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# Measurement by Ion Selective Electrodes

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## Why Use Ion Selective Electrodes?

- 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 water or wastewater*
  - *Residual chlorine in water or wastewater*
  - *Chloride in water or wastewater*
  - *Cyanide in water or wastewater*
  - *Fluoride in drinking water*
  - *Nitrate in drinking water or 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*

## What Are ISE's?

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




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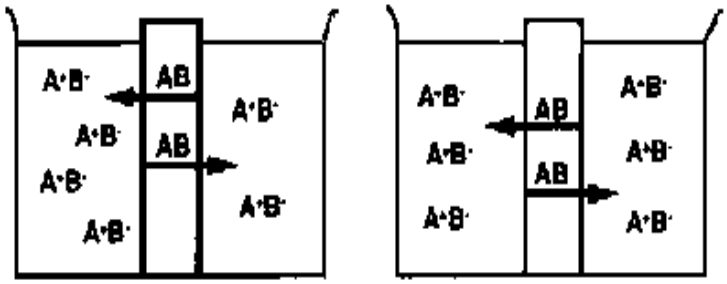
## How Do ISE's Work?

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



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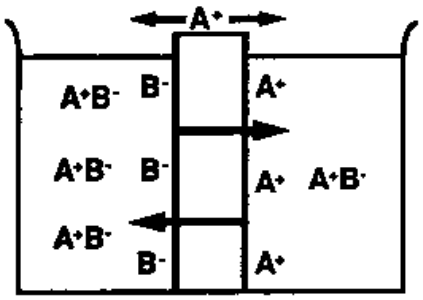
## How Do ISE's Work?

- 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



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## 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



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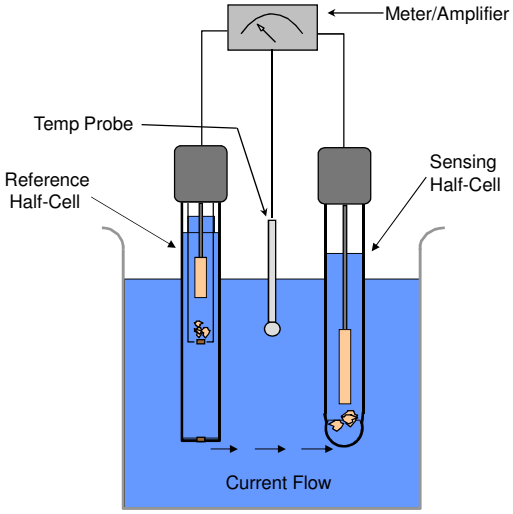
## The Electrode Measurement System

- **The meter measures the voltage potential (mV) difference between the sensing electrode and the reference electrode.**
- **Sensing electrode potential changes with sample concentration.**
- **Reference electrode potential does not change to compare sensing potential to.**



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## ISE Meters

- **ISE meters report concentrations**
  - ***No manual calibration curves are required***
  - ***The potentials of known standards are stored in memory to produce a calibration curve***
  - ***The potential of the sample is then compared to the calibration curve to determine the concentration***
- **ISE meters generate sophisticated curves which are held in the meter's memory**
  - ***Run standards***
  - ***Run unknowns***
  - ***Read results***




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## Types Of Sensing Electrodes

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



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## Glass Membrane Electrodes

- pH
- Sodium




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## Glass Membrane Electrodes

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




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## Types Of Sensing Electrodes

- **Solid State**




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## Solid State Electrodes

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



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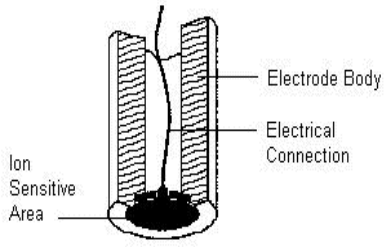
## Solid State Electrodes

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



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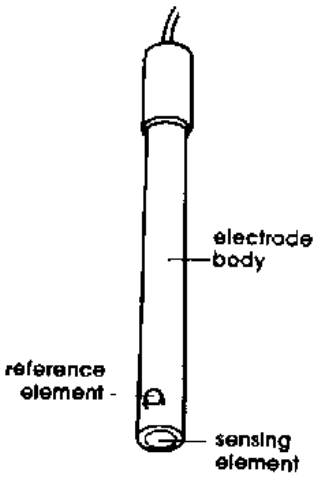
## Solid State Electrodes

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



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## Types Of Sensing Electrodes

- **Liquid Membrane**




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## Liquid Membrane Electrodes

- Ammonium
- Calcium
- Chloride
- Fluoroborate
- Nitrate
- Perchlorate
- pH
- Potassium
- Surfactant



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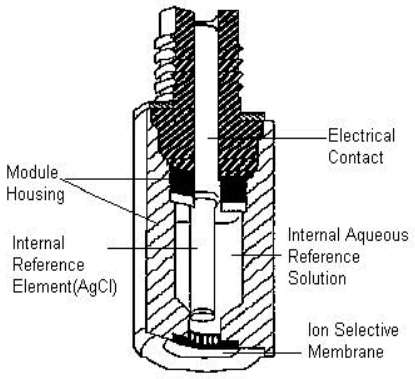
## Liquid Membrane Electrodes

- 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



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## Liquid Membrane Electrodes

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




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## Gas Sensing Electrodes

- **Ammonia**
- **Carbon dioxide**
- **Nitrogen dioxide**
- **Oxygen**




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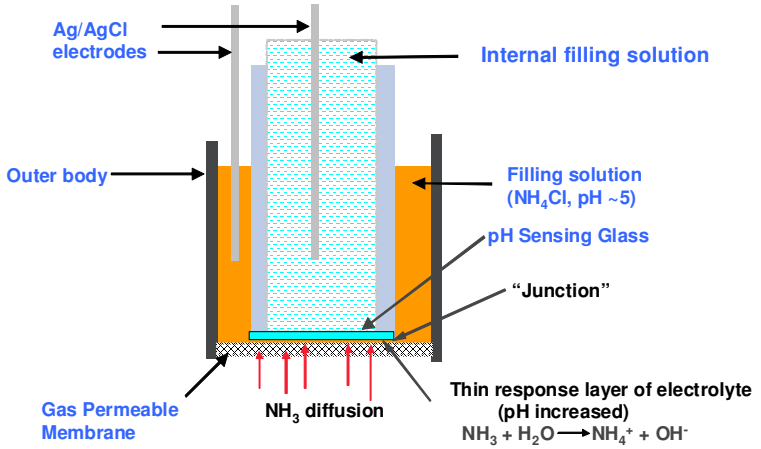
## Gas Sensing Electrodes: Ammonia

- **Gas sensing electrodes work by measuring the pH change caused by diffusion of the gas through a hydrophobic but porous membrane**



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## Ammonia ISE Measurement

- Measure from 0.01 ppm to 17,000 ppm ammonia
  - Also use for ammonium and organic nitrogen
- Must adjust sample pH
- pH electrode – Measures change in pH across the membrane
- EPA approved method for waste water
- Must pay attention to manufacturer's instructions



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## Ammonia Electrode Setup

Glass sensing surface protruded relatively to the outer body
*(view without gas membrane)*

Membrane on outer body without the inner sensing stem
*(retaining cap not shown)*

Membrane on outer body with the inner sensing stem protruded
*(retaining cap not shown)*



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## Ammonia Tips

- Tilt the electrode in sample or standard
- Rinse probe by immersion
  - More effective than squirting with rinse bottle
  - Does not disturb layer of inner fill solution between membrane and inner stem
- Conditioning electrode.
  - Exposure to ammonia prior to calibration/use greatly improves performance
  - 15 minutes in 1mg/L standard (with ISA) greatly improves performance



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## Ammonia Tips

- **Electrode Assembly –** Get rid of air bubbles by tapping on electrode body. Pull gently on cable or move sensor up and down
- **Rinsing Electrode –** Rinse generously between measurements, blot dry. Immerse rather than squirt.
- **Position Electrode at Slant** – This will make easier to view and dislodge bubbles
- **Inspect Membrane Surface** – Remove any bubbles from surface of membrane by wiggling or tapping electrode
- **Electrode Storage** – If storing the electrode overnight or up to 1 week, store in the electrode fill solution
- **Stirring** – Stir vigorously but avoid creating bubbles



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## Classic 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




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## Classic Ammonia ISE Storage

- 9512BNWP Only
- 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



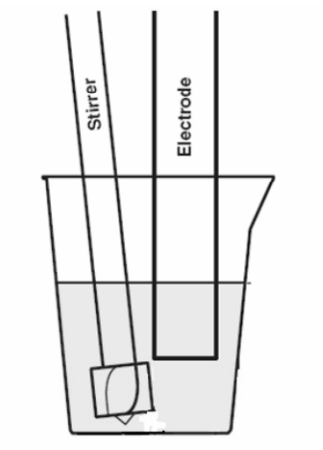


## High Performance Ammonia ISE Hints

- 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 or storage solution (951213)
- Between measurements use 1 ppm standard with 1 ml alkaline reagent
- Use Low Level Ammonia ISA (951210). Do not use standard ISA (951211) for any calibrations or measurements below 10 ppm
- Or use 1 ml of alkaline reagent (951011) per 100 mls sample or standard
- Do not reuse fill solution

## Ammonia Trouble Shooting Tips

- Make sure you have fresh standards and are using the correct amount of ISA
- Verify the electrode been conditioned
- Check slope and drift of electrode
- If you have a poor slope or drift, change the membrane and fill solution. Recheck slope and drift
- Check electrode inner body. Gently handle inner body
- Stir vigorously but without creating bubbles



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## How Are ISE's Used?

- **Direct measurement**
- **Incremental methods**
- **Titrations**
- **Gran methods**



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## Direct Measurement

- Preferred method in most cases:
  - *Many samples with similar backgrounds*
  - *High volume of samples*
  - *Wide range of concentrations*
  - *Easy*
- Calibrate by comparison with known standards
- Read by preparing calibration curve or using ISE meter
- Precision is +/- 2%



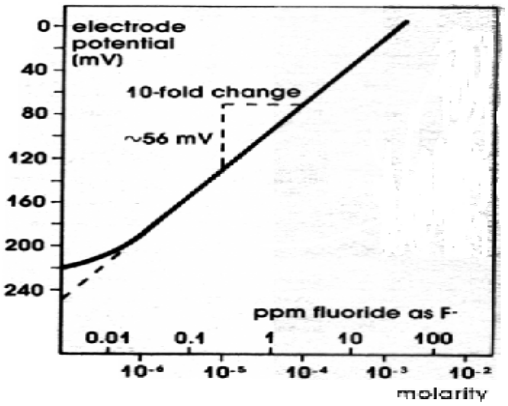


## Direct Measurement

- 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

## Direct Measurement

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



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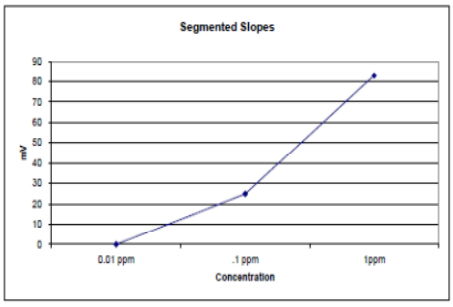
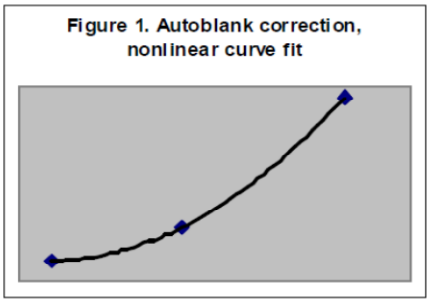
## How Meters Calibrate Slope

- Slope Segmented
  - Point-to-point calibration
- Auto-Blank for Low Levels
  - Smooth curve through points



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## Incremental Methods

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



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## 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



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## 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***



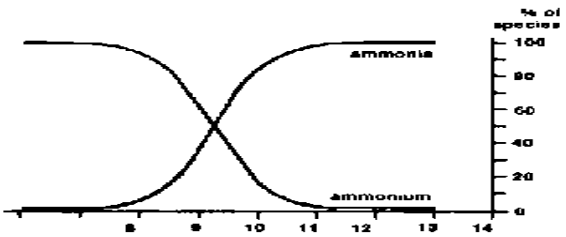


## Practical Considerations

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

## 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
  - Example Fluoride may be complexed by aluminum
- ISA's can adjust pH to proper range



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## 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

| Temp (°C) | Slope (mV) |
|---|---|
| 0 | 54.2 |
| 10 | 56.2 |
| 20 | 58.2 |
| 25 | 59.2 |
| 30 | 60.2 |
| 35 | 61.2 |
| 40 | 62.1 |
| 50 | 64.1 |



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## 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

## Troubleshooting pH Problems

- Troubleshooting ISE Meters
  - Use meter shorting strap
  - Reading should be 0 mV +/- 0.2 mV
  - Use meter self-test procedure
- Troubleshooting Standards
  - Use Fresh Standards for calibration
  - Verify expiration date
  - Verify when standard was opened
  - Stir standards during calibration



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## 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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- Contact us for any technical questions
- Technical Service: (800) 225-1480
- Web site: www.thermoscientific.com/water





## Q&A