Wastewater Laboratory Fundamentals

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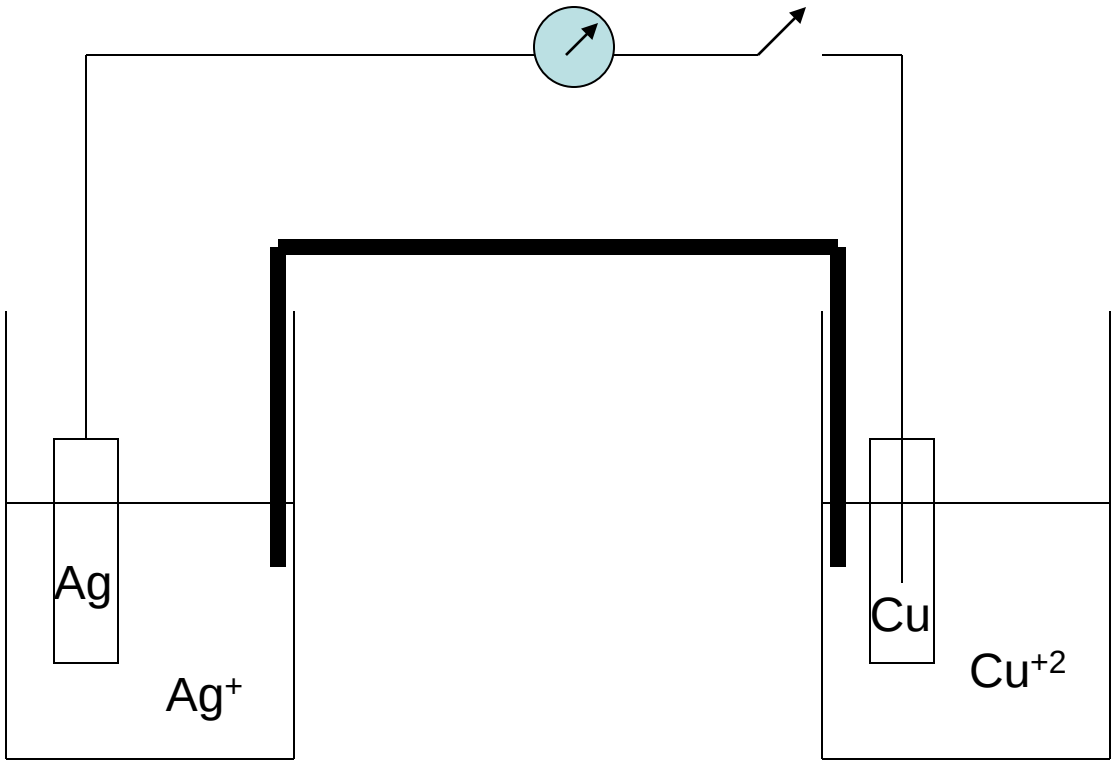
Ion Selective Electrodes

- Fundamentals of electrode chemistry
- Applications
  - pH
  - Ammonia
  - Dissolved Oxygen
- Dissolved Oxygen
  - Azide modification of the Winkler method

Electron transfer



Electrons flow from Cu to Ag

$$Cu + Ag^{+} \leftrightarrow Ag + Cu^{+2}$$

- Oxidation: $Cu \rightarrow Cu^{+2} + 2e^{-}$
- Reduction: $Ag^{+} + 1e^{-} \rightarrow Ag$

Potential for Oxidation/Reduction?

- Standard electrode potentials
  - Reduction potentials
  - Potentials relative to reduction of hydrogen to form hydrogen gas = 0 volts
  - Chemicals desiring electrons want to be reduced – positive potentials
  - Chemicals wanting to give up electrons want to be oxidized – negative potentials
  - $Ag^{+} + 1e^{-} \rightarrow Ag$ +0.80 volts
  - $Cu^{+2} + 2e^{-} \rightarrow Cu$ +0.34 volts

Calculating potential

$$Cu + Ag^{+} \leftrightarrow Ag + Cu^{+2}$$

- Oxidation: $Cu \rightarrow Cu^{+2} + 2e^{-}$
- Reduction: $Ag^{+} + 1e^{-} \rightarrow Ag$

- $Cu \rightarrow Cu^{+2} + 2e^{-}$ $E^{0} = -0.34$ volts
- $2(Ag^{+} + 1e^{-} \rightarrow Ag)$ $E^{0} = +0.80$ volts
- Total potential = +0.46 volts

Nearnst Equation

$$E_{cell} = E_{cell}^{0} - \frac{0.059}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

- $aA + bB \rightarrow cC + dD$
- Enables corrections for environmental conditions (concentrations of chemicals, temperature, etc.)

Applications to ISE

- To measure voltage, need “ground” – a constant reference point
- Use a reference electrode to provide constant reference voltage
- Standard calomel
  - $Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$
  - $E = E^0 – (0.059/2)\log[Cl^-]^2$
  - $E = E^0 – 0.059 \log[Cl^-]$
  - Potential is a function of chloride concentration

Ion Selective Electrode Basics

- Electrode typically contains a sensing element and a reference element
- A millivolt (potential) reading is developed by the sensing electrode in response to concentration of the analyte
- The reference element provides a constant potential against which the sensing element is compared.
- In combination electrodes, the sensing element and the reference element are contained in one electrode.
- Calibration creates a relationship between mV and concentration, and is done with known concentration solutions (standards)

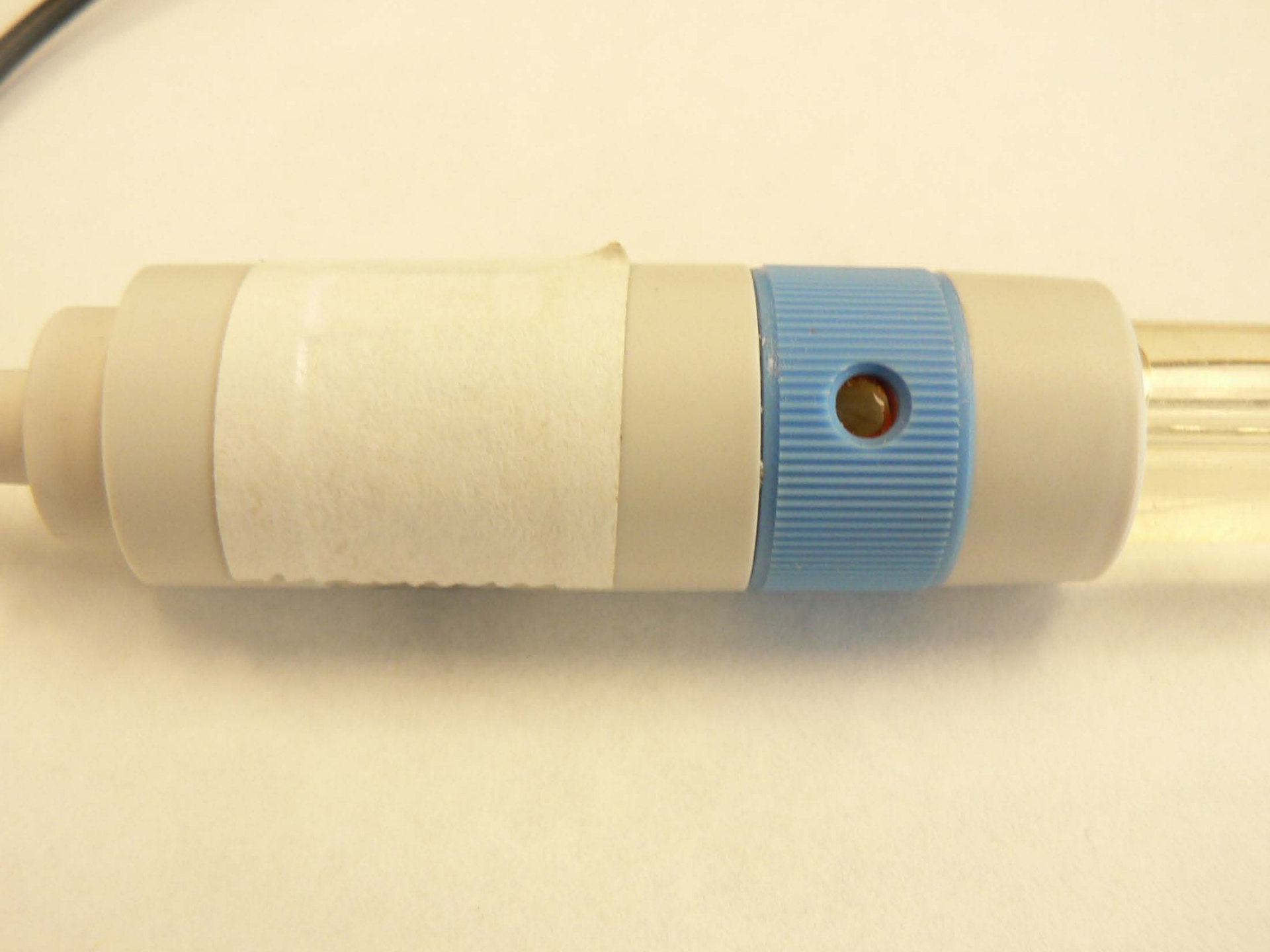
Example electrode systems

- pH
- Ammonia
- Dissolved Oxygen

pH measurement

- standard procedure is to use pH electrode attached to a meter
- glass electrode filled with a constant pH solution
- mV potential develops across the glass ball at the electrode tip due to difference between the inner hydrogen concentration and the solution hydrogen concentration
- glass electrode potential is measured against a reference electrode of constant potential

close
open



0-287

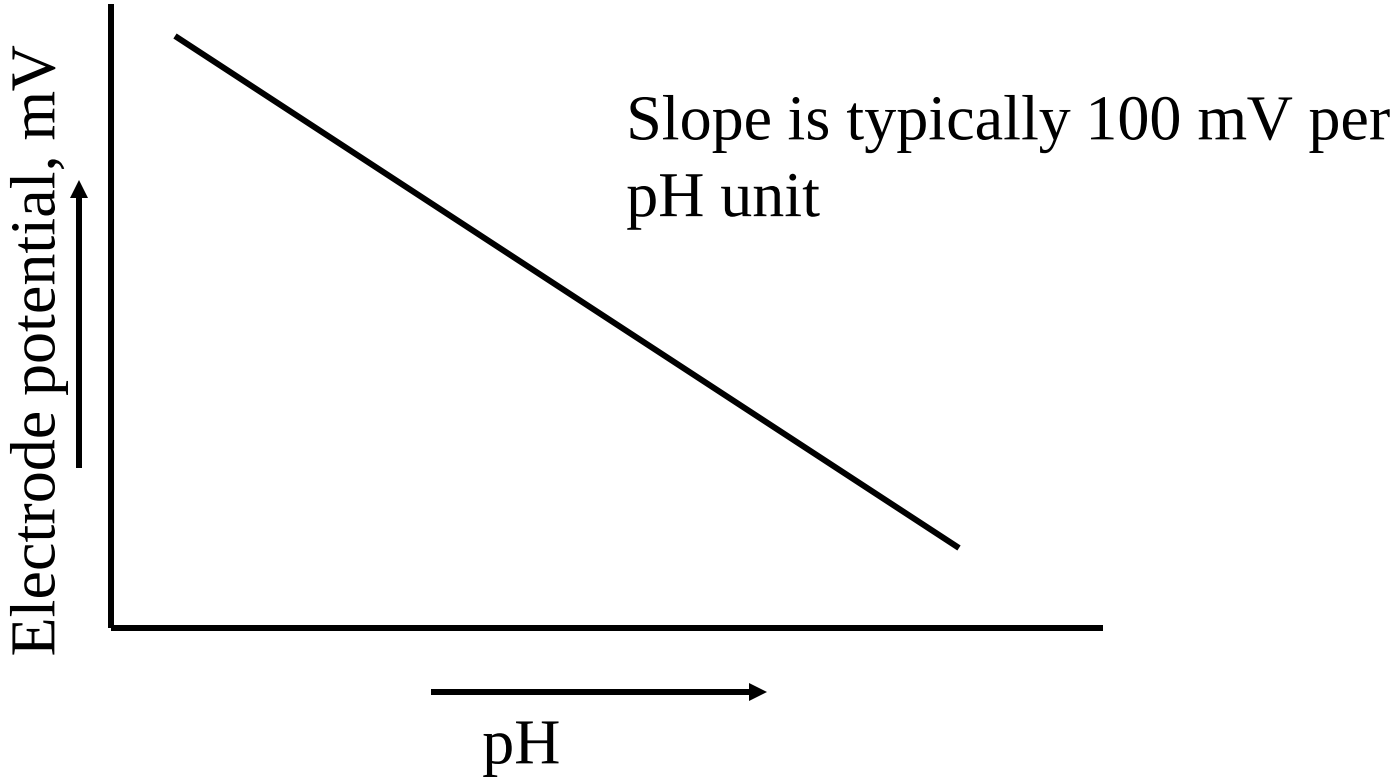
Nearnst Eqn - pH

$$E = E^0 - 0.059 \log \frac{[H^+]external}{[H^+]internal}$$

- Since internal hydrogen ion conc. is constant, can be incorporated into E^0
- $E = E^* - 0.059 \log[H^+]external$
- Since $pH = -\log[H^+]$
- $E = E^* - 0.059\ pH$

Electrode/meter use

- Standards set the slope and intercept of the electrode response to hydrogen ion concentration



pH meter/electrode use

- Standardize at same temperature as sample
  - ATC can help
- ceramic junction electrodes must be stored in a solution - if the junction dries out, the electrolyte flow slows, and the response is slower
- accumulation of solids on the glass tip slows down the response
- rinse with DI water between solutions - pH of weakly buffered samples (low alkalinity) will be changed by small amounts of standardization solutions

pH results

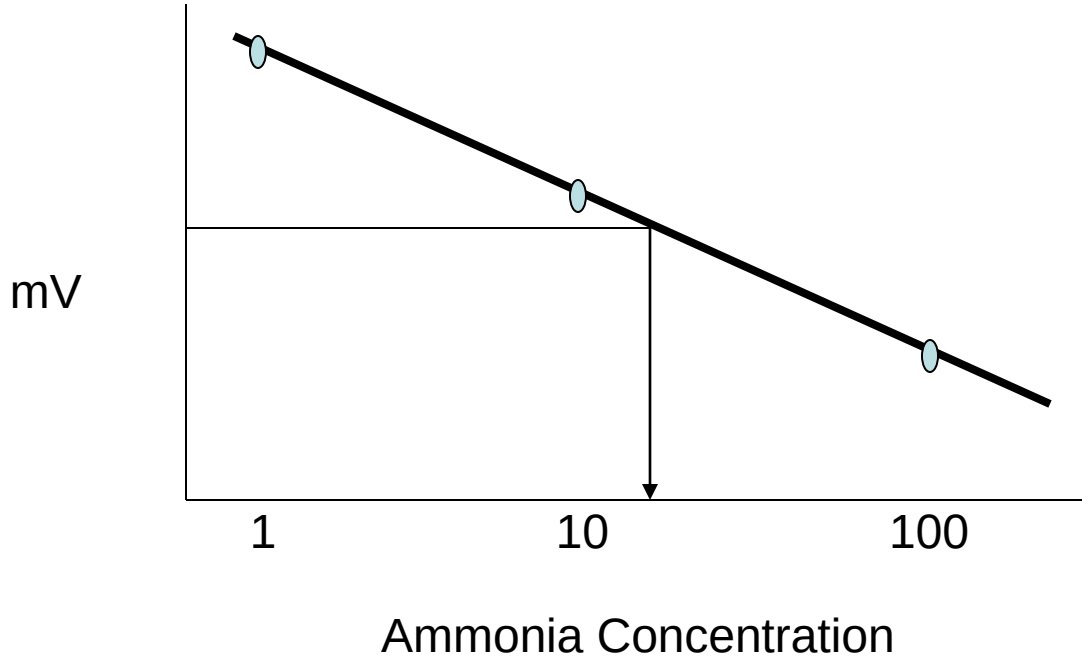
- Expressed as pH units
- Since these are log numbers, they CANNOT be averaged with a typical averaging calculation
- Also, you cannot calculated a weighted average pH when mixing two waters having differing alkalinities

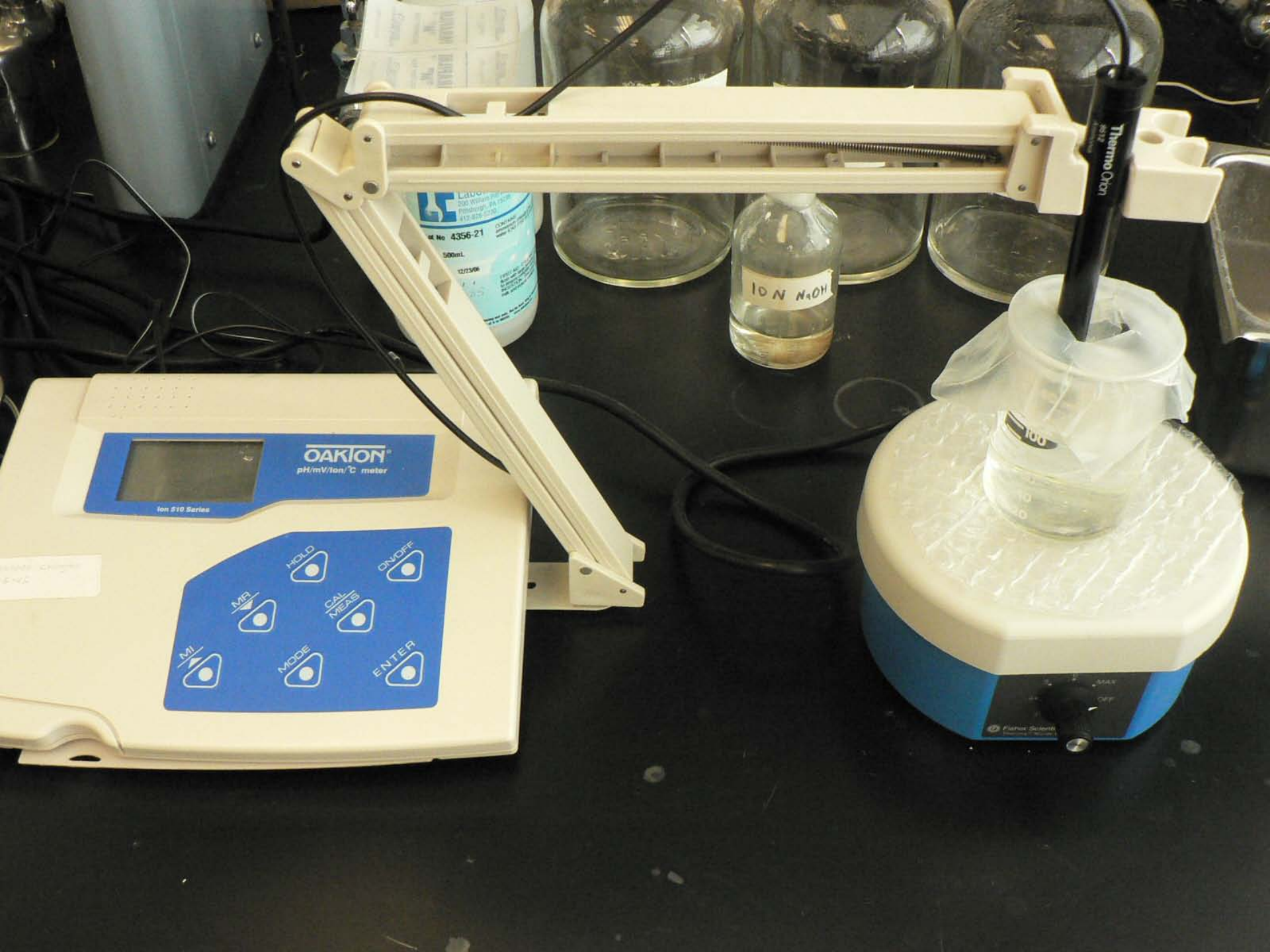
Ammonia

- Importance ?
- Typical Concentrations?
- Analytical Procedures
  - Ion Selective Electrode (compliance monitoring)
  - Colorimetric method (using Nessler’s method) operations and control

Ion Selective Electrode

- gas permeable membrane – ammonia gas moves into the electrode and creates a mV reading as it interacts with chemistry inside the electrode




OAKTON
pH/mV/Ion/°C meter
Ion 510 Series
HOLD
ON/OFF
MR
CAL MEAS
MI
MODE
ENTER
10 N NaOH
Thermo Orion
Fisher Scientific

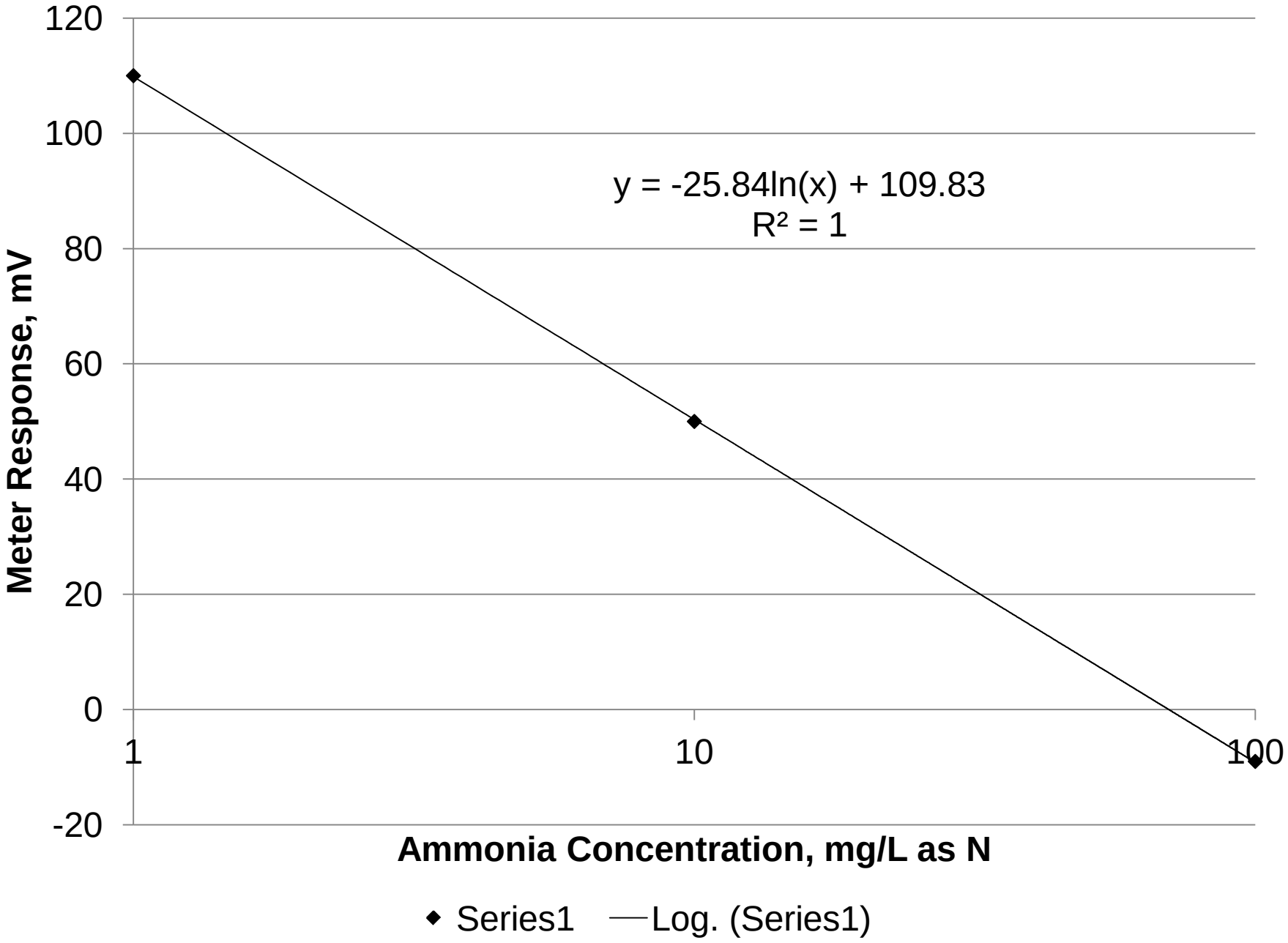
Theory of Operation

- Ammonia diffuses through membrane
- $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
- Constant = $\frac{[NH_4^+]\,[OH^-]}{[NH_3]}$
- Internal solution – high conc of ammonium chloride: $[OH^-] = [NH_3] \cdot \text{constant}$
- Electrode responds to changes in OH^- which is directly proportional to NH_3
- $E = E_o - S \log [NH_3]$

Procedure

- prepare electrode (stabilize reading)
- 100 ml of sample/standard placed in beaker
- pH raised with 10 N NaOH (1 mL)
  - $NH_4^+ \leftrightarrow NH_3 + H^+$
- record reading after reading is stable

- Same procedure for standards and samples
- develop standard curve and interpolate sample results using standard curve


120
100
80
60
40
20
0
-20
Meter Response, mV
y = -25.84ln(x) + 109.83
R² = 1
1
10
100
Ammonia Concentration, mg/L as N
Series1
Log. (Series1)

Dissolved Oxygen

- Essential to aerobic resipiration
  - Need for aquatic life in receiving streams
  - Used as an electron acceptor in biological wastewater treatment facilities
- Used in the BOD test
- Solubility is a function of TDS and Temperature
  - ↑ temperature, ↓ DO saturation
  - ↑ TDS, ↓ DO saturation
- Analysis
  - Winkler (wet chemistry)
  - ISE

Measuring DO with ISE

- Electrode/meter
  - Gas-sensing electrode
  - Water sample is collected in a DO bottle
  - Calibrated electrode is submerged in the bottle – stirrer insures flow past the electrode surface
- Calibrate with Azide Modification of the Winkler Method

DISSOLVED OXYGEN METER
YSI
5100
MODE
ENTER

Dissolved Oxygen Procedure

- Azide Modification of Winkler Method

1. Manganese sulfate and alkali iodide azide added to sample

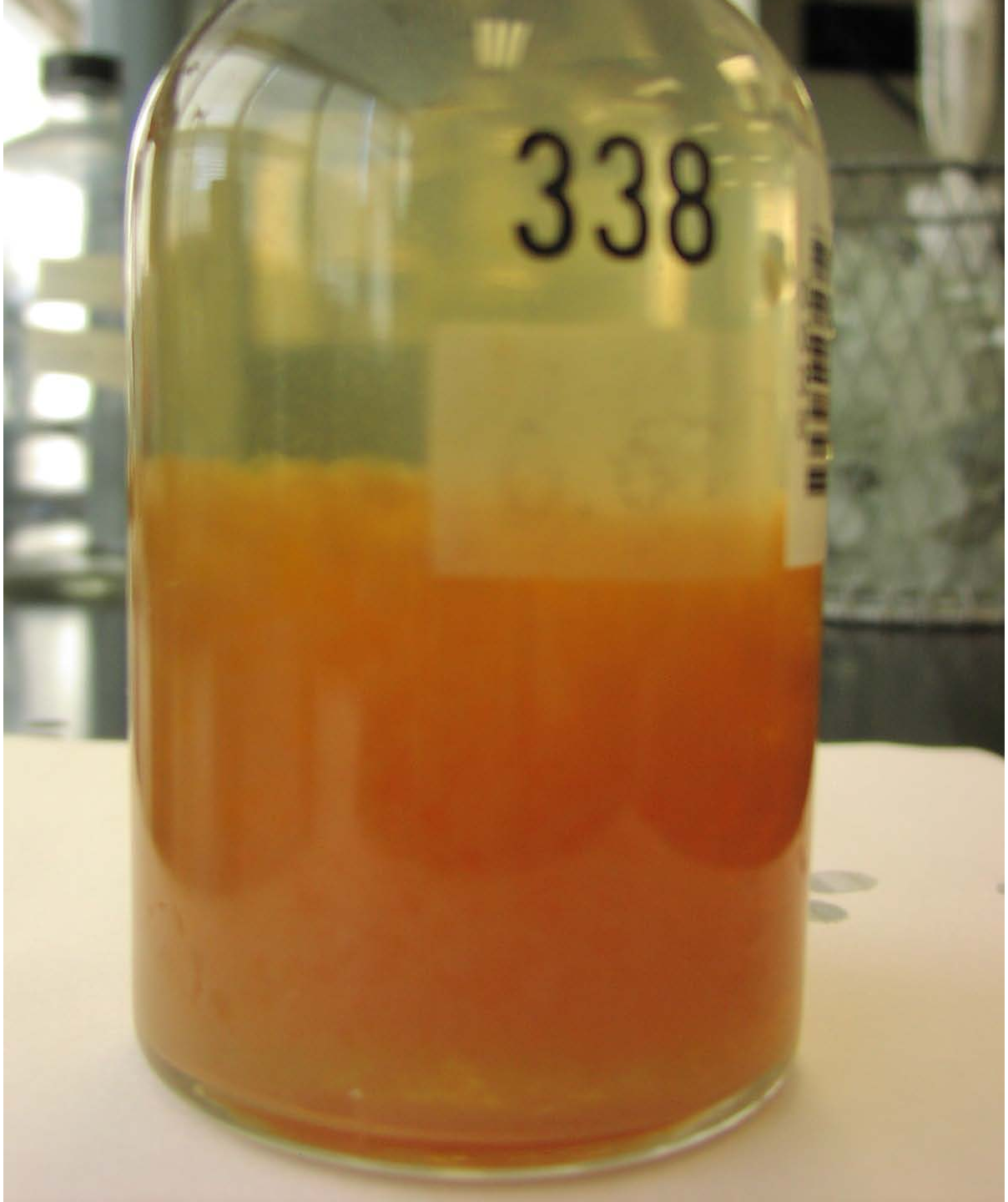
- No Oxygen

$Mn^{+2} + 2OH^{-} \rightarrow Mn(OH)_2\downarrow$ (white precip)

- Oxygen Present

$Mn^{+2} + 2OH^{-} + 0.5O_2 \rightarrow MnO_2\downarrow + H_2O$

(red/brown precipitate)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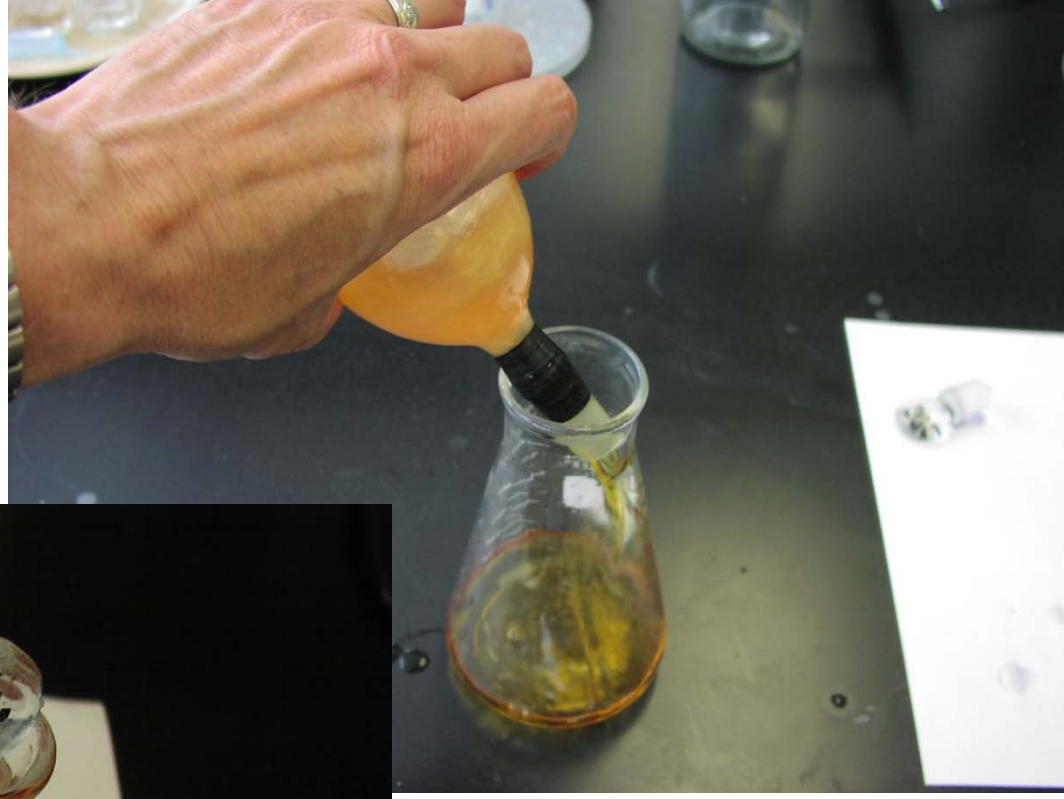
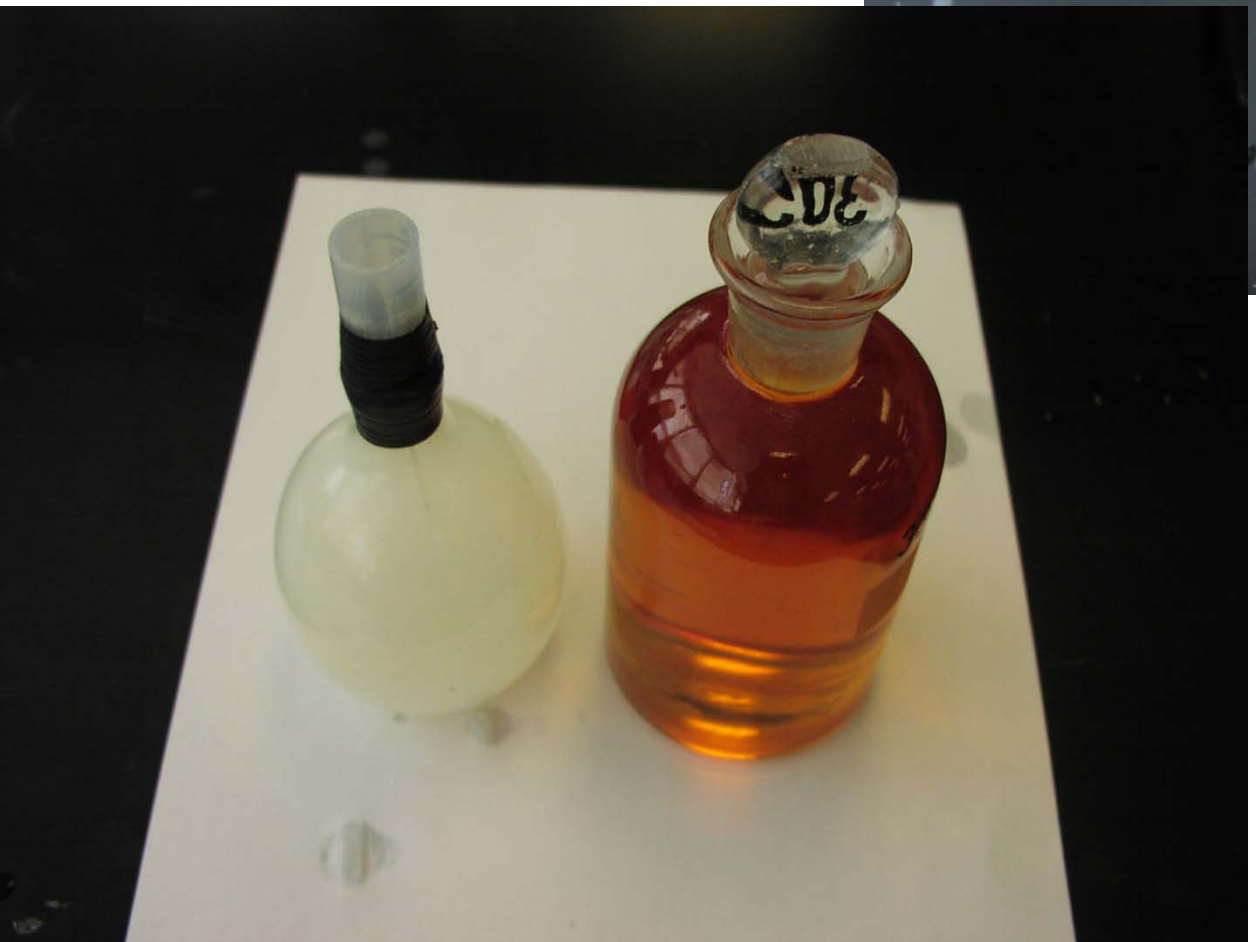
Dissolved Oxygen (winkler method)

2. Brown precip allowed to settle until an inch of clear liquid is present – then add concentrated sulfuric acid

$$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{+2} + I_2 + 2H_2O$$

- allow precipitate to totally dissolve oxidized iodide to iodine, leaving a yellow-brown color



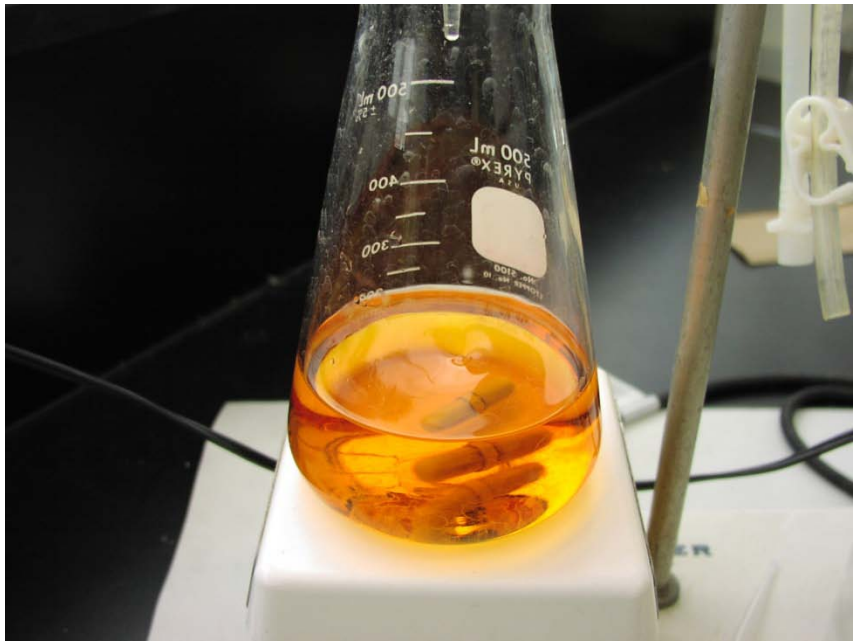


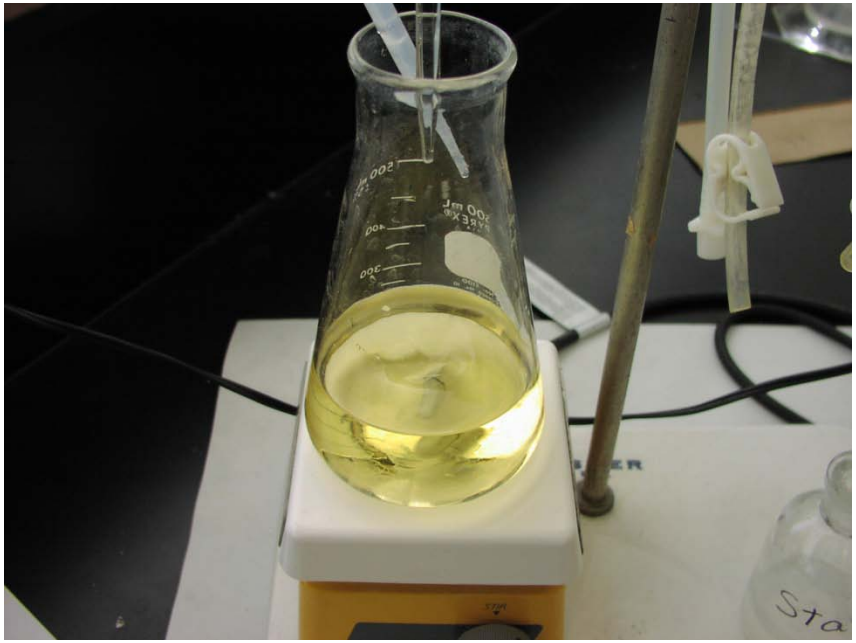
Dissolved Oxygen (winkler method)

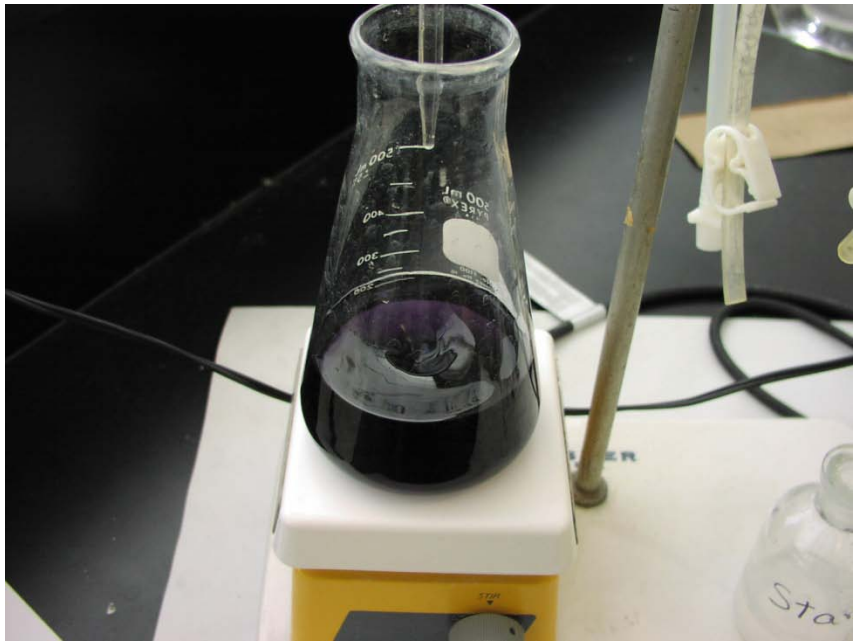
3. Titrate sample with 0.025 N sodium thiosulfate

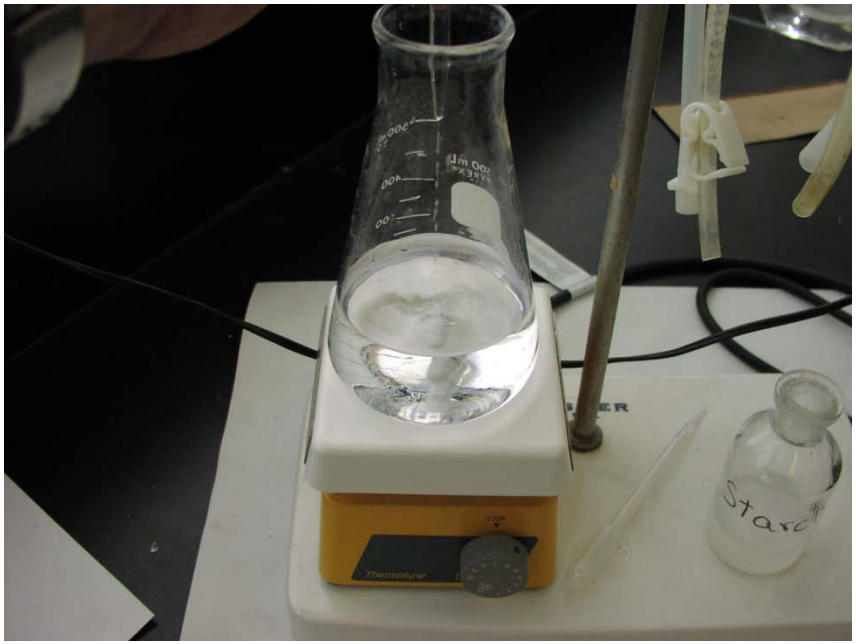
$$2Na_2S_2O_3 \bullet 5H_2O + I_2 \rightarrow Na_2S_4O_6 + 2NaI + 10H_2O$$

iodine is reduced to iodide, turning solution clear – starch used to clarify endpoint – (blue to clear endpoint)


500 ml
PYREX







Dissolved Oxygen (winkler method)

- nitrite oxidizes iodide to iodine which causes a reappearing endpoint

$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$

$N_2O_2 + 0.5O_2 + 2H_2O \rightarrow 2NO_2^- + 2H^+$

- azide breaks the interference

$NaN_3 + H^+ \rightarrow HN_3 + Na^+$

$HN_3 + NO_2^- \rightarrow N_2 + N_2O + H_2O$

(this is the azide modification)

Volumetric Analyses

- Titrant (standard solution of known strength)
- Instrument to measure titrant accurately (buret, digital titrator)
- Endpoint Indicator (solution, dry, meter)
- Pipette to measure sample accurately

measure required volume of sample, add indicator, titrate to endpoint - noting initial and final titrant readings, calculate result

Volumetric Analyses

- Use a solution of known concentration that reacts with the analyte (substance you are measuring) on an equivalent basis - one equivalent of the titrant reacts with one equivalent of the analyte
- $C_{titrant}\ V_{titrant} = C_{sample}\ V_{sample}$
- $C_{sample} = C_{titrant} \times V_{titrant} / V_{sample}$
- $mg/L = \dfrac{ml_{titrant} \times Normality_{titrant} \times Eq\ Wt_{analyte} \times 1000}{ml_{sample}}$

$$mg/L_{\text{ as } CaCO_3} = \frac{ml \times 0.025\ eq/L \times 8\ g/eq \times 1000\ mg/g}{200\ ml}$$