

BRIEF GENERAL NOTES & GUIDELINES FOR ONLINE ION SELECTIVE MEASUREMENTS

Statement of Purpose and Limitations for this General Guide to Online Ion Selective Measurement

- While these guidelines and technical notes are not intended as an exhaustive guide to online ion selective measurement, they are good general starting point for those unfamiliar with online ion selective measurement to better understand many of the capabilities and limitations of PVC (organic membrane) and solid-state based industrial ion selective sensors.
- This short guide is not meant as a replacement for the thorough technical treatment of the topic of ion selective electrodes and measurement posted at http://www.astisensor.com/indexrefresh_ISE_Tech_Papers.htm. In addition, an older and simplified treatment on the topic of ion selective electrodes and measurement is available at http://www.astisensor.com/indexrefreshprodoc_misc.htm
- This general guide is also not a replacement for the specific instructions (ISE Addendums) for use of specific ASTI industrial ISE sensors in conjunction with Rosemount industrial ion selective analyzer as posted at http://www.astisensor.com/indexrefreshprodoc_isemanuals.htm.
- Each industrial ion selective sensor has specific capabilities and limitations indicated for each ion selective sensor model. These specification sheets for each ISE sensors are posted at http://www.astisensor.com/indexrefreshproise_organicguide.htm for PVC (organic membrane) ISE sensors and at http://www.astisensor.com/indexrefreshproise_solidstateguide.htm for solid-state ISE sensors. Care should be taken to review these capabilities and limitations to ensure that you particular intended use falls within the specified parameters.
- **NO** technical document is a replacement for direct technical support and consideration of your particular ion selective applications from the ASTI factory by a qualified chemist (or an authorized ASTI independent distributors and/or agent). It is only through the approval of the factory (or qualified agent) that you will be able to purchase the online ISE measurement system for a particular application, and receive the technical support and consideration necessary for a successful inline ISE measurement.
- This general guide is intended to answer the most frequently asked questions for prospective customers and agents that are familiar with the field of controls and instrumentation, but not greatly familiar with the field of online ion selective measurement and control. If a greater theoretical background is desired, please consult the appropriate resources on our website or contact the factory.



Goal of this Guide

Once a two-point calibration for slope has been performed with your industrial ISE sensor using suitable calibration standards (following the procedures in the ISE addendum) and the recommended one point offset (grab sample standardize) adjustment is performed, you will be able to monitor the ion activity in accordance with accuracy, precision and performance of any other ion selective measurement system provided by ASTI. This precision meets or exceeds the industry standards for online ion selective analysis as proscribed for online control of ion activity and regulatory compliance.

Conditioning

The PVC (organic membrane) or solid-state ISE sensors must be sufficiently conditioned to give optimum stability and performance. The PVC (organic membrane) based industrial ion selective sensors have an active sensing element that is an organic ion selective electrode based on plasticized PVC, specialized ion sensitive ligand (ionophore) and some other necessary components for industrial use. All such electrodes containing these organic measuring membranes need conditioning before use allowing the organic system to get in equilibrium with the aqueous solution. This is best performed by soaking the sensor in the lower concentration of calibrating solution for about 16-24 hours. Solid-state ion selective sensing elements also require conditioning time for optimum performance, although satisfactory performance may be gained for many customer's applications in a period shorter than the recommended 16-24 hour period for organic membrane based industrial ISE sensors.

Calibration

The calibrating solutions employed should be not more than one decade apart bridging over the anticipated concentration of your sample. If there are any other constituents in the sample to be measured, there need to be additions of these constituents to the calibrating solution to mirror (reflect) the actual sample background. One needs to be careful with such ionic background if there are interfering ions in the sample. Many factors must be taken into account to fabricate an optimal calibration standard. These include but are not limited to the total ionic strength (total concentration all of the ionic species), typical process concentration of interfering ions, dissociation (and activity coefficients) of the salt providing the analyte ion to be measured, and the typical pH. The ASTI factory can readily assist customers and agents to properly choose calibration standard formulations (and preparation procedures) that will provide for suitable calibration standards for their given application.

Once having done this you should establish a procedure for performing the calibration with the industrial analyzer. Rinse the conditioned sensor with the first calibrating solution. This should reduce the overall response time. Once you have established the first calibration point, rinse again the sensor with the second calibration solution. Rinsing with D.I. (or distilled water) will dilute the solution on the surface of the sensor, thus the sensor has to start its potential development process with a much lower concentration and develop a longer response curve (which is exponential in its nature) and response time. Addendums (quick guides) for your given online ion selective measurement are posted at http://www.astisensor.com/indexrefreshprodoc_isemanuals.htm. The ISE addendums posted are specific to particular ASTI ISE sensor model(s), and the specific type of Rosemount ISE analyzer.



Temperature Considerations

The reading you obtain either during calibration or measurement are temperature dependent as described in the Nernst equation which is the basis for every potentiometric measurement. There is a built in temperature sensor which is about 1.5 inches (38 mm) from the interface of the sensor to the measured solution in the standard configuration or about 0.5 inches (13 mm) from the interface of the sensor to the measured solution for the ACCU-TEMP option (-X). If there is a temperature difference in the solution the sensor has to become into equilibrium with the solution itself and not the air or other environment. The time for the temperature reading as based upon the resistance of the temperature compensation (TC) element (typically a PT100, PT1000 or Balco 3K element) to agree with the temperature of the measured solution, will depend upon the location of the TC element (standard or ACCU-TEMP) and the rate of the temperature change. This time for equilibration can vary from as little as 1-2 minutes to as much as 30-60 minutes under some conditions. If the temperature is fluctuating or the sensor temperature is not in equilibrium with the solution temperature so will your "reading" even if your analyte ion activity is unchanged.

Effect of Temperature Compensation on Online Measurements

The Nernstian defined effect of temperature on an electrochemical measuring systems (for monovalent cations such as NH_4^+ and anions such as F^-) is 1 mV for every 5° Celsius change in temperature. As the relationship between the activity of any analyte (measured) ion and the mV potential is logarithmic, in practical terms this means that a 1 mV change in potential will alter the concentration reading by at least 4% of any actual value. This 4% (minimum) value assumes that either NO temperature compensation is employed or that there is a 5° Celsius temperature offset between the temperature derived from the TC element and actual temperature. Simply stated, a 5° Celsius discrepancy in temperature measurement will result in changing the reading at least 4% of the actual value, assuming that no other factors are present that would cause a larger error (see points below for details).

- IT SHOULD BE NOTED, HOWEVER, THAT AS ION SELECTIVE SENSOR CAN ONLY MEASURE ACTIVITY RATHER THAN CONCENTRATION. THE TEMPERATURE INDUCED CHANGE IN THE ACTIVITY COEFFICIENT OF THE ANALYTE ION FOR A GIVEN CHEMICAL SYSTEM IS OFTEN GREATLY MORE THAN THE 4% CHANGE INDICATED FOR THE UNCOMPENSATED ISE SENSOR.
- THE DIRECTION TEMPERATURE INDUCED ACTIVITY COEFFICIENT CHANGE WILL DIFFER FOR EACH PARTICULAR CHEMICAL SYSTEM AND THUS CANNOT BE MORE GENERALLY PREDICTED.
- TEMPERATURE INDUCED CHANGES IN ION ACTIVITY CANNOT BE “*COMPENSATED*” IN THE SAME WAY THAT WE ARE ACCUSOMED TO “*COMPENSATING*” FOR TEMPERATURE IN pH MEASUREMENTS.
- EVEN FOR PH MEASUREMENTS, THE ASSUMPTION THAT ACTIVITY COEFFICIENT OF THE HYDONIUM (H^+ OR H_3O^+) ION DOES NOT SIGNIFICANTLY CHANGE WITH TEMPERATURE CAN PROVE INCORRECT AND CONTRIBUTE TO THE UNCERTAINTY OF THE MEASUREMENT. Information about accuracy and uncertainty in pH measurement can be reviewed in the article as posted at http://www.astisensor.com/minimizing_user_errors_ph.pdf

Optimum ISE measurement can be accomplished by calibrating the ISE sensor to concentration standards (even tough the ISE sensors only measure ION ACTIVITY) and ensuring that there are stable process and calibration solution temperatures.

Measurement may be possible under other circumstances with greater uncertainties produced as a result.



Some other Important Considerations

Like most analytical methods the potentiometric electrochemical methods are based on interpolation, bridging the sample concentration with the two point calibrating solutions. The extrapolation method is not acceptable and is not as accurate on any account. Different concentrations may have different ionic strength and activity coefficients which will contribute to the difference between interpolation and extrapolation. The other reason for using interpolation rather than extrapolation is there may be some non linearity of the response taking all the factors in account in which case extrapolation is not as satisfactory an analytical method. In some laboratory ion concentration measuring equipment there is an option to perform multipoint calibrations to increase accuracy of the system. Industrial analyzers (such as the 54e-ISE and 1056-ISE) typically do not provide such an option for a variety of reasons.

Uncertainty & Reproducibility in Electrochemical Measurements

The relationship between the activity of any ion and the measured potential is logarithmic, which in practical terms means that one (1) mV change in potential will change the concentration reading at least 4% of any actual value. Potentiometric electrochemical systems are at best defined under laboratory conditions to that degree of uncertainty, but there is often a greater degree of uncertainty in the industrial arena for many reasons. Such optimum laboratory arrangements (with an approximate uncertainty of 4% under ideal conditions) typically require special reference systems, salt bridges, strict temperature control. In addition, measurement of unknown samples is performed immediately after a two-point (or often a multi-point) calibration has been performed for sensitivity. In addition, sample conditioning and various background solutions are often added to the unknown sample to adjust the pH, ionic strength and minimize the difference between the background of the calibration and measured solution. Recalibration between tests as required is not uncommon and there are well established solution and equipment handling procedures in place to further minimize uncertainties.

The goal of reproducibility to within 5% (but no necessarily accuracy in the analytical chemistry use of the term) based upon good process sample and temperature stability is realistic, provided that a reliable laboratory method is available to determine the activity of grab samples for use with the industrial standardize (1-point) offset calibrations. Under ideal process control conditions (very stable process sample and calibration standards with nearly isothermal process and laboratory conditions) ASTI customers performing some ISE measurements have reported reproducibility to with +/- 0.5 mV (2%). Less optimum process and thermal stability may yield correspondingly greater amounts of uncertainty and error. The one-point offset calibrations are typically performed while leaving the sensor in service to reduce the heat cycling of the sensor and minimize the amount of time spend waiting for the sensor to obtain thermal and electrochemical equilibrium with the process sample. Significant changes in process sample composition, analyte concentration, pH and/or temperature may make the goal of reproducibility with 5% uncertainty difficult to achieve.



Industrial Process & Installation Conditions Effect on ISE Measurements

ASTI industrial ISE sensor can be installed into service by use of an inline installation (flow cell) or by immersion or submersion style installation. For inline installation, care should be taken to not exceed the flow pressure rating of that given sensor. Optimal performance will be achieved by having a slow continuous flow past the sensor. For immersion or submersion installations (submersion installations require the waterproofing option as posted at http://www.astisensor.com/indexrefreshprosub_pics.htm). Thermal equilibrium between the sensor and process solutions at elevated or depressed temperature (not at 25 degrees Celsius) is generally better achieved via immersion or submersion installation styles.

Care must be taken for both inline and immersion/submersion installation styles that air bubbles are not present on the sensing element. Air bubbles present on the sensing element can cause erroneous and erratic reading. This potential problem is best alleviated installing the ISE sensor at angle of approximately 45 above the horizontal (whether inline or in tank).

ASTI Ion Selective sensors should NEVER be installed in a horizontal or inverted configuration as this may lead to erratic and unreliable reading. In addition, most ASTI industrial ISE sensors are liquid or semi-liquid filled and as such may have a small air pocket inside the sensing element. To ensure that there is not an air pocket caught inside the sensing element, simply shake the ISE sensor gently downward. The small capillary force holding the air bubble in place inside the sensing element will be overcome by even a gentle downward shake.

Summary

ASTI strives to make online ISE measurement as accurate, simple and affordable as possible for all of our customers. Therefore, ASTI recommend to establish the sensitivity (slope) of your sensor with a two point calibration (repeat as necessary to validate the sensor sensitivity has not changed) and then start testing your process sample by installing the sensor into industrial service. Allow sufficient time to allow the sensor to come to equilibrium (assuming that the process conditions are stable). As required, take a grab sample from the process and adjust the concentration of the online analyzer to match the value of your established laboratory method using a one point offset calibration (standardize in Rosemount menu). Once you have reached this online operational level, you will be able to establish the relative accuracy and reproducibility of your inline measurement which will be influenced by host of factors including (but not limited to) the sample's temperature change (stability), ionic composition (background) amongst the various others factors as described above.

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