Ion Selective Electrodes for the Laboratory

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OTCO Water Laboratory Analyst Workshop

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Outline

- Review ISE measurement technology
- How to properly calibrate ISE sensors
- Best measurement practices
- Recommended maintenance and storage to help maximize sensor life

ISE Measurement Technology

Measurement Basics

- **ISEs measure ion activity (i.e. “effective concentration”)**

    -Ion activity < actual ion concentration due to interaction of ions in solution, reduces ions available to react

- ISEs are designed to measure specific ions, but other ions can interfere

    -Adding ionic strength adjustor acts to minimize/mask effect of interfering ions

- Aqueous (water-based) measurements
- Mono or half cell – only the ion sensor. This must be used with a separate reference electrode
- Combination – both the sensing electrode (half-cell) and reference electrode (half-cell) are housed in the same body

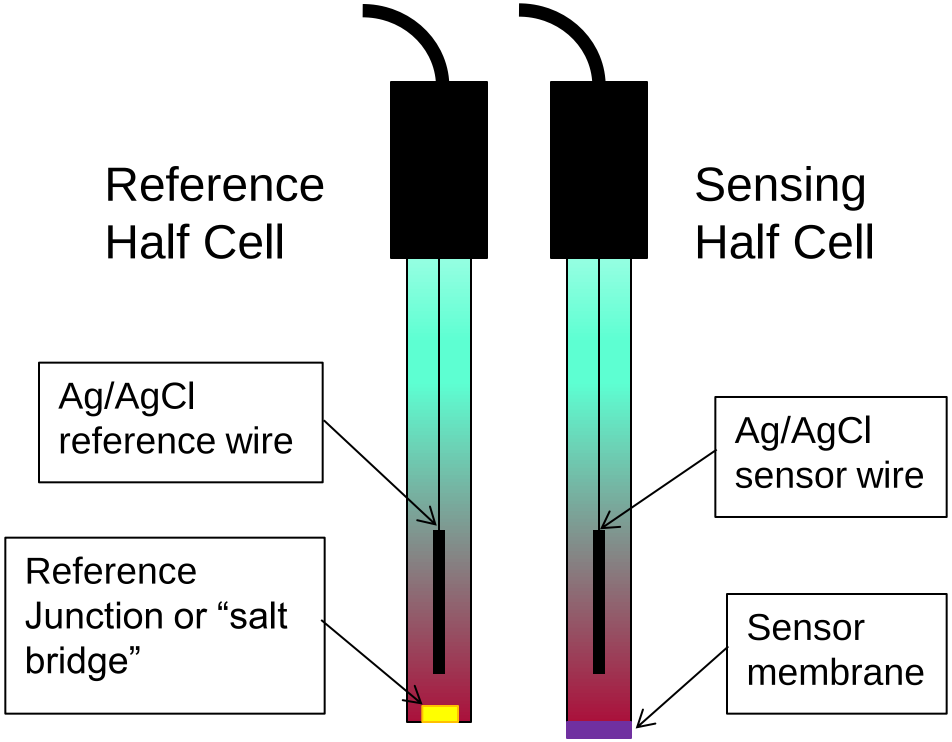
Measurement Basics

Very similar to pH electrodes

- pH electrode is just a “Hydrogen ISE”
- Output is in mV
- Follows the Nernst equation
- Calibration is critical
- Meters with an ISE mode, like YSI TruLab are best because they allow direct calibration in ion concentration units
- Differences: sensor designs (membranes), divalency (H^+ versus Ca^{+2}), use of Ionic Strength Adjustor (ISA), temperature compensation, range

ISE – How do they work?

Also much like pH electrodes…



Both half cells have similar chemistry and design:

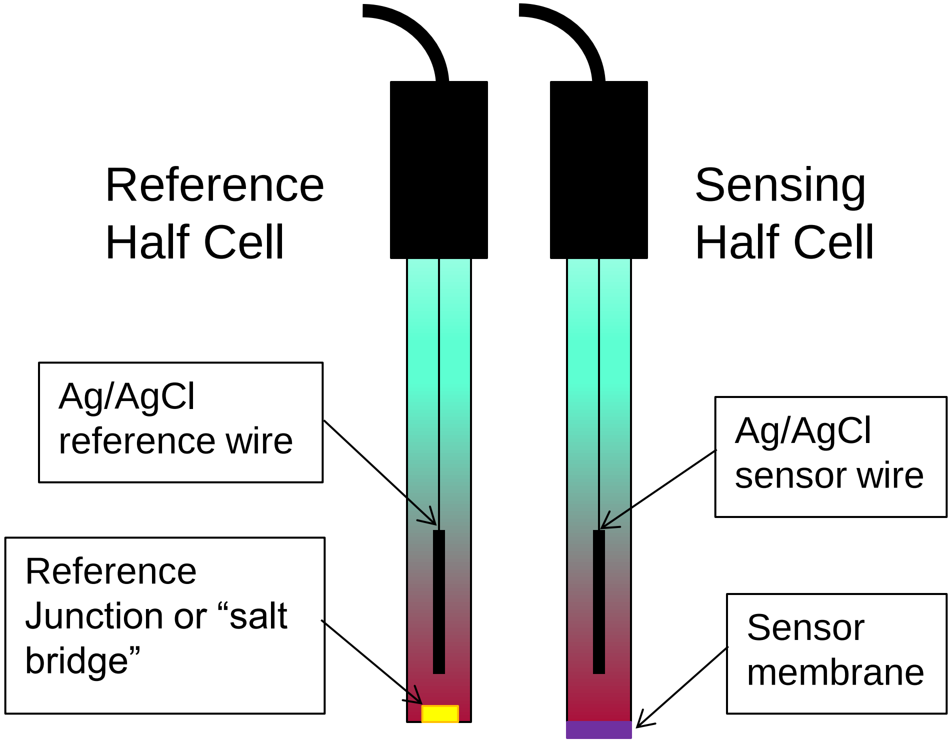
- Ag/AgCl wire bathed in a salty, chloride containing fill solution
- Both have ion exchange (interface) with the sample
- Both connected to the meter

The difference in the way they interface with the sample is KEY!

- The reference interfaces with the sample thru a salt bridge
- The sensing half cell interfaces via the sensor membrane

ISE – How do they work?

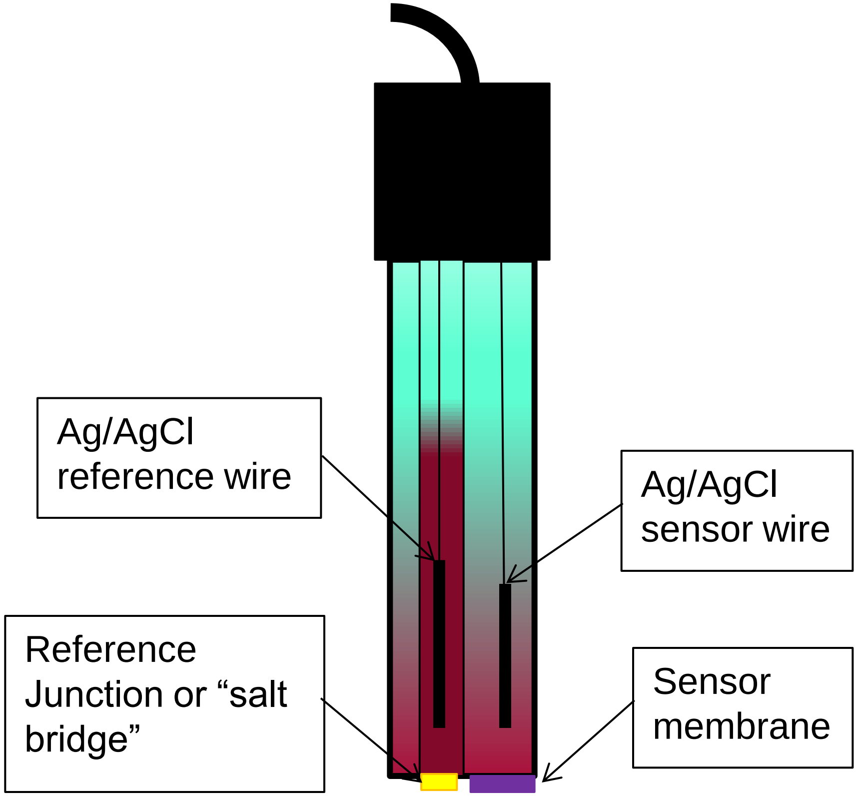
Think of it as if the Ag/AgCl wires are "antennas"



- Both antennas are similar and "connected" to the sample.
- Both SHOULD receive the same "signal" or potential
- However, because the sensing half cell interfaces with the sample **via the special ion-selective sensor membrane**, the difference in "signal" or potential is completely attributed to the target ion!
- The meter, via the calibration and the Nernst equation (software) can correlate ion concentration to this difference in potential

ISE – How do they work?

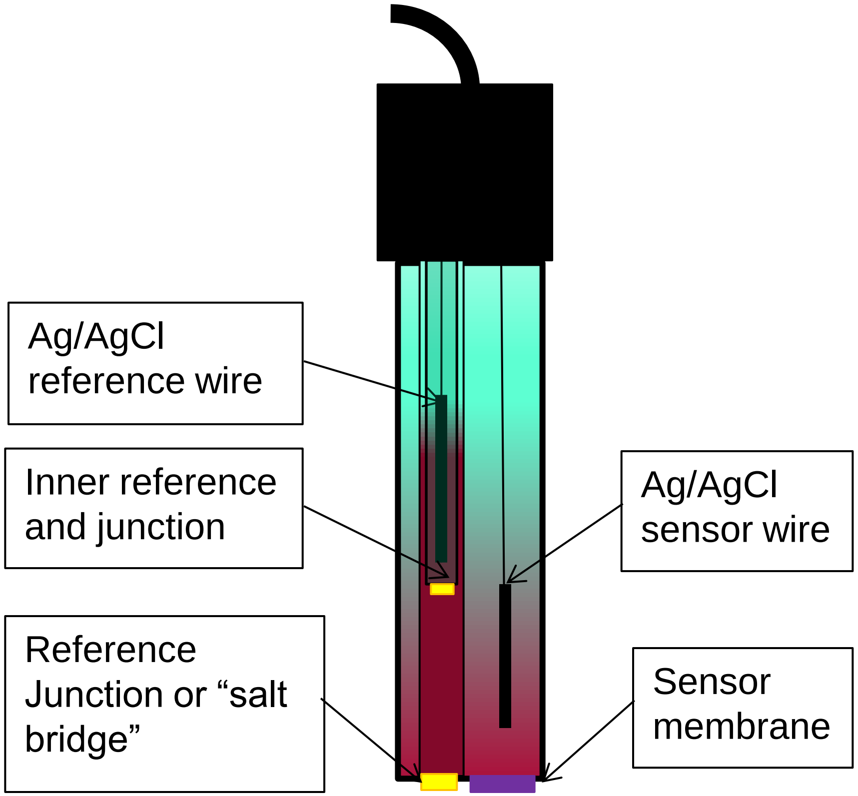
Now, combine these two half cells into one electrode body…



- And this becomes a convenient “**Combination Ion-Selective Electrode**”!
- Much easier to use
- Single-junction reference shown here
- An ISE with replaceable sensor membrane (modules) is the best option for some parameters

ISE – How do they work?

Many ISEs include a Double-Junction Reference



- If you add another “compartment” around the reference Ag/AgCl wire, and connect it to the rest of the reference system by ANOTHER junction or “salt bridge” – it is called a “Double-Junction Reference” design or “DJ”
- DJ references help avoid sample contaminants that could shorten the life of the ISE.
- They also allow the use of electrolyte that doesn’t contain silver (Ag) ions that could leak into the sample (certain application require metal-ion free electrodes)

ISE – How do they work?

ISE: Potential influenced by the activity of target ions in solution

Reference: Potential that is independent of the sample

The difference between these potentials (mV) is displayed on the meter.

Nernst equation establishes a relationship between the voltage and ion activity.

$$E = E^0 + (2.303RT/nF) \times \text{Log}(A)$$

- E = the total potential (in mV) developed between the sensing and reference electrodes.
- E^0 = is a constant which is characteristic of the particular ISE/reference pair. (It is the sum of all the liquid junction potentials in the electrochemical cell)
- 2.303 = the conversion factor from natural to base10 logarithm.
- R = the Gas Constant (8.314 joules/degree/mole).
- T = the Absolute Temperature.
- n = the charge on the ion (with sign).
- F = the Faraday Constant (96,500 coulombs).
- Log(A) = the logarithm of the activity of the measured ion.

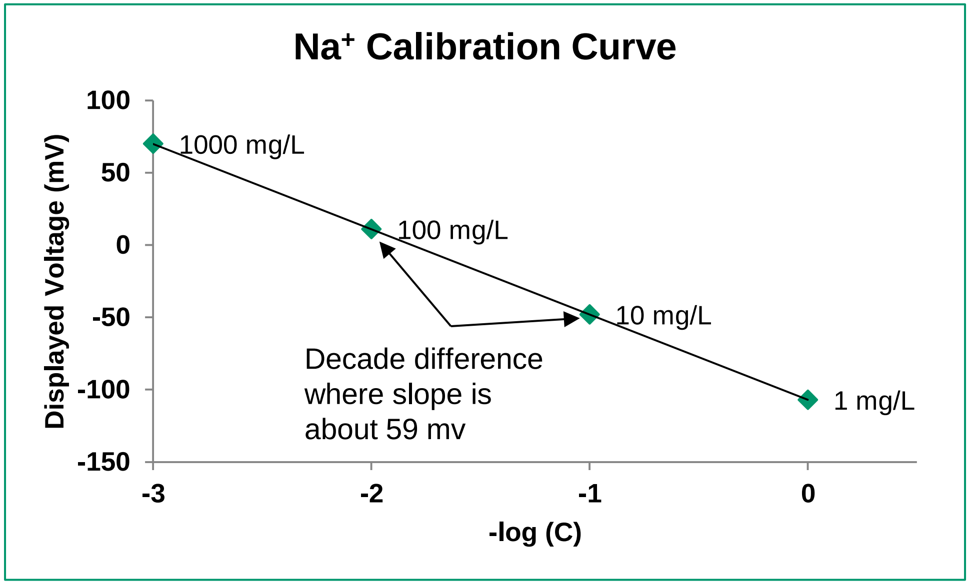
ISE – How do they work?

Slope?

- Slope of electrode: $2.303 * \frac{RT}{nF}$
  - The slope is typically ~**59 mV/decade** for a monovalent ion (e.g. Na^{+})
  - For a divalent ion like Calcium (Ca^{2+}), the slope is ~**29 mv/decade**

$$Slope\ (\mathrm{Ca}^{2+}) = 2.303 * \frac{8.314\ J}{\cancel{K}\ \cancel{mol}} * 298.15\ \cancel{K} * \frac{1}{2} * \frac{\cancel{mol}}{9.649 * 10^{4}\ C} = 2.958 * 10^{-2}\ J\ C^{-1} = 29.58\ mV$$

- Commonly, the ISE slope is lower than the ideal value of 59 mV/decade (or 29 mv/decade for a divalent ion like Ca^{2+} or Sulfide S^{2-})
- It is typical to see ISE slopes range from 53-59 mV/decade (26-29 mV/decade for divalent ions)

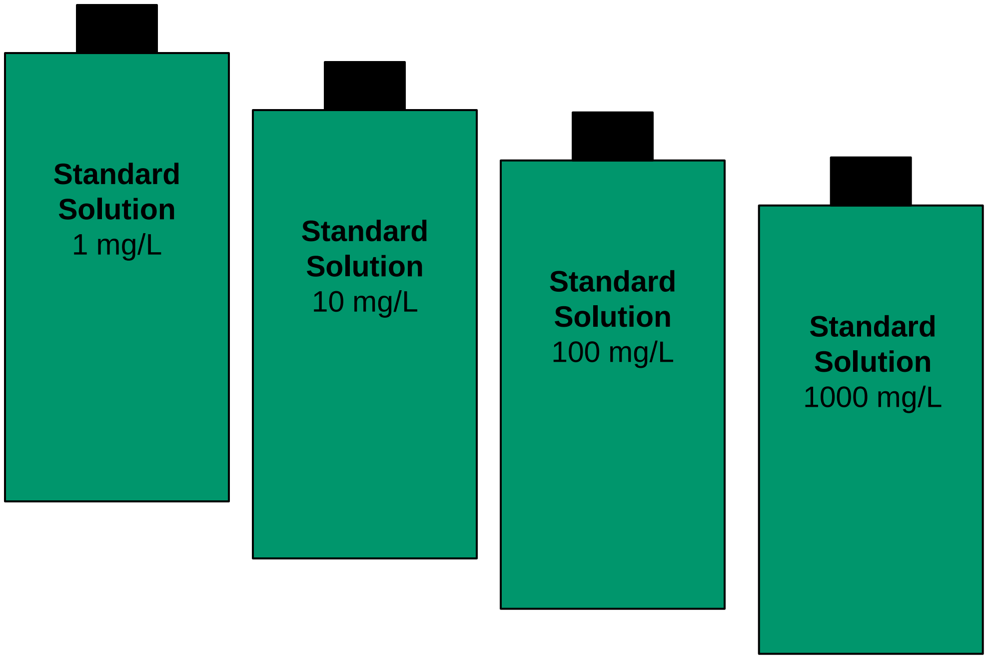


ISE – How do they work?

Decade?

- When discussing ISEs you will often hear this word "decade" – all that means is a 10-fold difference (like logarithm scale)
- For example, for pH a decade difference is the difference between pH 7 and pH 8

- For ISEs, it is important to have at least ONE decade difference represented in the calibration standards used. (e.g. 1 mg/L and 10 mg/L)
- On meters like the YSI TruLab, it is possible to include up to 7 calibration points! It is perfectly fine to "fill-in" between the decade.



The YSI TruLine ISEs…

Snapshot:

- 15 electrodes, 16 Parameters
- Electrode kit
- Made in the USA
- 4 Sensor Technologies:
  - Polymer/PVC membrane, Solid State, Gas Sensing and Glass membrane

The YSI ISEs…

What’s included in the box?

- Electrode – unfilled
- 1 sensor module for Polymer/PVC type electrodes (these sensors have a shorter shelf life than solid state types)
- 2 membrane modules for Ammonia ISE
- Reference Fill Solution – varies by parameter
- Ionic Strength Adjustor (ISA) – varies by parameter but serves as pH adjustment and ionic strength addition.
- Standard Solution – small bottle of the high standard (usually 1000 mg/L)
- Polishing strip for solid state electrodes
- Instruction sheet

ISE Technology

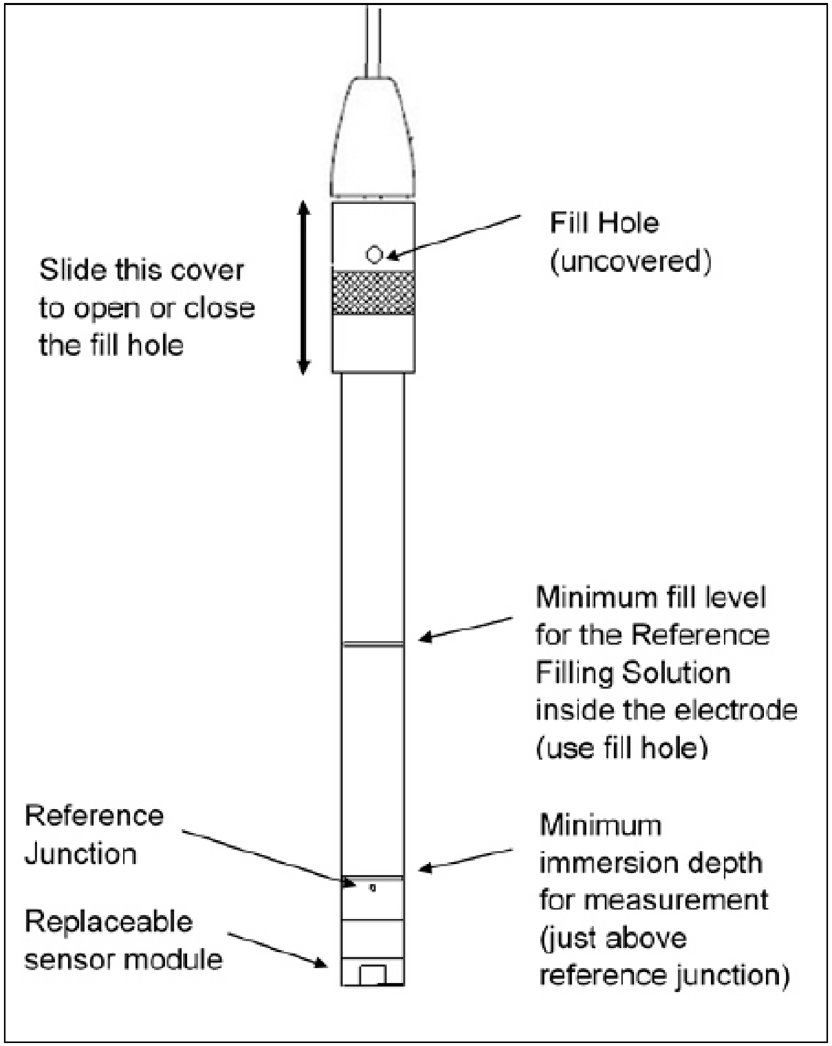
General guidelines

- Polymer/PVC type electrodes have shorter life expectancy (6-12 months) and therefore have replaceable sensors.
- Solid State types can last 36 months in some applications.
- All these ISEs are refillable and include a double-junction reference. It only takes about 1-2 mL to fill the electrode.
- Accuracy: Typically 2%-3% is very feasible. ISEs can be very technique sensitive.

ISE Use, Calibration and Maintenance

Getting started, preparing a new electrode

- Remove storage/soaker bottle
- Install sensor module (polymer/PVC) or membrane module (ammonia)
- Fill electrode with fill solution
  - Takes ~1-2 mL to fill electrode
- Condition in low concentration standard
- Perform calibration



Calibration tips

- Make sure to include at least one decade difference – most meters require it. It is ok to add calibration points in between a decade, especially in the non-linear low level measurement.
- Add ISA (ionic strength adjustor) to both standards and samples
    - 2 mL ISA per 100 mL of solution
- Calibration standard preparation needs to be done very accurately!
- Try to calibrate at the same or similar temperature as the expected sample temperature
    - For best results, calibrate within 5°C of sample temperature

Cleaning/maintenance

- Solid State sensors (not Fluoride) should be inspected regularly and buffed with a polishing strip if they look oxidized
- Fluoride ISE can be scrubbed with a small brush and some users use toothpaste to clean them!
- Polymer/PVC membrane and gas-sensing membrane ISEs are more difficult to clean – avoid touching or abrading the membrane. Use short (1 hour) soak in DI water to remove impurities. Recondition in a 100 mg/l standard before using.
- Glass electrode and pH electrode of Ammonia probe can be cleaned similar to pH electrodes
- Refill/refresh the electrolyte regularly

Storage

- Short term – the sensor can be stored in a low standard solution for 1-3 days with Reference Filling Solution full
- Long term – try to drain Reference Filling Solution and store dry, but protected from sunlight and preferably with a cover over sensor. Avoid contact with plastic materials on Polymer/PVC type sensors.
- After storage, it is important to refresh the electrolyte by shaking the remainder out of the fill hole and refilling with fresh solution

Troubleshooting

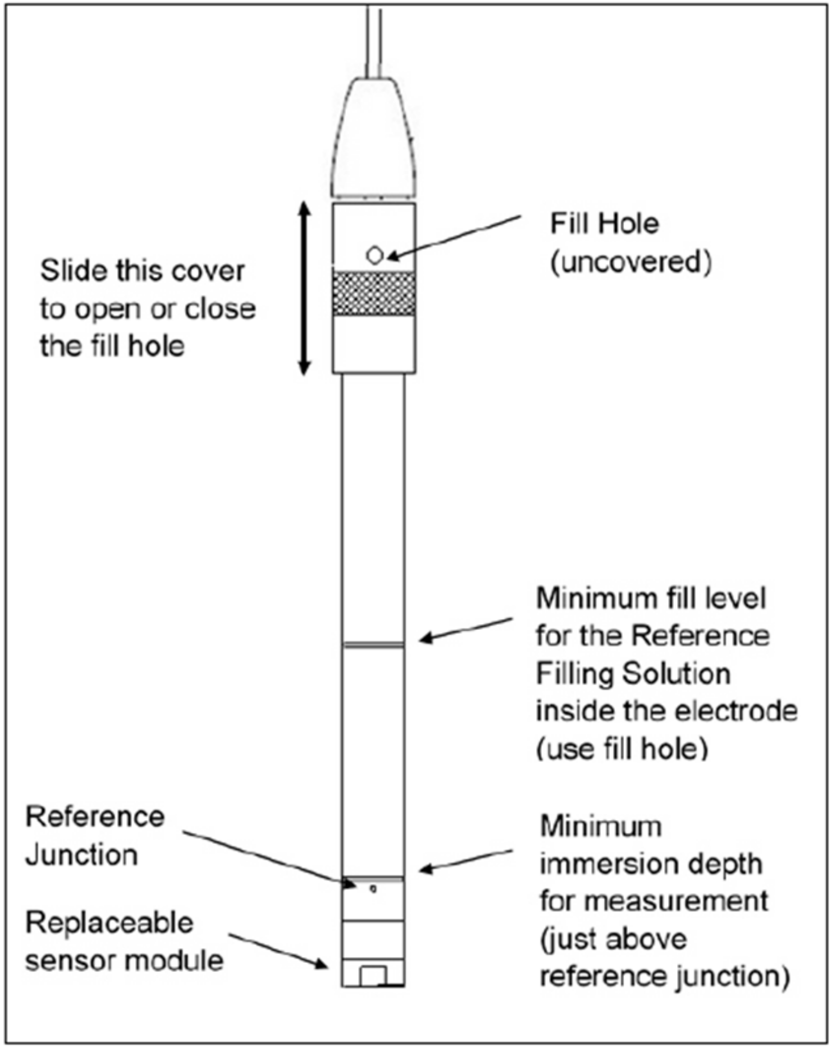
Common issues/problems:

- Conditioning – good to condition in the low standard solution and start with that standard to avoid carryover.
- Try a new sensor module (on polymer/PVC types)
- What is the measurement range? Non-linear curves may occur below 1 mg/L
- Interferences can be a problem – try known additions to quantify their impact as a false low or false high.
- Stirring can be important for some testing/applications.
- Observe mV readings over concentration to get a clearer picture of electrode response

Troubleshooting

Common issues/problems

- The fill hole should be OPEN during use to allow electrolyte to "leak" via the salt bridge. Close the hole only during storage
- It can be difficult to drain the ISE, however, on occasion it may be good to shake out the old electrolyte and refresh it (salt concentration). It might be easier to overfill it to accomplish this also.
- Make sure the Reference Filling Solution (electrolyte) is covering the inner junction (small white dot on inner body



Troubleshooting

Common issues/problems

- Make sure the Reference Filling Solution level is above the <u>sample</u> level (ensures electrolyte leaking into sample instead of sample coming into electrode)
- Make sure the correct Reference Filling Solution is being used! Each parameter has its own type!
- Polymer/PVC sensors should not be stored in contact with other plastics – the sensor membrane can bond to plastic materials

Measurement Methods

Direct measurement:

- Simple and most commonly used ISE method
- Measure mV output in samples and determine concentration based on calibration (i.e. just as is done with pH)

Incremental methods:

- Standard addition, standard subtraction, sample addition, sample subtraction
- Methods of spiking the sample
- Sample ion concentration calculated from change in potential
- YSI TruLab 1320 and MultiLab 4010-2/3 have all incremental methods preprogrammed

A brief review of a few ISEs

EPA Approved measurement methods

Species Measured	ASTM	Standard Methods	USGS
AMMONIA	D1426-89	4500-NH3 (F), (G)	I-1524
BROMIDE	D1246-05		I-1125-852
CHLORIDE	D512-04 (C)		
CYANIDE	D2036-09A	4500-CN F-99	
FLUORIDE	D1179-04B	4500-F (C) 97	
NITRATE		4500-NO3 D-00	
POTASSIUM		3500-D C 97	
SULFIDE	D4659-08	4500-S-2 G-00	

Ammonia (NH_3)

- ✓ **Technology:** Gas-sensing
- ✓ **Features:** Replaceable Membrane Modules, pH sensor inside
- ✓ **Range:** 0.02-17,000 mg/L
- ✓ **Slope:** 54-59 mv/decade
- ✓ **pH range:** Must be 11 or higher to make NH_3 gaseous. ISA has blue color at this pH
- ✓ **Interferences:** few, volatile amines
- ✓ **Applications/Notes:** Popular for wastewater, aquaculture, agriculture, industrial. pH shift caused by ammonia gas is correlated to concentration

Ammonium (NH_4^+)

- **Technology:** Polymer/PVC Membrane
- **Features:** Refillable, Replaceable Sensor Modules
- **Range:** 0.02-1,800 mg/L
- **Slope:** 54-59 mv/decade
- **pH range:** 4-10
- **Interferences:** few, Na^+, K^+
- **Applications/Notes:** Popular for wastewater, environmental, industrial, food/beverage

Bromide (Br^-)

- ✓ **Technology:** Solid State
- ✓ **Features:** Refillable, non-replaceable sensor
- ✓ **Range:** 0.4-79,900 mg/L
- ✓ **Slope:** 54-59 mv/decade
- ✓ **pH range:** <12
- ✓ **Interferences:** I^-, Cl^-, CN^-, NH_3^-
- ✓ **Applications/Notes:** industrial

Chloride (Cl^-)

- **Technology:** Solid State
- **Features:** Refillable, non-replaceable sensor
- **Range:** 1.8-35,500 mg/L
- **Slope:** 54-59 mv/decade
- **pH range:** 2-12
- **Interferences:** CN^-, Br^-, I^-, OH^-, S^{2-}, NH_3
- **Applications/Notes:** Very popular for industrial, wastewater, drinking water, food/beverage, environmental. This sensor is slightly photosensitive – store in dark place when not in use.

Fluoride (F^-)

- **Technology:** Solid State Crystal
- **Features:** Refillable, non-replaceable sensor
- **Range:** 0.02 mg/L - saturation
- **Slope:** 54-59 mv/decade
- **pH range:** 5-7 at low range, 11 at higher range
- **Interferences:** OH^-
- **Applications/Notes:** Very popular for drinking water, industrial. Lanthanum fluoride crystal is the sensor.

Nitrate (NO_3^-)

- **Technology:** Polymer/PVC Membrane
- **Features:** Refillable, Replaceable Sensor Modules
- **Range:** 0.4-62,000 mg/L
- **Slope:** 54-59 mv/decade
- **pH range:** 2.5-11
- **Interferences:** few, ClO_4^-, ClO_3^-, I^-, F^-
- **Applications/Notes:** Very popular for environmental, industrial, agriculture, food/beverage

Potassium (K^+)

- ✓ **Technology:** Polymer/PVC Membrane
- ✓ **Features:** Refillable, Replaceable Sensor Modules
- ✓ **Range:** 0.04-39,000 mg/L
- ✓ **Slope:** 54-59 mv/decade
- ✓ **pH range:** 2-12
- ✓ **Interferences:** Cs^+, NH_4^+, Tl^+, H^+, Ag^+,$Tris^+$, Na^+, Li^+
- ✓ **Applications/Notes:** Popular for agriculture, food/beverage, environmental, industrial

Thank you for your attention!

Any questions?