

Instrumental Methods

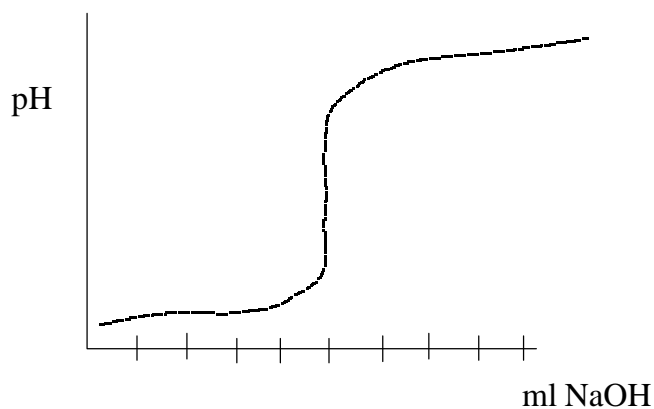
I. Overview

- A. Potentiometry
- B. Spectroscopy
- C. Fluorescence
- D. Flame Emission
- E. Atomic Absorption
- F. Polarography

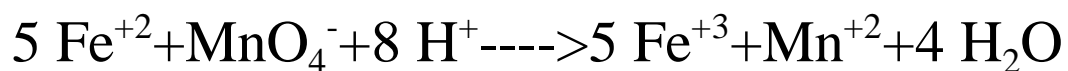
II. Potentiometric Methods

- A. Use of a potential to detect the endpoint of a reaction (Indirect Potentiometry)

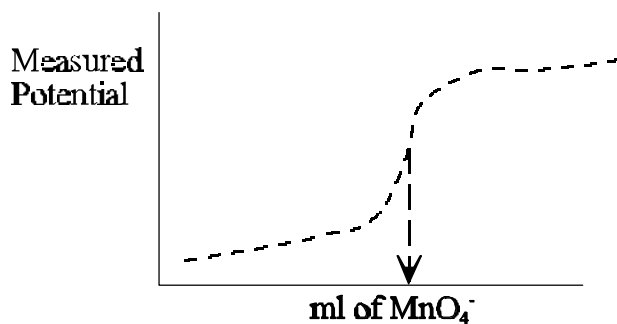
1. Glass electrode vs SCE (pH meter)



2. Platinum electrode vs SCE to measure potential as a function of ml of titrant (Indirect Potentiometry)



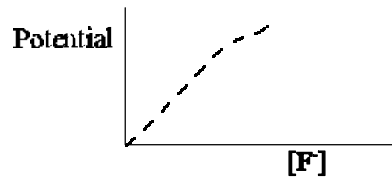
10.00 ml of Fe^{+2} $[\text{Fe}] = ??$



B. Use of the potential to determine the concentration of ions (Ion selective electrodes + potentiometer) - Direct

1. Fluoride, F^- , sensitive electrode

a. Set up a standard curve



b. Relate potential of unknown to $[F^-]$

2. Ca^{+2} sensitive electrode

3. Problems of ion selective electrodes

- a. Electrodes are not specific
- b. Electrode response may not be linear over a large concentration range
- c. pH may be involved in electrode response

III. Spectroscopy

A. Visible & Ultraviolet

1. Visible spectroscopy used if

a.

b.

2. UV spectroscopy used if

a.

b.

3. Beer's Law

$$A_{\text{max}} = a_{\text{max}} \cdot b \cdot c$$

B. Other types of spectroscopy

1. Infrared spectroscopy - IR

a. What it measures

b. Why it is useful for Quantitative

c. Uses of IR

2. Nuclear magnetic resonance spectroscopy-NMR

a. What it measures

b. What it is used for analytically-

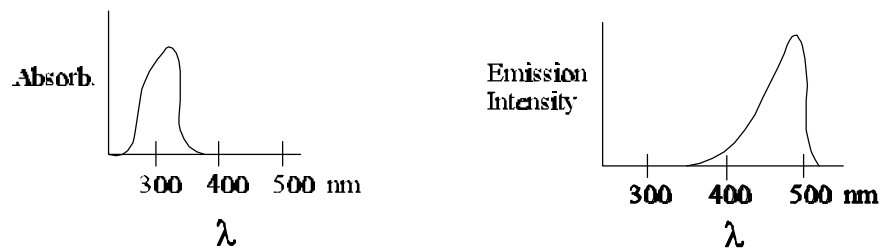
c. Function of NMR

IV. Fluorescence

A. The phenomenon

1. Some molecules will absorb light of one λ and will emit light of a higher λ (lower energy)
2. Fluorescence- if the emission is instantaneous

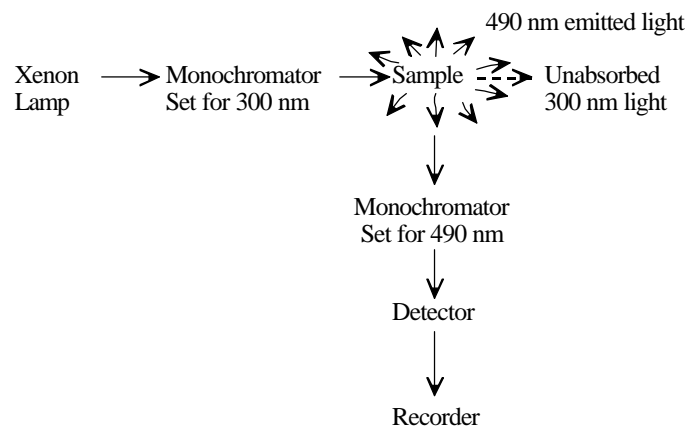
3.



- a. Absorbs light at 300 nm - UV light
Emits light at 490 nm - Visible light

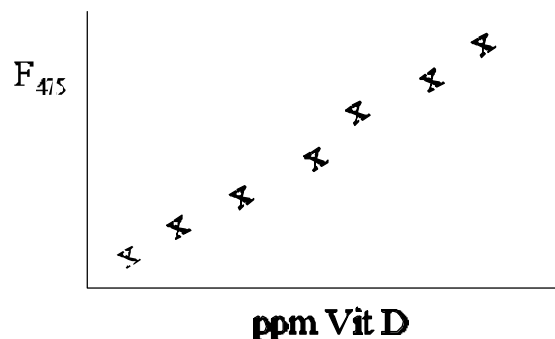
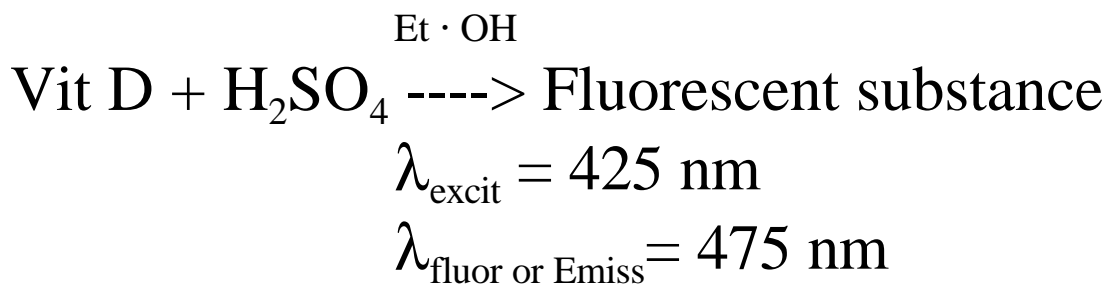
- b. If we irradiate with UV light at 300 nm & measure the intensity of light emitted at 490 nm
- We will measure fluorescence

4. Instrument Design



5. Analysis

- a. For a system where all factors are held constant, one may construct a calibration curve (standard curve) if you have:
 1. Fluorescent substance
 2. Substance that will react \rightarrow Fluorescent substance
- b. Eg

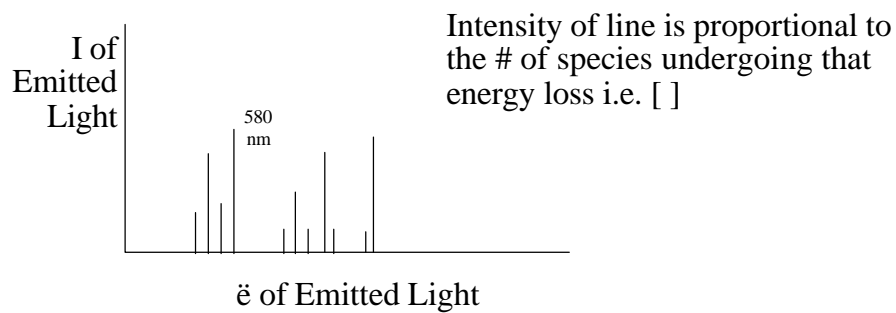


V. Flame Emission Spectroscopy

A. Sample placed in flame

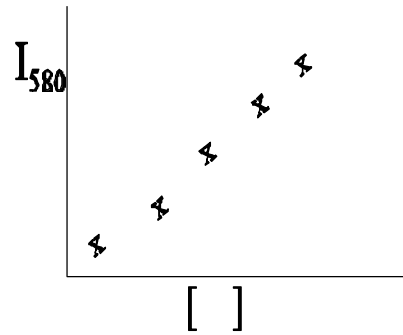
1. H₂O evaporated
2. Sample is converted to
 - a. Atoms
 - b. Excited atoms- electrons raised to higher energy levels
 - c. Ions-electrons have been lost by over- excitation
 - d. Excited Ions - some of the remaining electrons have been raised to higher energy levels
3. Excited atoms & ions- Electrons will return to their “ground level” - lower energy level
 - a. Energy released in the form of light
 - b. ϵ of light depends on amount of energy lost
low energy = long λ
high energy = short λ

- c. Measure intensity of emitted light as a function of the wavelength of the emitted light- Get **Emission Spectrum**



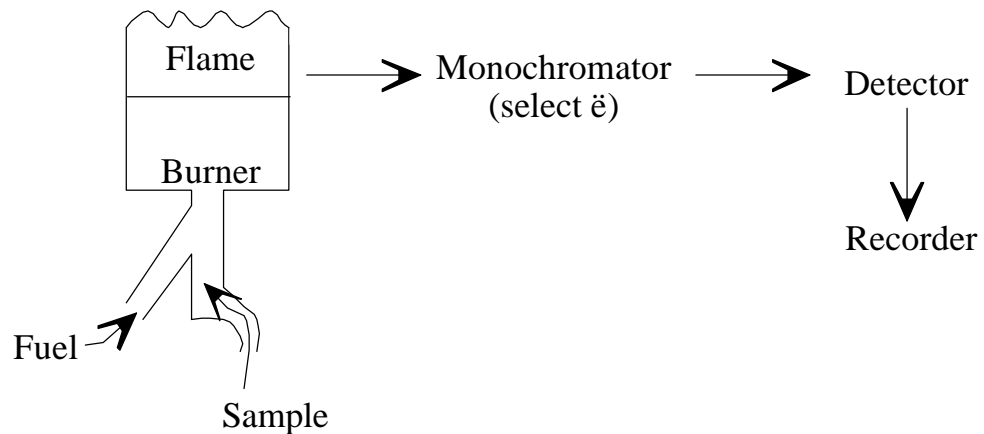
For any given line- the more the excited atoms giving that transition, the more intense the line

- d. Vary the [] of substance & determine I_{580} as a function of []



- e. For Unknown- Determine I_{580} & relate it to []

B. Instrument



VI. Atomic Absorption Analysis

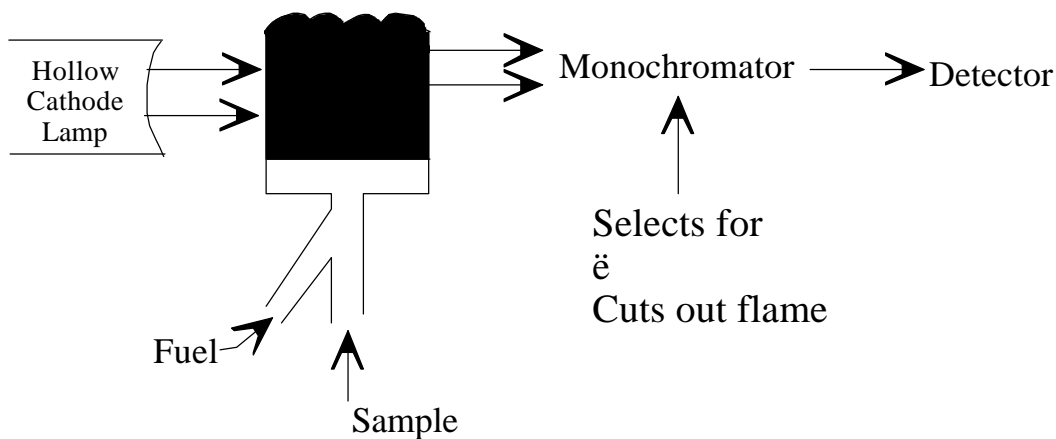
A. Analysis

1. Sample placed in flame (as with flame emission)
Now concerned with the unexcited atoms in the flame
2. Irradiate vaporized atoms with light & determine how much light they absorb
3. The greater the [], the more the vaporized atoms and the more light they will absorb

B. The Irradiating Light

1. Use hollow cathode lamps constructed of the element you are analyzing for
 - a. If analyzing for Ca- Use hollow cathode lamp made of Ca
2. Light emitted by hollow cathode lamp will be the exact λ 's that the atoms in the flame need to absorb

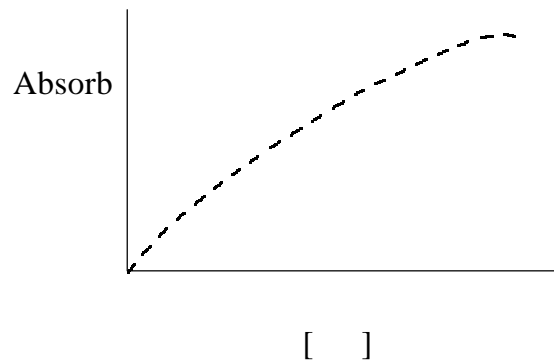
C. Instrumental Design



D. How to Perform The Analysis

1. Select hollow cathode lamp for element
2. Select major line of excitation spectrum
3. Set monochromator
4. Using solutions of known concentration, measure the absorbance in the flame

5.



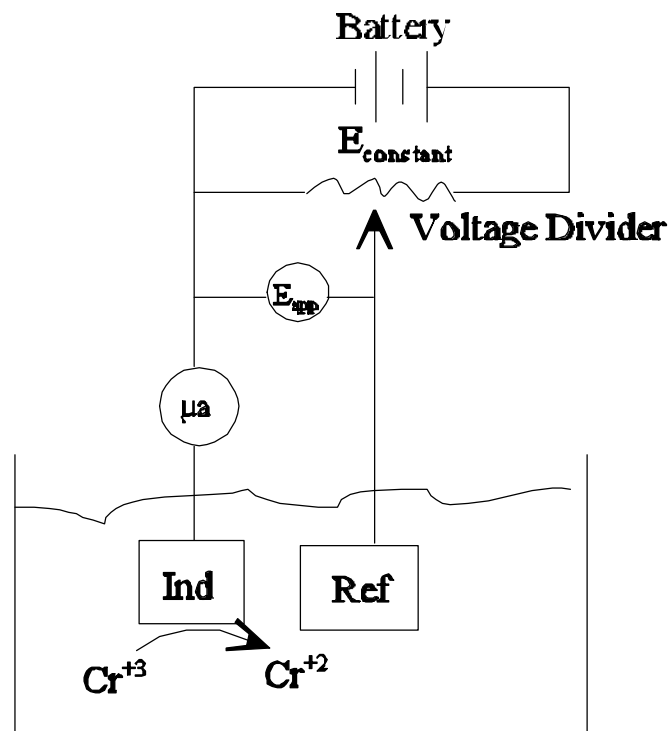
6. Run unknown & determine its concentration from the calibration curve

VII. Polarography

A. Basic Idea

1. Investigate the current- voltage relationship in a cell

B. Instrumental Design

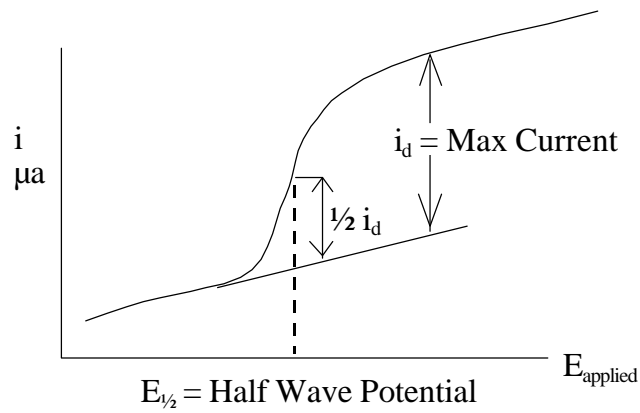


1. Vary E_{applied} & measure both

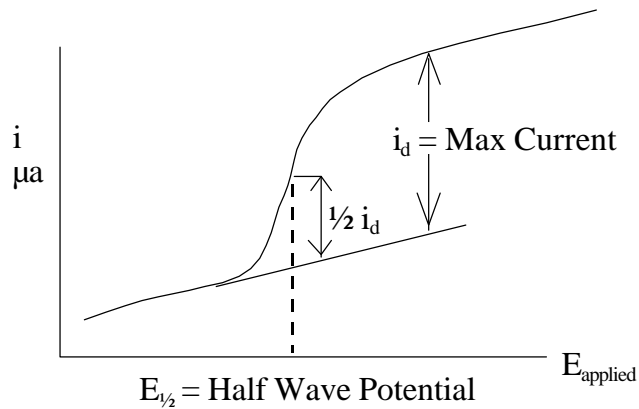
E_{applied} (volts)

i (ma)

2. Plot i vs E_{applied} to obtain a polarogram



C. Polarogram



i_d = limiting diffusion current

1. Limited by how fast Cr^{+2} can diffuse away from the electrode
2. Limited by how fast Cr^{+3} can diffuse to the electrode

$E_{1/2}$ = Applied potential where

$$i = 1/2 i_d$$

D. Qualitative Polarography

1. Determine $E_{1/2}$ of “sample” in some medium (supporting electrolyte) (graphically from polarogram)
2. Look in tables for $E_{1/2}$ in different media to distinguish between various possibilities

E. Quantitative Polarography

1. Concept

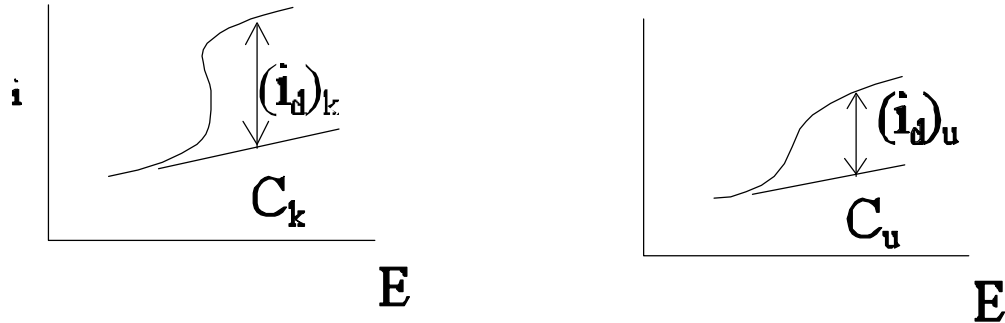
$$i_d = k \cdot C$$

i_d = limiting diffusion Current

k = “constant”

c = conc of Subst ($\frac{mmoles}{l}$)

2. Measure standard of known conc., then measure sample of unknown conc with the same apparatus



$$3. \quad \frac{(i_d)_k}{(i_d)_u} = \frac{k C_k}{k C_u} = \frac{C_k}{C_u}$$

$$C_u = C_x \cdot \frac{(i_d)_u}{(i_d)_k}$$

4. Pilot Ion Method- Add a known amount of an Internal Standard To the sample
 - a. The internal standard (known amt) and the “unknown” are entirely diff. compounds
 - b. Conditions
 1. Unknown must not contain any endogenous internal standard compound
 2. Standard must have a wave before or after the unknown & the wave must be displaced enough to enable the two limiting currents to be determined

- c. Waves should be influenced by conditions in about the same manner.

$$\frac{(i_d)_k}{(i_d)_u} = K \frac{C_k}{C_u}$$

Determine K in advance using STD known mixtures of C_k & C_u measuring $(i_d)_k$ & $(i_d)_u$

Then

$$C_u = K \cdot C_k \cdot \frac{(i_d)_u}{(i_d)_k}$$

5. Standard Addition Method

a. STD is the same compound as the “unknown”

b. Measure $(i_d)_u$ at some potential

$$(i_d)_u = K \cdot C_u$$

c. Add a known amount of Substance of known Concentration (i.e. standard) C_s & V_s

Measure $(i_d)_{\text{mix}}$ under the same conditions

$$(i_d)_{\text{mix}} = K \left(\frac{C_u V_u + C_s V_s}{V_u + V_s} \right)$$

C_u = Conc. of Unknown

C_s = Conc of STD Sol'n

V_u = Volume of Unknown started with

V_s = Volume of STD added

d. Two Equations with Two unknowns
Solve for K & Cu

Polarography Problems

1. A solution that is 17.0 mmolar in Co (III) produces a limiting diffusion current of 32.0 microamps. A solution that contains an unknown concentration of Co (III) measured in the same polarographic cell yields a limiting diffusion current of 6.0 microamps. What is the concentration of Co (III) in the unknown?

2. A solution containing an unknown amount of Cr (III) was made 8.0 mmolar in Pb (II). The limiting diffusion currents of the Cr (III) and Pb (II) were 16.2 microamps and 25.0 microamps, respectively in this solution. Previously, a solution 18.0 mmolar in Cr(III) and 16.0 mmolar in Pb (II) yielded limiting diffusion currents of 21.0 microamps and 50.0 microamps for the Cr(III) and Pb(II), respectively. What was the concentration of Cr(III) in the unknown solution?

3. A solution containing an unknown concentration of Ni(II) when measured in a polarographic cell, yielded a limiting diffusion current of 18.2 microamps. 50.00 ml of the unknown Ni(II) containing solution were mixed with 25.00 ml of a 10.0 mmolar Ni(II) solution, and the mixture was measured in the same polarographic cell. the limiting diffusion current of the mixture was found to be 25.0 microamps. What was the concentration of Ni(II) in the original unknown?