ionic species where an ion selective electrode does not exist. With these methods, the electrodes sense a reagent species that has been added to the sample before titration.

Orion pH, ORP and ISE Applications

ISEasy™ Electrode Applications

Orion ion selective electrodes form the basis of the one analytical technique that gives direct measurement of both cations and anions - common ions like sodium, chloride, potassium etc. Some electrodes also measure dissolved gases such as ammonia, nitrogen dioxide and carbon dioxide. By using indirect analysis methods, the number of species that can be measured greatly increases. Our technical support and extensive application notes are available to assist customers with a wide range of analyses.

	ISEasy Electrode Applications
Industry Type	**Species Measured**
Agriculture	
Soil	Nitrate, nitrite, calcium, sodium, potassium, bromide, chloride, ammonia, fluoride and boron are measured
Animal Feed	Determination of Kjeldahl nitrogen, calcium, chloride, fluoride, iodide, nitrate, sodium and potassium assures product quality
Plant Tissue	Nitrate, chloride, fluoride, iodide, cyanide, calcium, sodium and potassium can be measured consistently
Fertilizer	Nitrate using the ammonia electrode and the nitrate analysis test kit, potassium in potash, fluoride in phosphate rock and Kjeldahl nitrogen
Aquaculture	Ammonia in fresh and salt water, nitrate, nitrite and hardness
Biomedical Research	
Culture Media	Calcium, carbon dioxide and ammonia in biological cultures (1)
Tooth enamel	Calcium and fluoride determination in dental research
Education	
Various ISEs	Electrodes are used in most science departments of colleges and universities, in both teaching and research applications
Food Processing	
Processed Meat and Fish	Chloride, nitrate, nitrite in fish products and fluoride in fish protein
Milk and Dairy Products	Chloride in cheese, butter, ice cream and milk. Fluoride and iodide are monitored to control levels of these toxins
Soft Drinks and Juices	Chloride, fluoride, carbon dioxide and residual chlorine
Spirits, Wine and Beer	Alcohol, potassium, sodium, carbon dioxide, fluoride, bromide, calcium, dissolved oxygen and residual chlorine
Vegetables	Nitrate in canned vegetables and baby food. Chlorine in wash waters
Geology and Mining	Fluoride and calcium in various rocks, pH of solutions containing hydrofluoric acid
Metallurgy and Metal Plating	Fluoride in cryolite, aluminum, fluoride and tungsten. Cupric, free cyanide, total cyanide, fluoride, fluoroborate, nitrate, chlorine and ammonia in plating baths
Pulp and Paper	Sodium, chloride, calcium and sulfite in white, green and black liquors
Petroleum Refining Stack Gases	Ammonia, hydrogen sulfide, hydrogen cyanide, hydrogen fluoride and hydrogen chloride gases after scrubbing, low level chloride in desalting water, mercaptans in naphtha and gasoline
Pharmaceuticals	Fluoride in vitamins and toothpaste
Sewage Treatment	Nitrate, ammonia, residual chlorine, nitrite, ORP, dissolved oxygen and Kjeldahl nitrogen
Steam and Power Generation	Chloride levels in boiler cleaning solution, boiler feed water and high purity water; sodium as an indicator of contamination; residual chlorine
Water	
Drinking Water	Total residual chlorine, nitrate, nitrite, chloride, ORP, water hardness and fluoride; aluminum in aluminum sulfate (used as a flocculant)
Natural Water	Bromide, calcium, chloride, fluoride, nitrate, nitrite, ORP, potassium, silver, sodium, carbonate and dissolved oxygen
Sea Water	Sodium, chloride, fluoride, nitrate and ammonia

Key

(1) Not approved for in vitro or in vivo diagnostic use