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# ISE Measurement Seminar

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# Why Use ISE's?

- **Responsive over a wide concentration range**
- **Not affected by color or turbidity of sample**
- **Rugged and durable**
- **Rapid response time**
- **Real time measurements**
- **Low cost to purchase and operate**
- **Easy to use**

# Why Use ISE's?

- **There are many types of ISE applications:**
  - *Ammonia in wastewater*
  - *Residual chlorine in water or wastewater*
  - *Chloride in wastewater*
  - *Cyanide in water or wastewater*
  - *Fluoride in water*
  - *Nitrate in drinking water or wastewater*
  - *Nitrite in water*
  - *Sulfide in wastewater*

# Why Use ISE's?

- EPA approved methods
  - *Acidity*
  - *Alkalinity*
  - *Ammonia*
  - *Bromide*
  - *Chloride*
  - *Residual Chlorine*
  - *Cyanide*
  - *Fluoride*
  - *Total Kjeldahl Nitrogen (TKN)*
  - *Nitrate*
  - *Dissolved Oxygen/BOD*
  - *pH*
  - *Sulfide*

# New EPA ISE Approvals

- Nitrate in wastewater
  - 0.1 ppm as N detection limit
  - Direct calibration and read method
- Chloride in wastewater
  - 1.8 ppm detection limit
  - Direct calibration and read method
- Sulfide in wastewater
  - 0.003 ppm detection limit
  - Direct calibration and read method
- Cyanide (total) in wastewater
  - 0.2 ppm detection limit
  - Direct calibration and read method

# New EPA ISE Approvals

- 40 CFR Part 122, 136, et al.
- Nitrate (as N) in wastewater
  - SM 4500-NO<sub>3</sub>-D
- Sulfide in wastewater
  - SM 4500-S<sup>-2</sup>-G
  - ASTM D4658-03
- Chloride in wastewater
  - ASTM D512-89(99)(C)
- Cyanide (total) in wastewater
  - SM 4500-CN<sup>-</sup> F
  - ASTM D2036-98A

SM = Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition

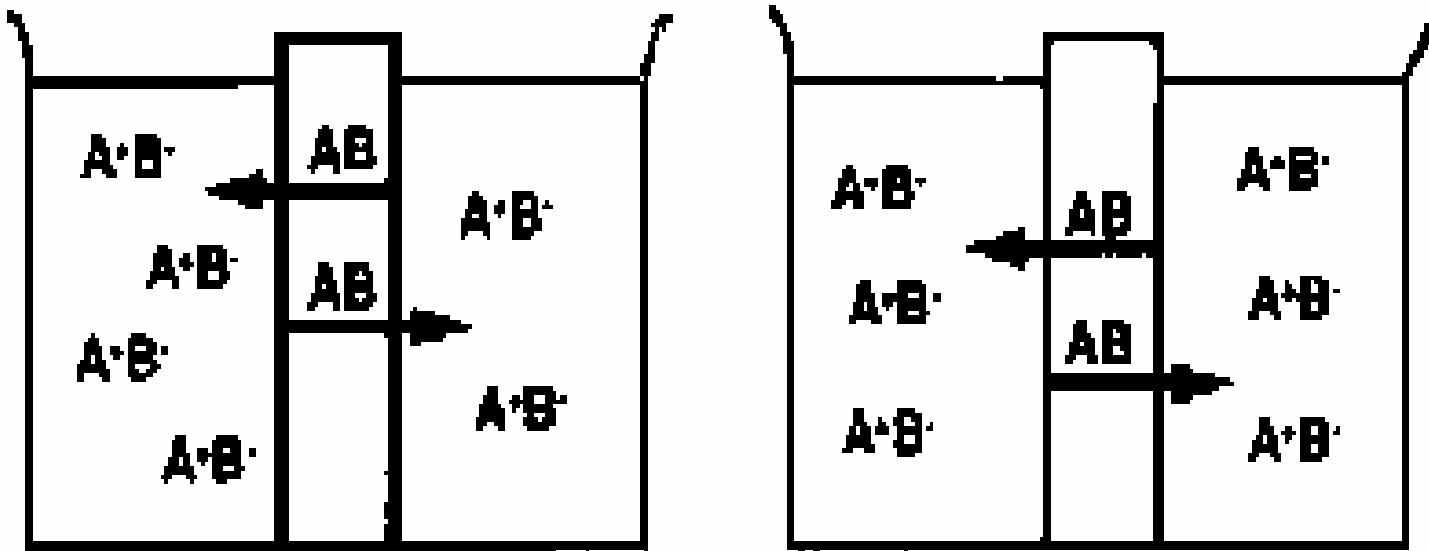
ASTM = Annual Book of Standards, Volumes 11.01 and 11.02, D19 Water

# What Are ISE's?

- **Electrodes are devices which detect species in solutions**
- **Electrodes consist of a sensing membrane in a rugged, inert body**

# How Do ISE's Work?

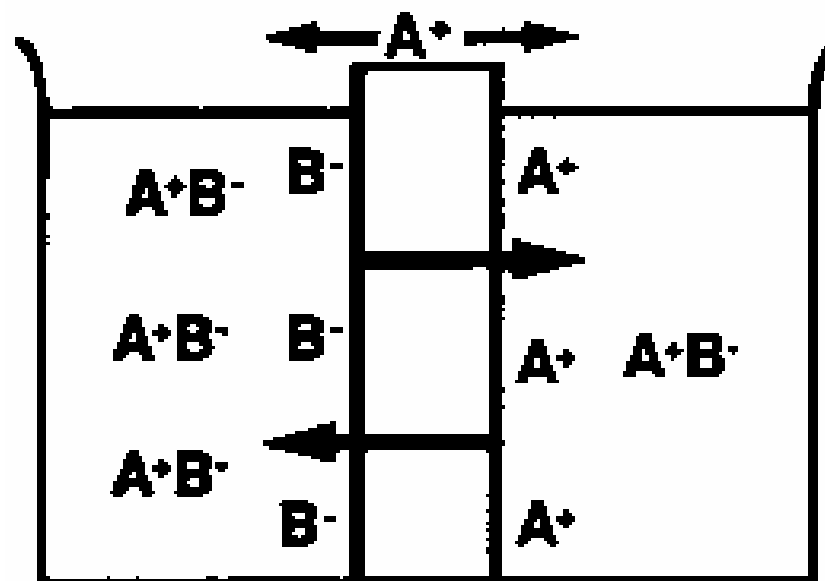
- If two solutions are separated by an ion-permeable membrane, they will equilibrate:





# How Do ISE's Work?

- If the membrane is permeable to only one species, a charge quickly develops which opposes further movement
- The charge is proportional to the difference in concentration on the two sides
- The total number of ions that diffuse is very small

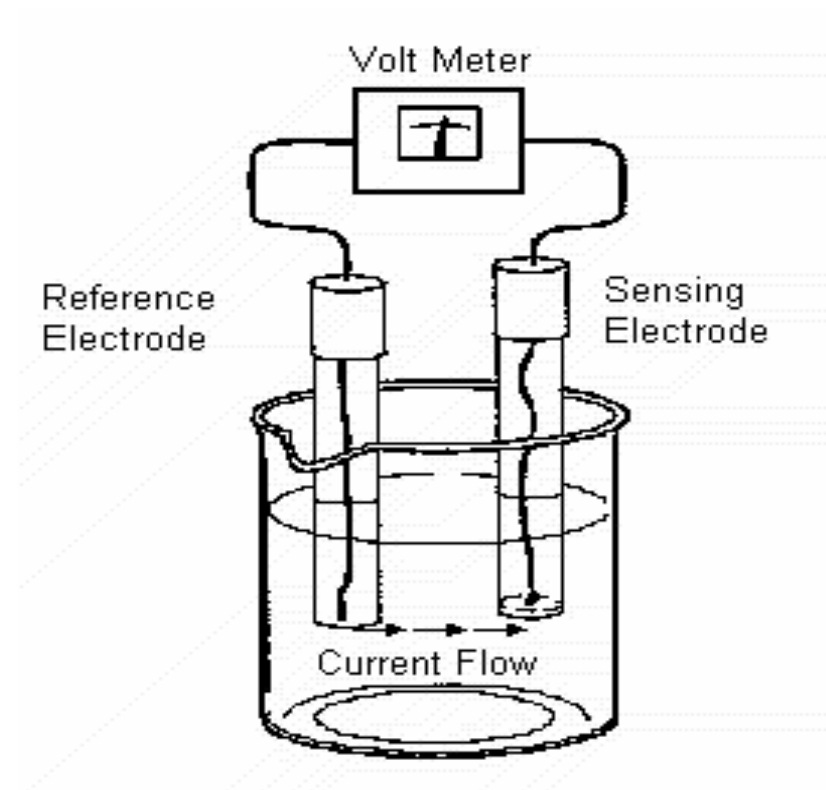


# How Do ISE's Work?

- The reference electrode completes the circuit to the sensing electrode (ISE)
- Reference electrodes have a small leak to establish contact with the sample
- The reference solution (usually KCl) in contact with the reference keeps the reference potential constant

# How Do ISE's Work?

- The ISE meter measures the voltage potential (mV) difference between the sensing electrode and the reference electrode



# ISE Meters

- ISE meters report concentrations
  - *No manual calibration curves are required*
- ISE meters generate sophisticated curves which are held in the meter's memory
  - *Run standards*
  - *Run unknowns*
  - *Read results*

# Types Of Sensing Electrodes

- **Glass Membrane**
- **Solid State**
- **Liquid Membrane**
- **Gas Sensing**

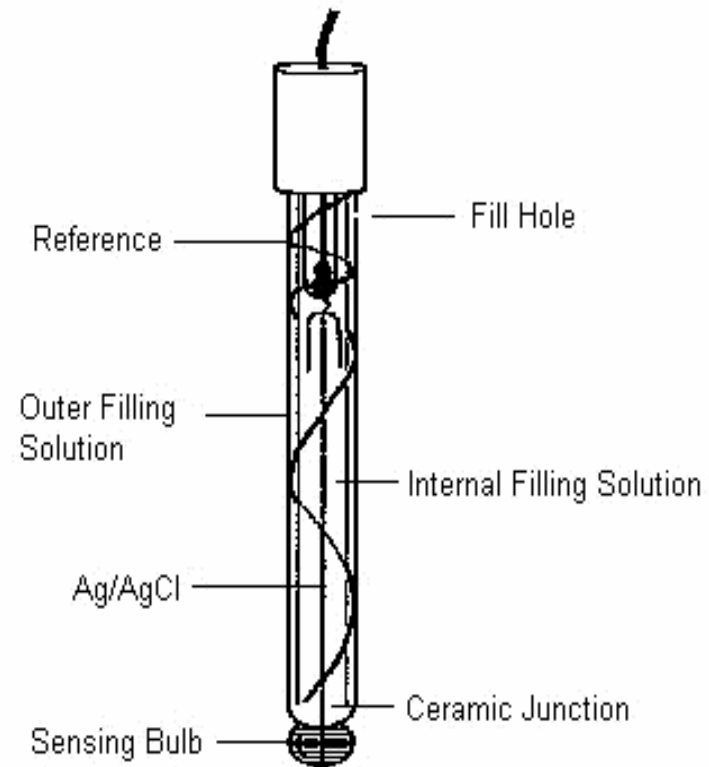
# Glass Membrane Electrodes

- pH
- Sodium



# Glass Membrane Electrodes

- The sensing element is a special type of glass
  - *Combination or half-cell electrodes*
- Store glass membrane electrodes wet in storage solution
- Recondition when sluggish



# Glass Membrane Electrodes

- **Example: Sodium**
  - *0.02 detection limit*
  - *Available in combination or half-cell versions*
  - *Ross or Ag/AgCl references*





# Types Of Sensing Electrodes

- Solid State

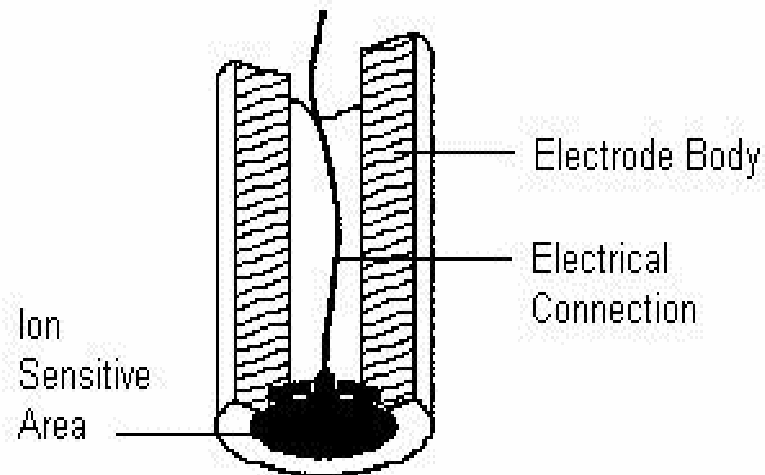


# Solid State Electrodes

- Bromide
- Cadmium
- Chloride
- Chlorine
- Copper
- Cyanide
- Fluoride
- Iodide
- Lead
- pH
- Silver
- Thiocyanate

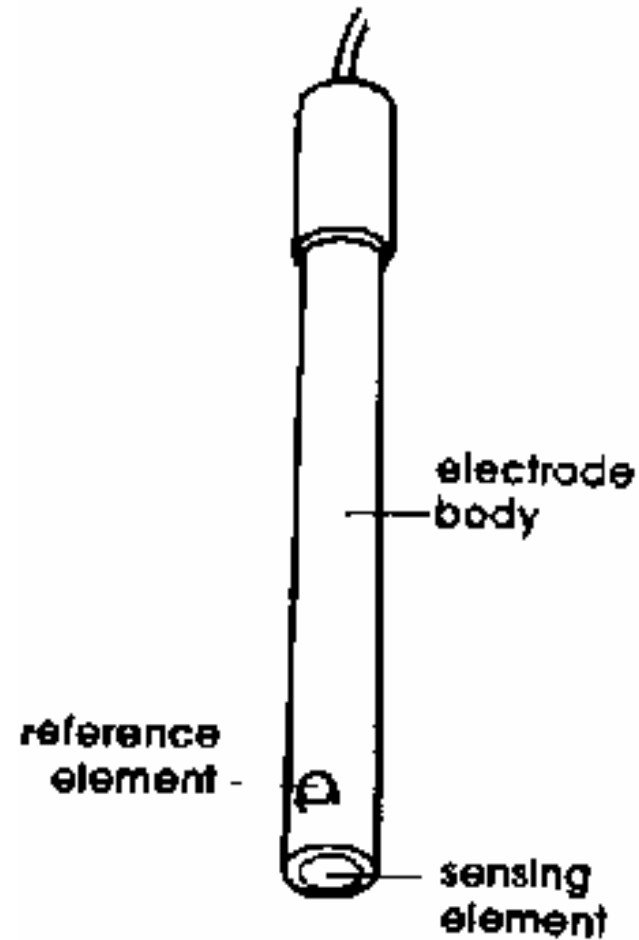
# Solid State Electrodes

- Sensing element is a solid crystalline material
- Store combination electrodes in dilute standard
- Store half-cell electrodes dry
- Polish solid state electrodes to rejuvenate



# Solid State Electrodes

- **Example: Chlorine**
  - *EPA approved for drinking water or wastewater*
  - *0.01 detection limit*
  - *Combination electrode*



# Chlorine ISE Slope Check

- Prepare chlorine water by diluting 1 ml of 5% hypochlorite solution (bleach) to 500 ml with DI water
- Add 1 ml iodide and acid reagents to 100 ml DI water
- Add 1 ml chlorine water and stir *gently* for 2 minutes
- Add 10 ml chlorine water and stir *gently* for 2 minutes
- Record readings: slope range 26-30 mV

# Chlorine ISE Calibration

- Dilute 100 ppm standard to bracket range of samples with at least a ten fold concentration difference between standards
- Can calibrate with multiple standards
- Add 1 ml of iodide reagent and 1 ml of acid reagent to diluted aliquot of standard, mix, then add DI water
- Slope range: 26-30 mV

# Chlorine ISE Hints

- Do not use bleach as standards, only as slope check
- Polish reference element with polishing strip when response is sluggish
- Polish platinum sensing surface only as last resort
- *Gentle* stirring is acceptable during calibration and measurement
- Store Chlorine ISE dry

# Fluoride ISE Slope Check

- Place electrode in 100 mls of 1ppm standard w/TISAB II
- Record mV reading, rinse electrode
- Place electrode In 100 mls of 10 ppm standard w/TISAB II
- Record mV reading
- Slope range: 54-60 mV



# Fluoride ISE Hints

- Store electrode in 100 ppm standard
- Flush fill solution weekly
- Polish electrode when response is sluggish or slope is low
- Polish with fluoridated toothpaste/water for 30 seconds

# Types Of Sensing Electrodes

- Liquid Membrane

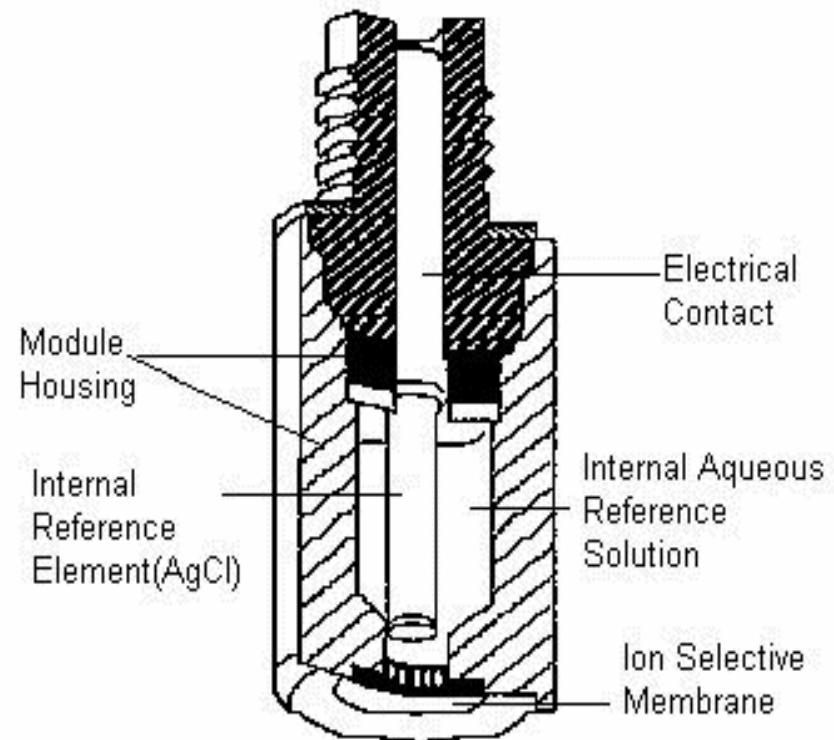


# Liquid Membrane Electrodes

- Ammonium
- Calcium
- Chloride
- Fluoroborate
- Nitrate
- Nitrite
- Perchlorate
- pH
- Potassium
- Surfactant
- Water Hardness

# Liquid Membrane Electrodes

- Sensing membrane is an ion carrier dissolved in a soft plastic
- Store electrodes in dilute standard for short-term
- Store module dry in vial for long-term



# Liquid Membrane Electrodes

- **Example: Nitrate**
  - *EPA approved for drinking water or wastewater*
  - *0.1 ppm detection limit*
  - *Available in combination or half-cell versions*



# Nitrate ISE Assembly

- Replace module every 2-6 months
- Do not over-tighten module
- Replace fill solution weekly
- Do not immerse electrode beyond o-ring on half cell module
- Use full strength ISA or Optimum Results as fill solution

# Nitrate Slope Check

- Prepare 100 mls DI water
- Add 2 mls ISA
- Add 1 ml 1000 ppm nitrate standard
- Record mV reading
- Add 10 mls 1000 ppm nitrate standard
- Record mV reading
- Slope range: 54-60 mV

# Nitrate ISE Hints

- Check slope with ISA not ISS
  - Depressed slope normal when using ISS
- Use ISS with interfering anions
- Soak module In DI water for cleaning
- Store module in 100-1000 ppm standard
- Make sure junction flow is adequate
- Calibrate with standards that bracket sample concentration



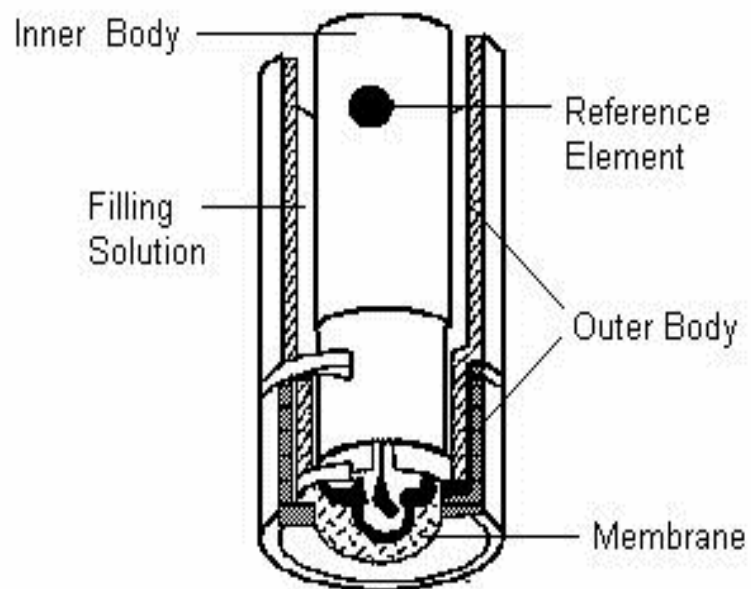
# Gas Sensing Electrodes

- Ammonia
- Carbon dioxide
- Nitrogen dioxide
- Oxygen



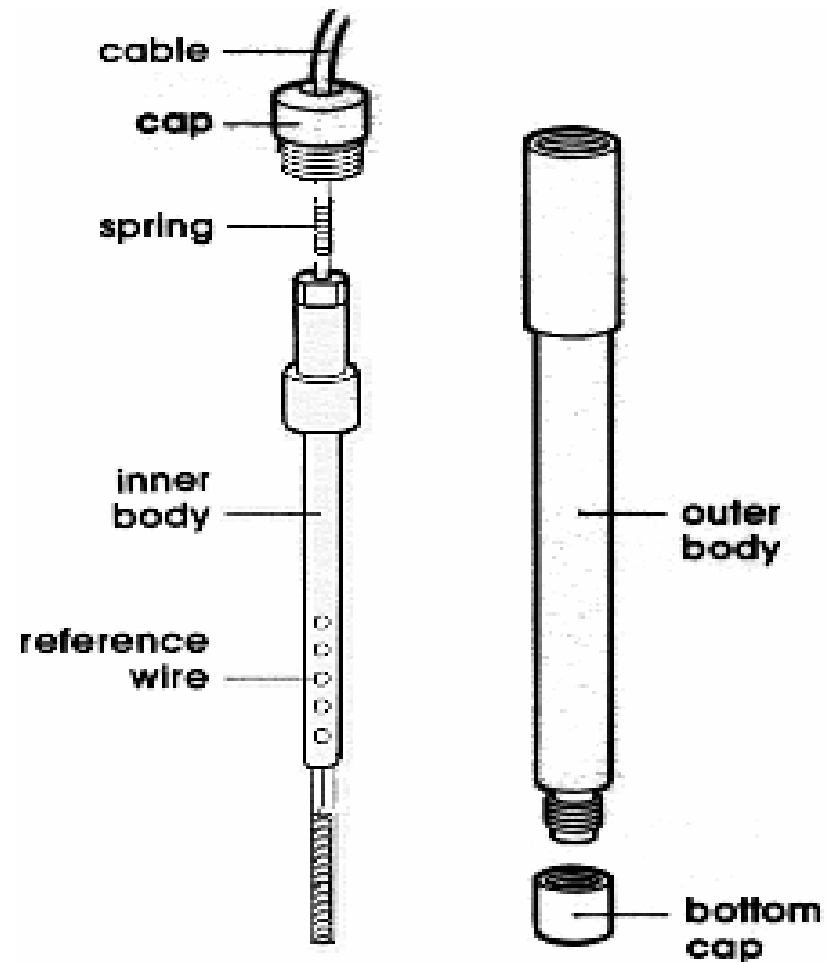
# Gas Sensing Electrodes

- Gas sensing electrodes work by measuring the pH change caused by diffusion of the gas through a hydrophobic but porous membrane
- Store in dilute standard for short term
- Store dry for long term

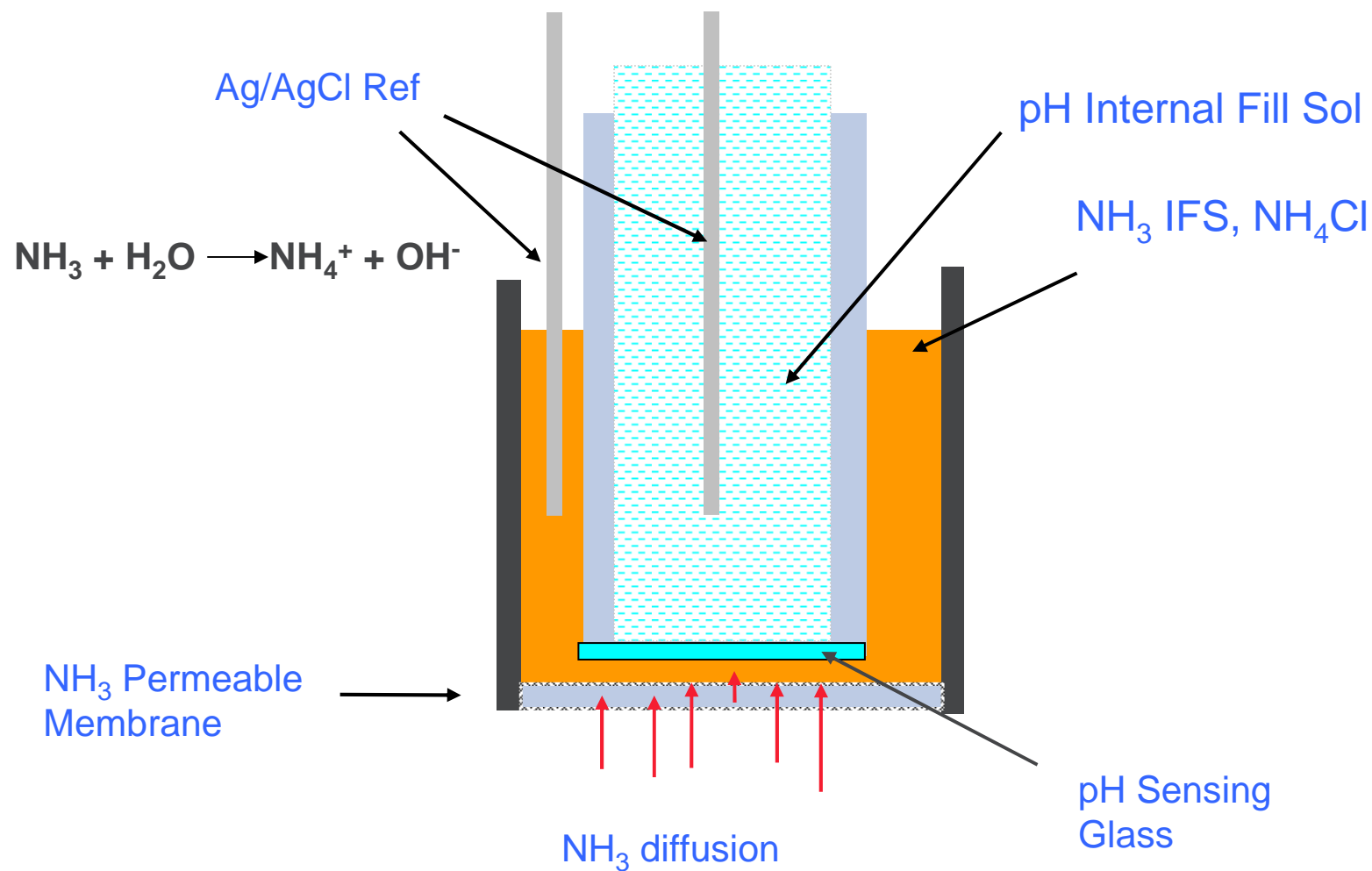


# Gas Sensing Electrodes

- **Example: Ammonia**
  - *EPA approved for wastewater*
  - *0.01 ppm detection limit*
  - *Combination electrode*
  - *Replaceable membranes*



# Electrode Structure



# Older Ammonia ISE Assembly

- Soak inner body in fill solution for 2 hrs.
- Replace the membrane every 2-4 weeks
- Use tweezers to handle membrane
- Stretch membrane until taut
- Use 2.0 - 2.5 mls of fill solution
- Shake electrode down after assembly
- Pull on the electrode cable to allow fresh supply of fill solution to the membrane but re-calibrate after this is done



# Older Ammonia ISE Storage

- Store in 10-100 ppm ammonia standard
- Between measurements store in 10 ppm standard with NaOH (ISA)
- Condition electrode in pH 4 buffer for several minutes before starting low level calibration

# Ammonia ISE Inner Body Check

- Place electrode in pH 7 buffer: read mV
- Rinse electrode
- Place electrode in pH 4 buffer
- mV's should change by at least 100 after 30 seconds
- mV's should change by at least 150 after 3 minutes

# Ammonia Slope Check

- Prepare 100 mls DI water
- Add 2 mls ISA
- Add 1 ml 1000 ppm ammonia standard
- Record mV reading
- Add 10 mls 1000 ppm ammonia standard
- Record mV reading
- Slope range: 54-60 mV



# Ammonia ISE Hints

- Use electrode at a 20 degree angle: check for bubbles at membrane
- Calibrate with standards that bracket sample concentration
- Samples should be acidified if stored
- Replace membrane/clean inner body in 0.1M HCl when response is sluggish or slope is low

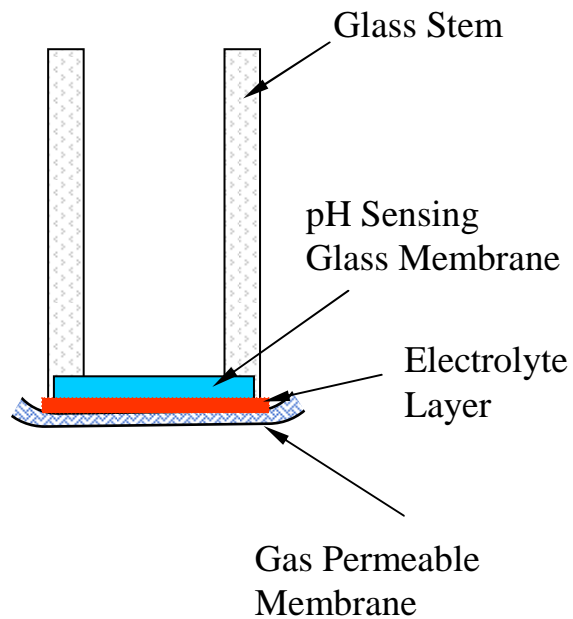
# New High Performance Ammonia ISE

- Low limit of detection
  - 0.01 ppm
- Faster response
  - <2 minutes at 0.05 ppm
- Greater linear response
  - 0.01 ppm to 14,000 ppm
- Unique outer body design
  - Entire outer body is replaced, bonded membrane attached
  - \$20 replacement cost
  - Translucent body with fill line mark to avoid overfilling
  - Can also use loose membranes with cap
  - Lock in feature to prevent membrane damage during assembly
  - Back seal to prevent leakage
- Started shipping January 2008



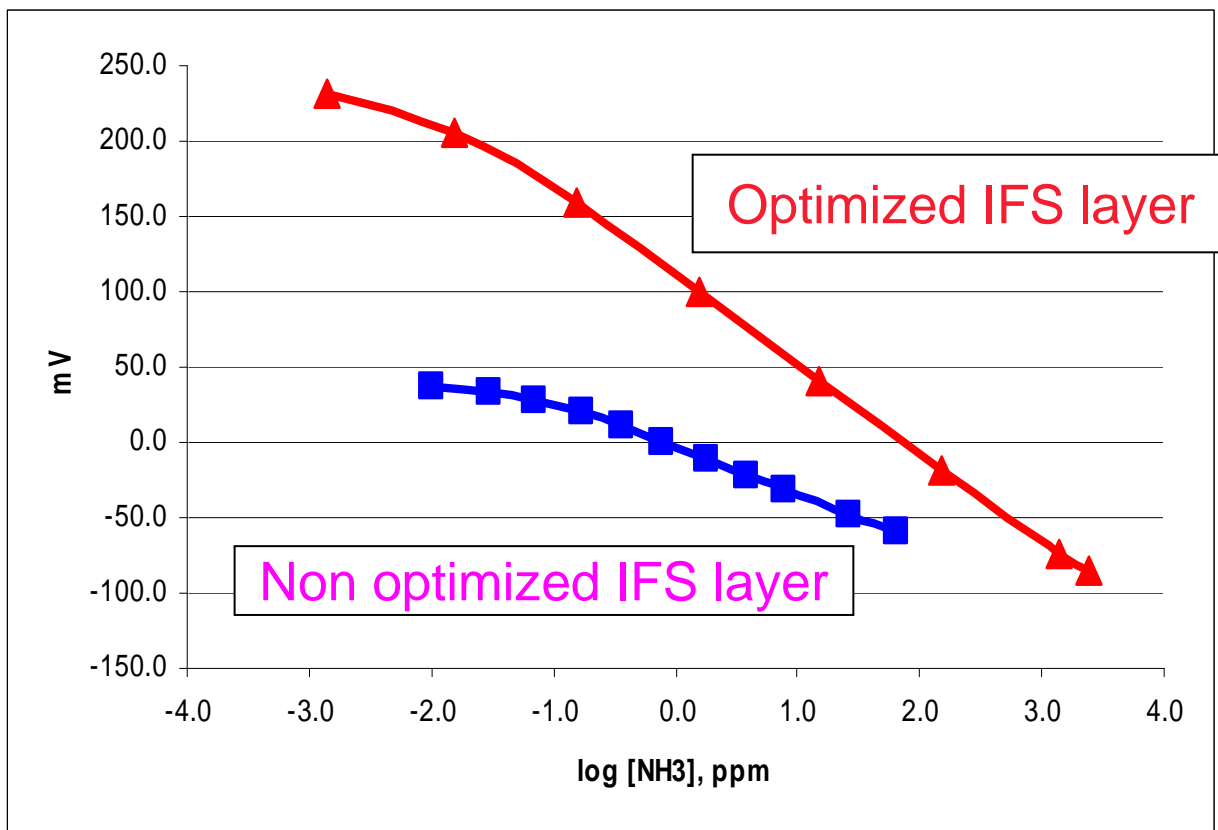
# Electrode Design Highlights

Thin, Uniform Electrolyte Layer Covering Whole Sensor Area

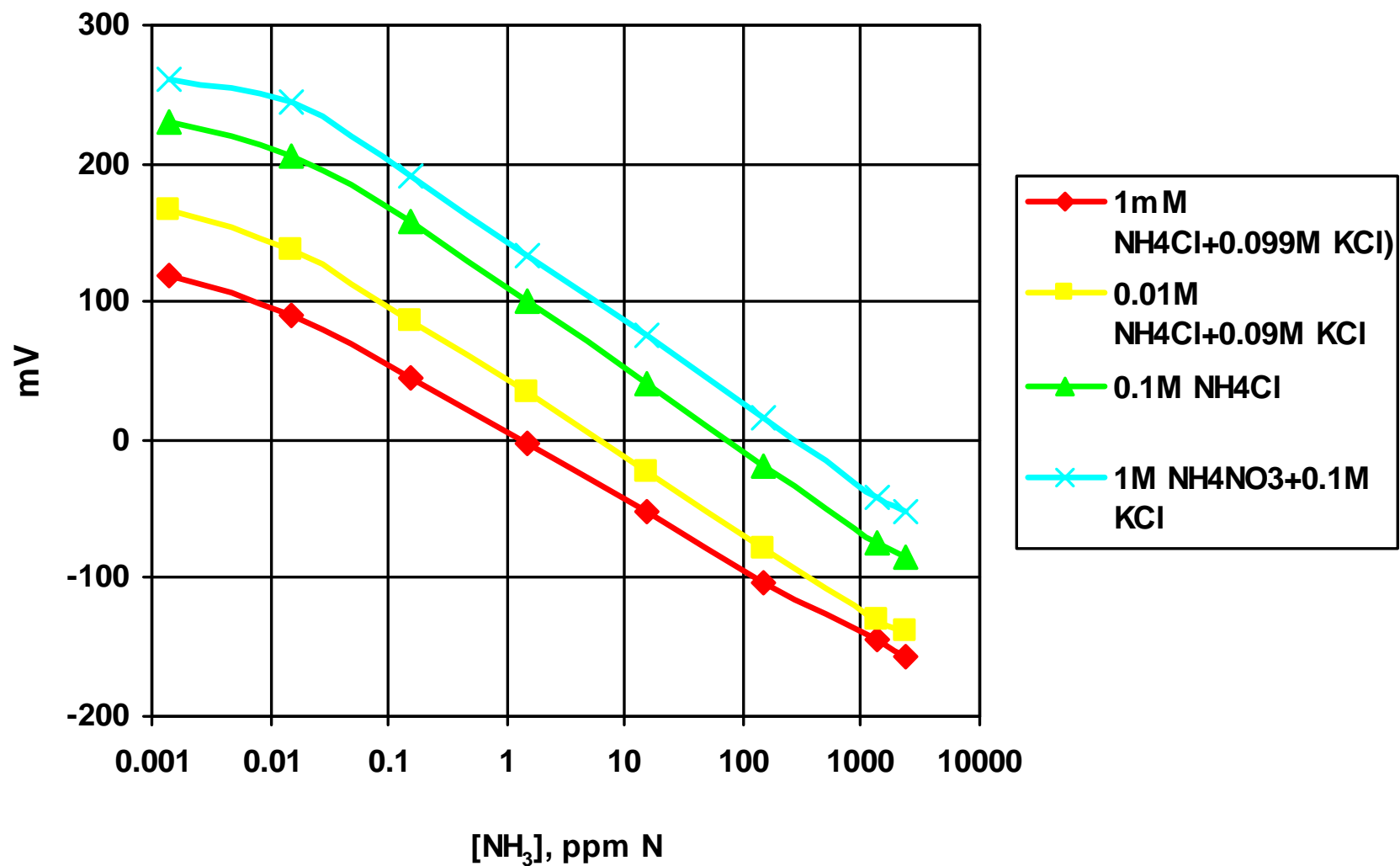


- Glass stem with small diameter
- Flat sensor surface
- Mold parts for tight tolerance

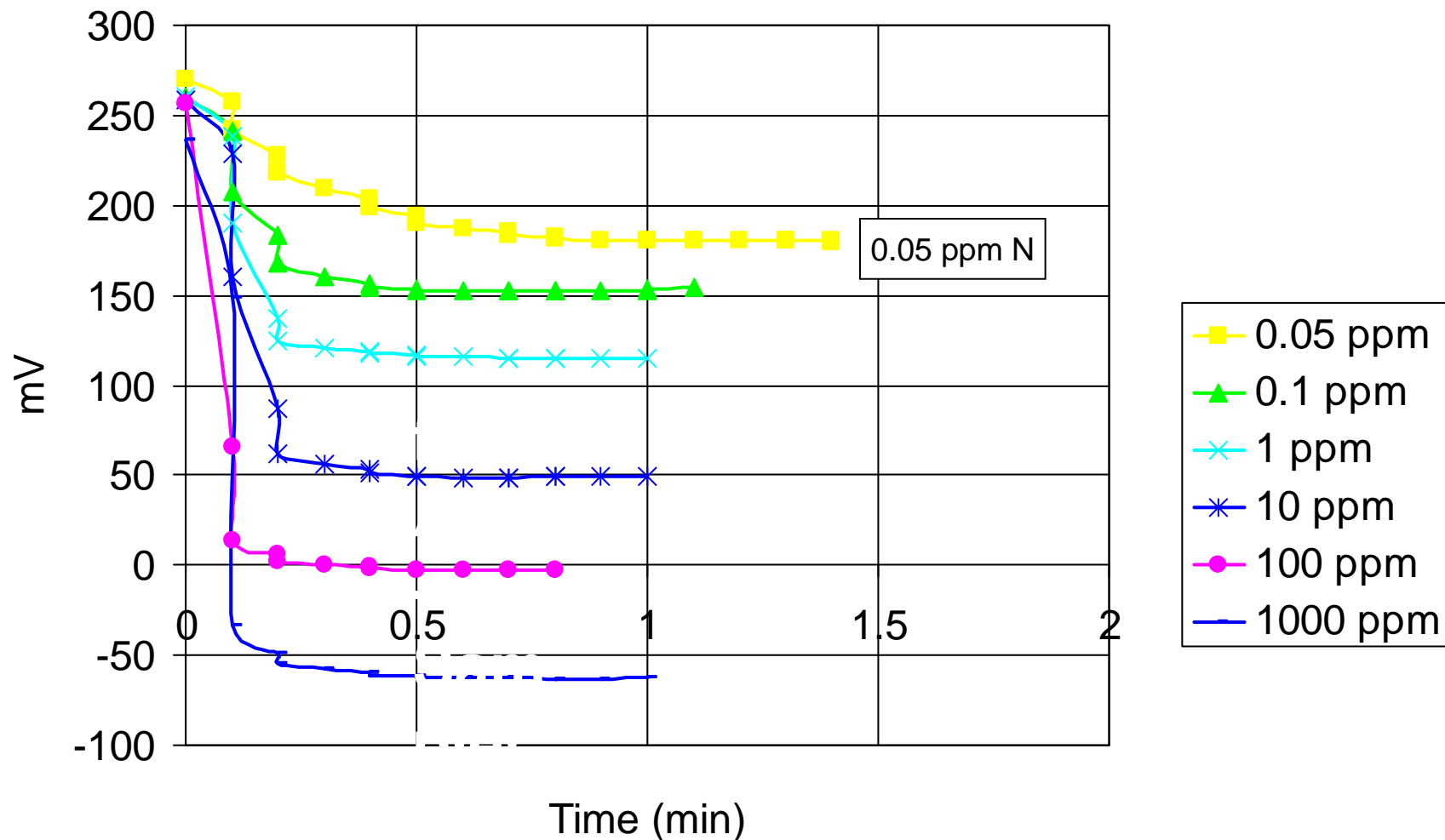
# Improve Performance by Optimizing Fill Solution



# Calibration Curves of New NH<sub>3</sub> Electrode



# Response Time of NH<sub>3</sub> Electrode



# New High Performance Ammonia ISE Hints

- Membranes and fill solution are NOT interchangeable between old and new electrodes!
- Do not stretch new membrane
  - Just smooth over and pull tight
  - Can use outer bodies with assembled membranes
- Fill electrode to just below fill level line
- Condition assembled electrode overnight in electrode fill solution
- Store the electrode in electrode fill solution
- Between measurements use 1 ppm standard with 1 ml alkaline reagent
- Do not use blue ISA (951211) for any calibrations or measurements below 10 ppm!
- Use 1 ml of alkaline reagent (951011) per 100 mls sample or standard
  - Required in low range
  - Can use in any range
- Dip the electrode in beaker of DI water rather than using rinse bottle
- Do not reuse fill solution
- Stir standards and samples vigorously
  - Not to the point of causing bubbles to collect on the membrane

# New High Performance Ammonia ISE Troubleshooting

- Drifting
  - 15 minute condition with 1 ppm standard and alkaline reagent
  - In mV mode after 15 minutes electrode drift should be less than 0.5 mV/min
  - Check for air bubbles trapped underneath electrode membrane
  - Pull on electrode cable to refresh inner fill solution and recalibrate
  - Change membrane or membrane body, use fresh fill solution and condition again
  - Clean inner body with 0.1M HCl for 30 minutes
  - Check inner body performance with buffers
  
- Low Slope
  - Use fresh standards, check expiration dates
  - Add ISA immediately before measuring
  - Stir standards during calibration
  - Follow Drifting recommendations



# Reference Electrodes

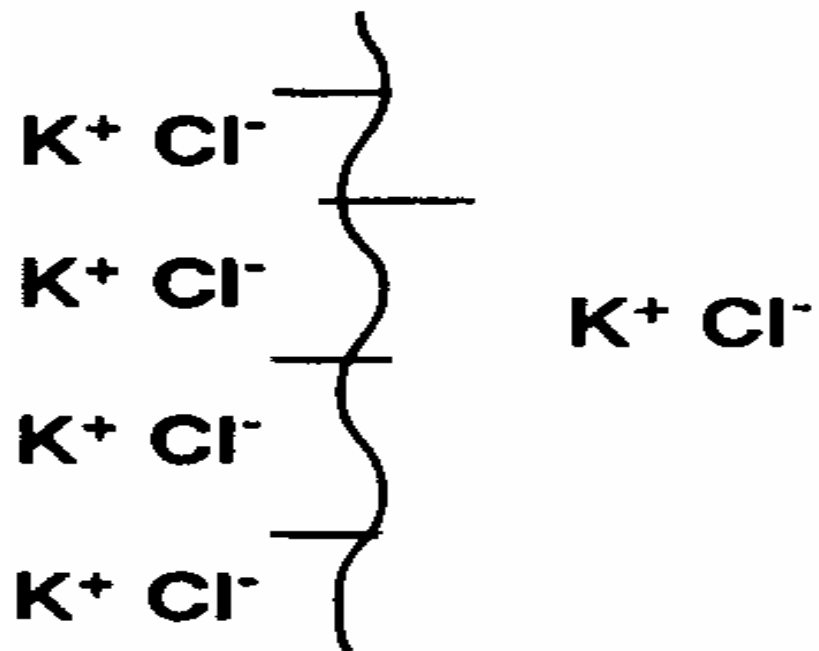
- **Reference electrodes are critical to getting good results**
  - *The reference chosen must match the internal reference in the sensing electrode which is typically Ag/AgCl*
  - *Any change in reading at the reference junction will be interpreted as a change in the sample concentration: liquid junction potential*

# Reference Electrodes

- A reference electrode with a sleeve-type liquid junction is highly recommended
- The filling solution should be:
  - High in ionic strength and equitransferent
  - Nonreactive and noninterfering with sample
    - Don't use KCl solutions for low levels of  $\text{Cl}^-$  or  $\text{K}^+$
    - $\text{Ag}^{++}$  containing solutions will react with sulfides, proteins, etc.

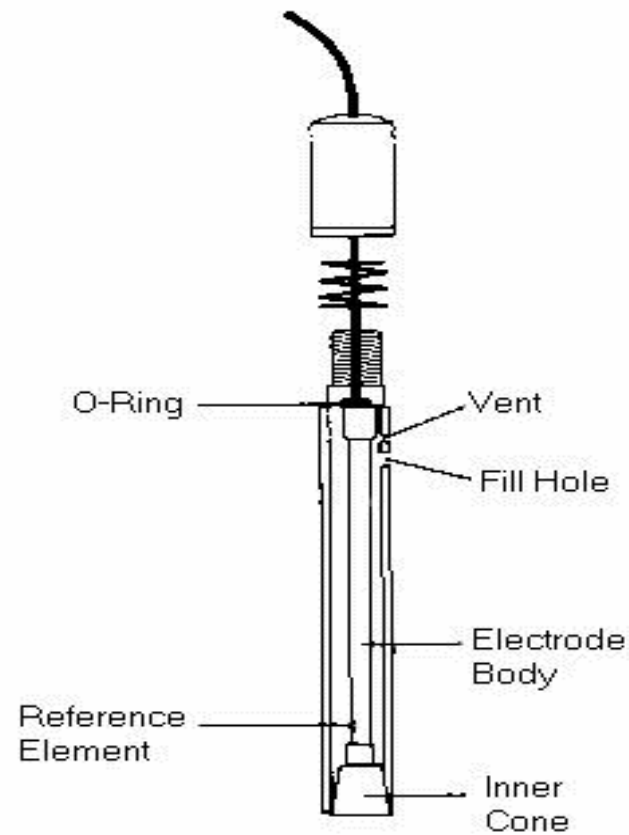
# Liquid Junction Potentials

- There is a “liquid junction” between the solution inside the reference electrode and the sample
- If the positive and negative ions in the fill solution do not diffuse at the same rate, a potential develops



# Single Junction Reference

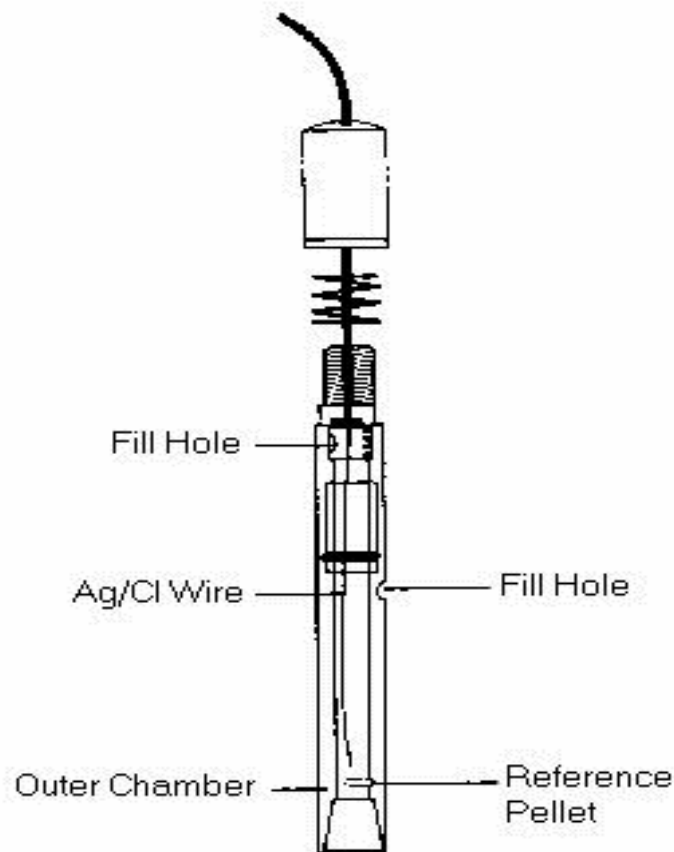
- Ag/AgCl reference
- Sleeve junction
- Equitransferent filling solution saturated with AgCl
- Store in filling solution



Single Junction

# Double Junction Reference

- Ag/AgCl reference
- Sleeve junction
- Equitransferent inner filling solution saturated with AgCl
- 10%  $\text{KNO}_3$  for outer chamber
- Store in filling solution



Double Junction

# How Are ISE's Used?

- **Direct measurement**
- **Incremental methods**
- **Titration**
- **Gran methods**

# Direct Measurement

- Preferred method in most cases:
  - *Many samples with similar backgrounds*
  - *High volume of samples*
  - *Wide range of concentrations*
  - *Easy*

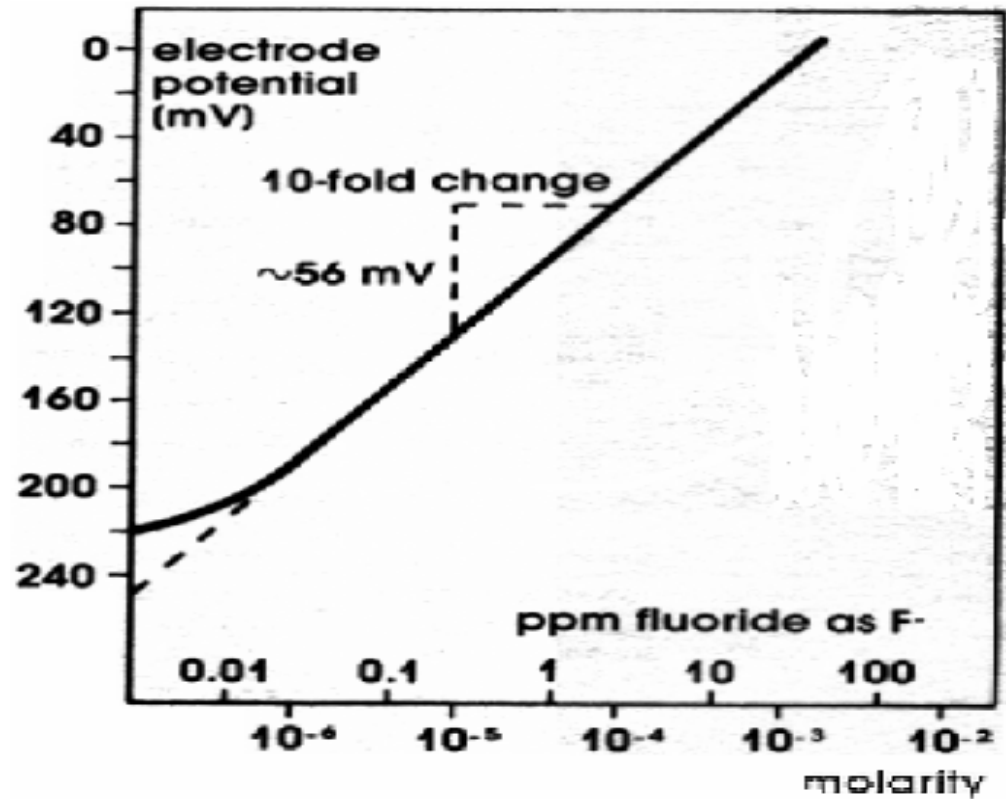
# Direct Measurement

- **Calibrate by comparison with known standards**
- **Read by preparing calibration curve or using ISE meter**
- **Precision is +/- 2%**



# Direct Measurement

- Two-point calibration for linear portion of curve
- Low-level measurements require non-linear multi-point calibration or blank correction



# Direct Measurement

- **Low level measurement considerations:**
  - *Solubility of membrane material*
  - *Absorption*
  - *Contamination*
  - *Presence of interferences*
  - *Time response*

# Direct Measurement

- **Limits of detection**
  - *Use a meter which calculates the blank from the calibration curve*
    - No separate blank has to be run
    - Equivalent to drawing a smooth curve through the lowest three calibration points and extrapolating to zero concentration
  - *Use incremental techniques*

# Direct Measurement

- **Calibrate every 2 hours**
- **Always calibrate with standards that bracket expected concentration range**
- **Always use at least two standards that are ten fold apart in concentration**
- **Slope range for monovalent ions: 54-60 mV**
- **Slope range for divalent ions: 26-30 mV**

# Incremental Methods

- **Known addition**
- **Analate addition**
- **Known subtraction**
- **Analate subtraction**

# Known Addition

- A technique which adds a known amount of the species being measured into the sample
- This incremental method eliminates the need for a separate calibration curve for each sample
- Single, double, or multiple known additions possible
- 2-4 times more accurate than direct read

# Known Addition

- **Known addition is preferred when:**
  - *Number of samples is small*
  - *Backgrounds vary and cannot be fixed*
  - *Working at very low levels*
  - *Excess complexing agent is present*

# Analate Addition

- A variation of standard addition where the sample (analate) is added to the standard
- Typically used with concentrated samples
- Analate addition is used to avoid complications due to pH extremes, viscosity, and complex sample matrices
- Can be used to diminish the effects of varying sample temperatures



# Known Subtraction

- A variation of the known addition method
- An addition of a known amount of standard reacts stoichiometrically with the ion of interest
- Useful technique when there is no direct sensing electrode

# Analate Subtraction

- A variation of the known subtraction technique
- The sample (anilate) is added to a standard which reacts with the ion of interest
- Useful technique when there is no direct sensing electrode

# Titration

- **Quantitative analytical technique for measuring the concentration of a species by incremental addition of a reagent that reacts with the sample species**
- **There must be a reaction with the species of interest which can be followed by an electrode**
- **Increased precision to +/- 0.1%**

# Titration

- Many analyses can be done by reacting a species that cannot be measured with an ion that can be measured directly
  - *Sulfate by titration with lead to give lead sulfate*
  - *Aluminum by titration with fluoride to give aluminum fluoride*
  - *Phosphate by titration with lanthanum in the presence of fluoride*

# Titration

- **Modern instruments are available which control the addition of titrant, use sophisticated algorithms to determine the endpoint(s), and calculate concentration**
- **Certain instruments will predict the endpoint without performing the entire titration**

# Gran Method

- In starting a titration, each step is like a known subtraction: each addition removes part of the ion of interest
- Since the theoretical concentration at the endpoint is zero, extrapolation to zero after just a few additions of titrant gives the endpoint

# Gran Method

- **Multi-incremental technique**
- **Improves precision and accuracy**
- **Useful technique to linearize titration curve to determine weak inflection points**
  - *E.g. low level chloride*
- **Gran is a plot of the antilog of the mV potential vs. concentration**

# Practical Considerations

- **Method interferences**
- **Electrode interferences**
- **Temperature effects**



# Method Interferences

- **Complexing agents may be present**
  - *Fluoride may be complexed by aluminum*
- **pH of sample may be in wrong range**
  - *Ammonia may be present as ammonium ion*
- **Ionic background varies from sample to sample**
  - *Chloride in ground water samples which vary in background*

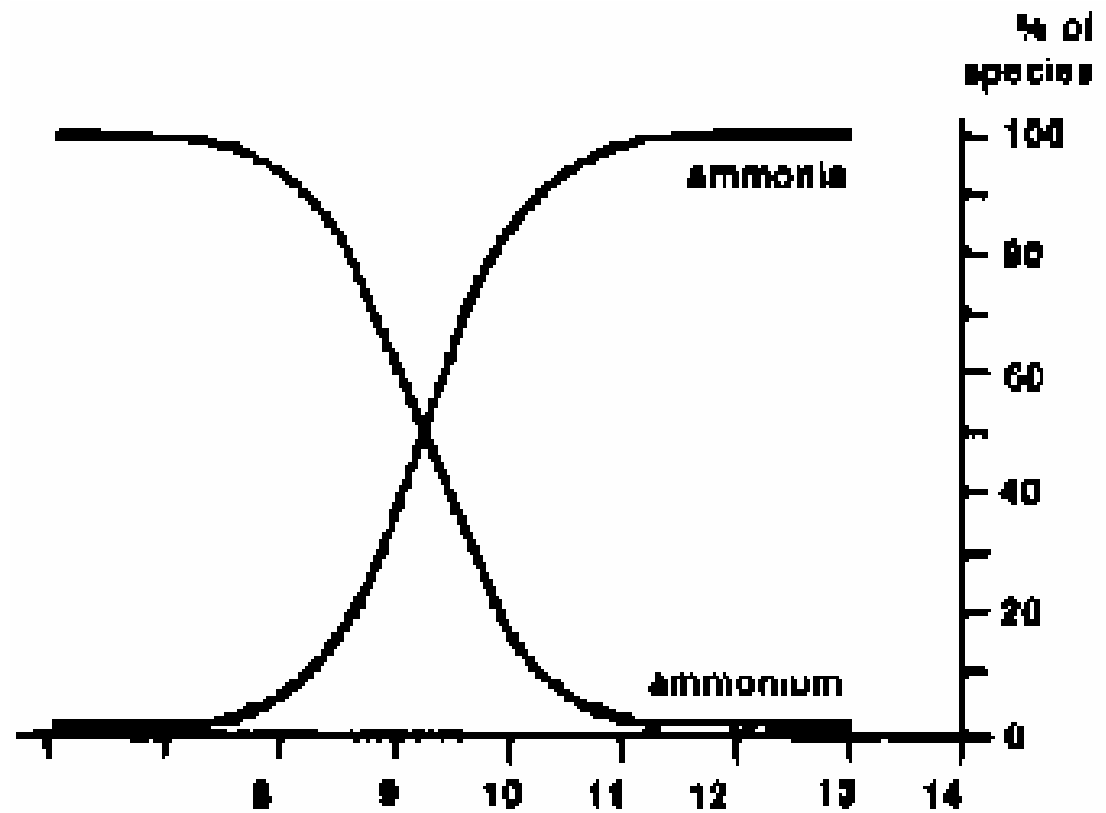
# Method Interferences

- Many method interferences can be overcome by using Ionic Strength Adjusters
- ISA's are added to samples and standards to maintain constant background
- ISA's minimize ionic strength differences
- ISA's can complex interferences
- ISA's can adjust pH to proper range

# Method Interferences

- ISA example

- Ammonia ISA adjusts pH to proper range for conversion to ammonia



# Electrode Interferences

- **There are some species which cause increased electrode response**
- **For some ISE's, there is a maximum allowable ratio**
  - **Example: not more than 400x as much chloride for the bromide electrode**

# Electrode Interferences

- **For some ISE's, interferences introduce a gradual error**
  - Example: at 10 ppm nitrate, a level of 760 ppm chloride will cause a 10% error
- **For some ISE's, interference suppressors are available**
  - Example: Sodium ISA removes H<sup>+</sup> interferences for the sodium electrode

# Temperature Effects

- A change in temperature will cause electrode response to shift and change slope
- On average, a 1 °C change in temperature gives rise to a 2% error for monovalent ISE's
- On average, a 1 °C change in temperature gives rise to a 4% error for divalent ISE's

# Temperature Effects

- **Temperature compensation is possible only if the isopotential point of the electrode is used to adjust the calibration curve**
- **For most situations make sure standards and samples are at the same temperature**

# Troubleshooting Sequence

- **Meter**
- **Standards**
- **Reference electrode**
- **Sensing electrode**
- **Sample**
- **Technique**



# Meter Troubleshooting

- Use meter shorting cap or strap
  - Reading should be 0 +/- 0.2 mV
  - Use meter self-test procedure



# Measurement Variables

- **Concentration range**
- **Ionic strength**
- **Temperature**
- **pH**
- **Stirring**
- **Interferences**
- **Complexation**

# Making Accurate Measurements

- **Maintain a constant reference potential**
- **Adjust ionic strength**
- **Remove method interferences**
- **Remove electrode interferences**
- **Operate at a constant temperature**
- **Stir standards and samples gently**
- **Bracket sample with standards**

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