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Radiochemistry Ph.D. Program

Fuel Cycle Separations Subgroup

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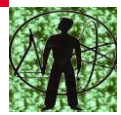

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Radiochemistry Research Program Concepts

- **Research areas**
  - Radiochemical materials synthesis and characterization
  - Fuel cycle separations
  - Radioanalytical separations
- **Chemistry based analysis of actinides and technetium**
  - Interested in chemical species and coordination, focus on radioelements
- **Research with radionuclides**
  - Kg quantity of Th and U
  - Gram amount of Tc, Np, Pu
  - Milligram quantity of Am and Cm
- **Research coupled with education program**
  - Provide undergraduate and graduate students with actinide research opportunities
- **Develop a center of excellence in radiochemistry**
  - Noted researchers, strong collaborations

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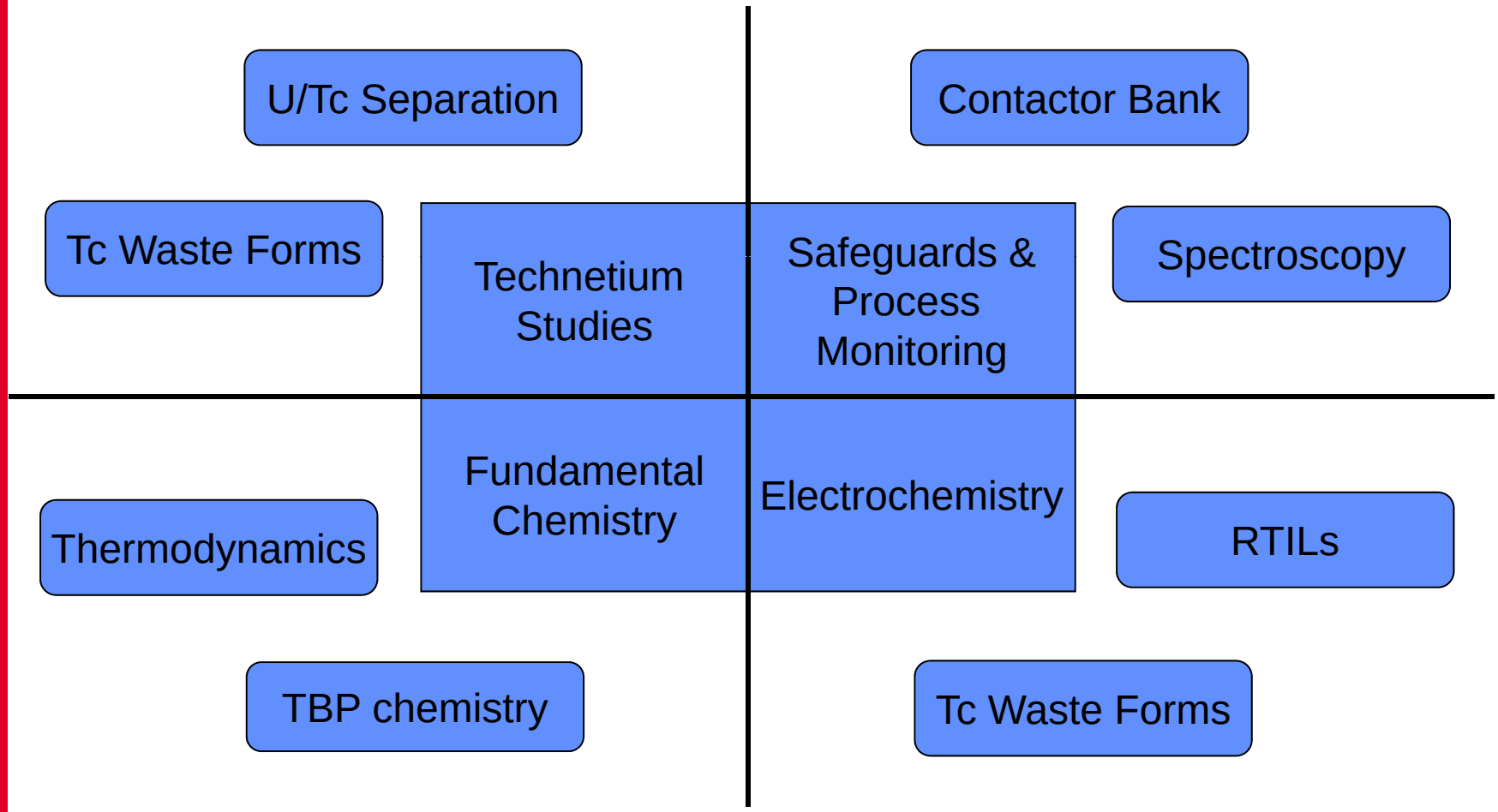
Program Resources

- **Spectroscopy**
  - UV-Visible
  - Laser Fluorescence
  - NMR
  - IR
  - EELS
  - *XAFS (APS @ ANL)*
- **Radiochemical separation and detection**
  - Gross alpha/beta counting
  - α-spectroscopy
  - γ-spectroscopy
  - Liquid Scintillation Counting
- **Thermal methods**
  - TGA, DSC
- **Scattering**
  - Powder XRD
  - Single crystal XRD
- **Contactors for Separations**
- **Analytical**
  - ICP-AES
  - ICP-MS
  - Electrospray-MS
  - Laser Ablation MS
  - Automated Titrator
- **Microscopy**
  - Optical
  - SEM
  - TEM
- **General Equipment**
  - Box/Tube furnaces
  - Glove Boxes
  - Arc Welder
  - Ultracentrifuge
  - Ball Mill
  - 10 tonne die press
  - Electron microscopy sample preparation

Separations Hierarchy



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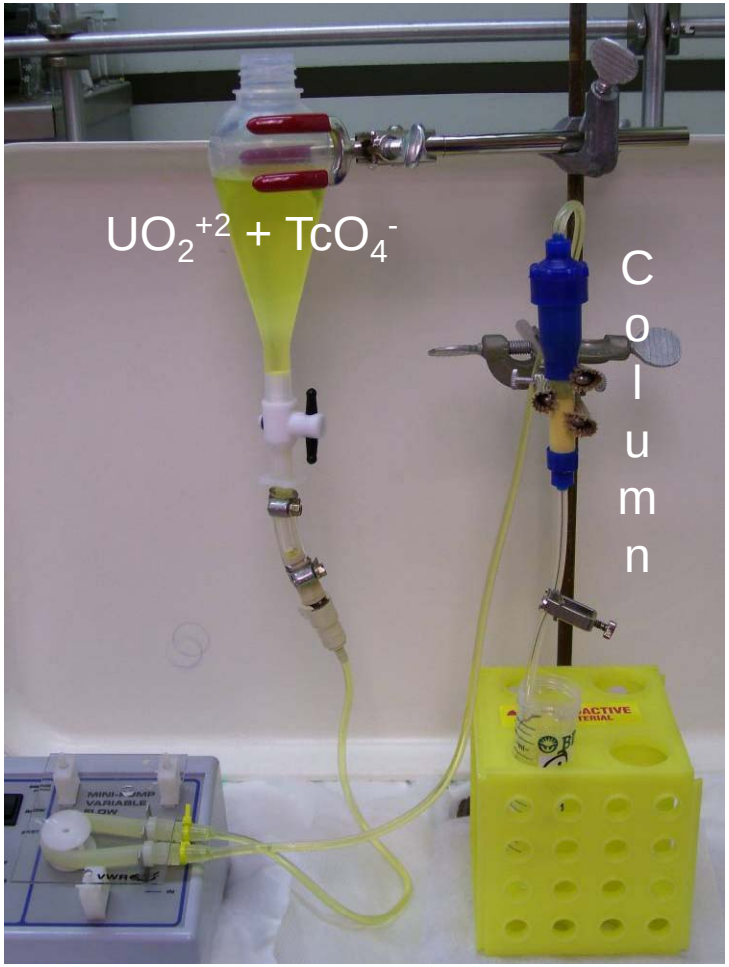
Technetium Studies

- **UREX process Tc/U separation**
  - Resins are tested for Tc loading and strip efficiency
  - Steam reforming process developed for conversion to Tc metal for waste form
- **Analysis of waste forms**
  - Suitability for repository storage
  - Leach characteristics
  - Electrochemical behavior

Tc metal



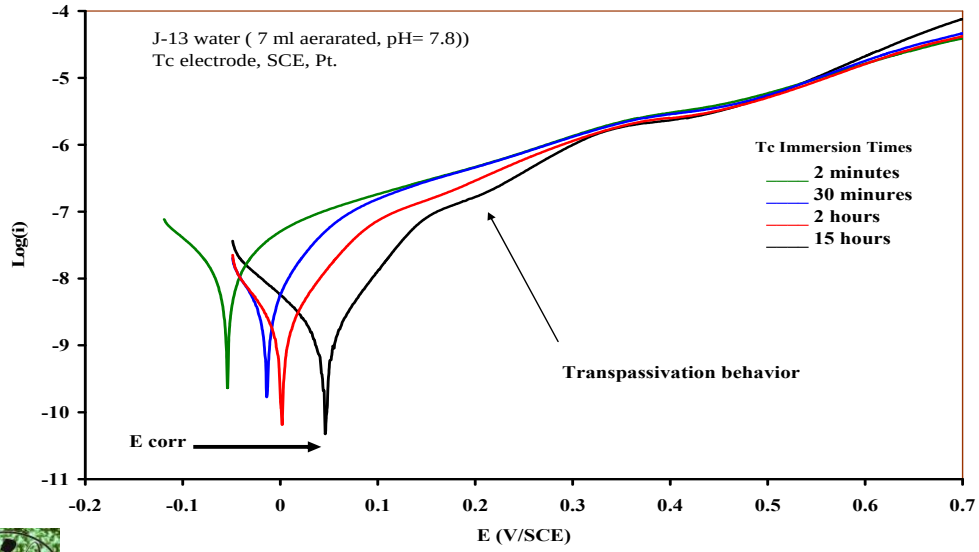
Electrochemical Corrosion Studies

Tc electrode: acceleration corrosion test

m= 80 mg, A= 3.3 mm²

Tc electrode

Set-up for corrosion exp

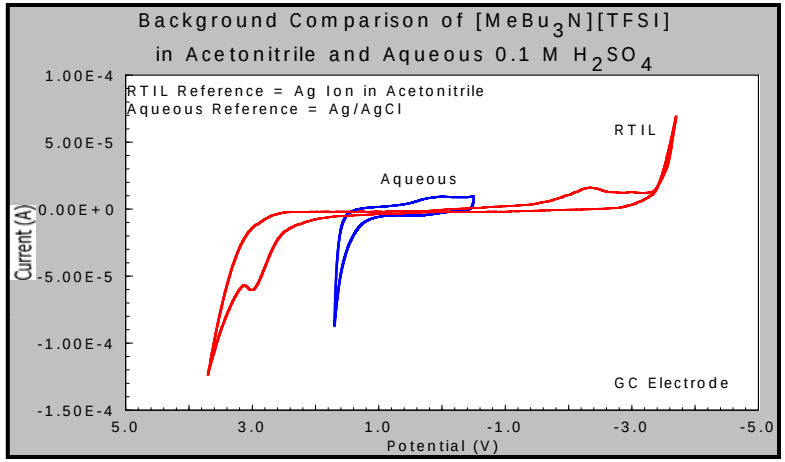


E_{corr} : shift from -54 mV (t= 2min) to +46 mV (t= 15 hours)

Transpassivation behavior around +195 mV

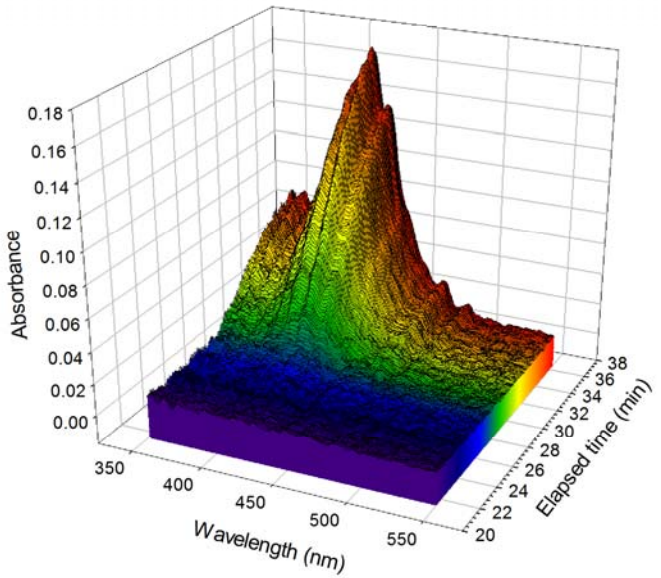
Room Temperature Ionic Liquids

- RTILs are becoming more popular
  - "Green" solvents (some exceptions)
  - No measureable vapor pressure
- RTIL Advantages
  - Electrochemical windows up to 7 volts
  - Water free systems
    - Organic & inorganic synthesis
    - Separations
    - Polymerization
- U(III) systems
  - Utilizing lower oxidation state in inert atmosphere provides more direct mechanism for metallic alpha uranium deposition
  - Metallic uranium has many potential uses
    - Vast interest in waste forms
    - Potential reactor fuel
    - Target material for generating medically useful ^{99}Mo



Process Monitoring & Safeguards

- **UV-Vis monitoring of process streams**
  - Confirm stated process chemistry
  - Detect diversion attempts
- **Fiber optic dip probe inserted into product of UREX demo in contactors at ANL for [UO_2^{2+}] measurement**
  - Spectral acquisition time of 250 µs
  - Focus on trends over time rather than single data points
  - Coupled with flow meters



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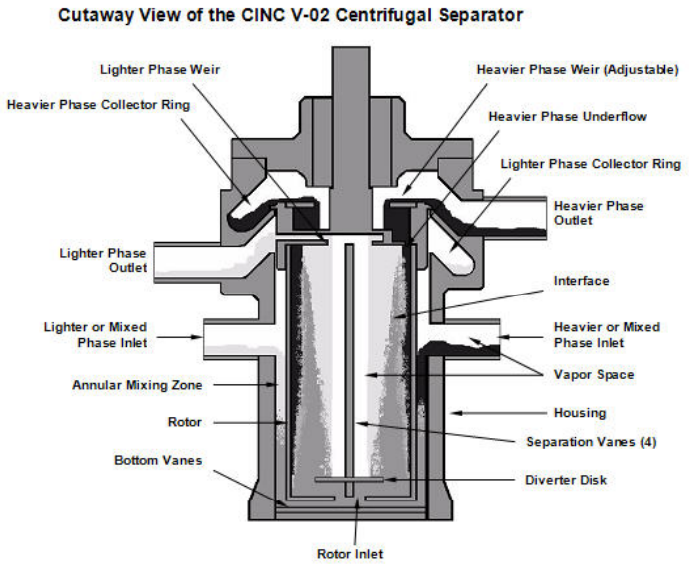
Contactor Bank

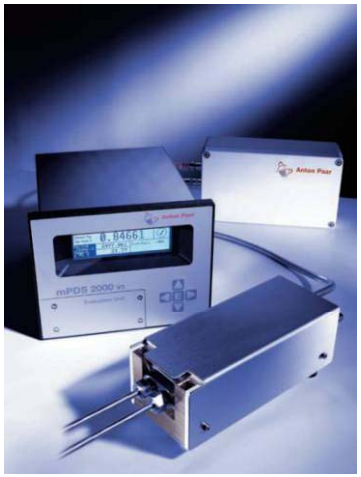
- **Purchased and installed 3 CINC V02 (2”) contactors**
  - 316 SS, suited for lab scale or pilot plant work
  - 1 or 2 phases (in the case of 1 mixed phase, can be used for separation)
  - 5 cm (2”) design reported to not exhibit pulsed flow problems
  - 1.9 LPM max throughput (combined phases)
  - 2000-6000 RPM, 100-900 Gs
  - 200 mL holdup volume
  - 220 V/3 phase, draws 0.2-0.4 amps
- **Experimental parameters**
  - Flow rate
  - Concentration
  - Process chemistry
  - Nuclide content
- **Used as a test bed for MC&A, process monitoring techniques**



TBP/dodecane/HNO_3 systems

- Basic physiochemical data incomplete in the available literature
  - Vapor pressure
  - Solubility
  - Density
- Investigation of properties as functions of T, $[HNO_3]$, $[HNO_2]$, [HDBP], $[UO_2^{2+}]$, and $[Zr^{4+}]$
- HNO_3 degradation in the presence of TBP has been studied over several decades
  - Discrepancies remain in hydrolysis rates, products and reaction heats
  - Thermal analysis with mass spectrometric analysis of gaseous reaction products proposed

Grabner MINIVAP VPXpert vapor pressure tester



Anton Paar DMA HPM density meter

Actinide Speciation and Spectroscopy

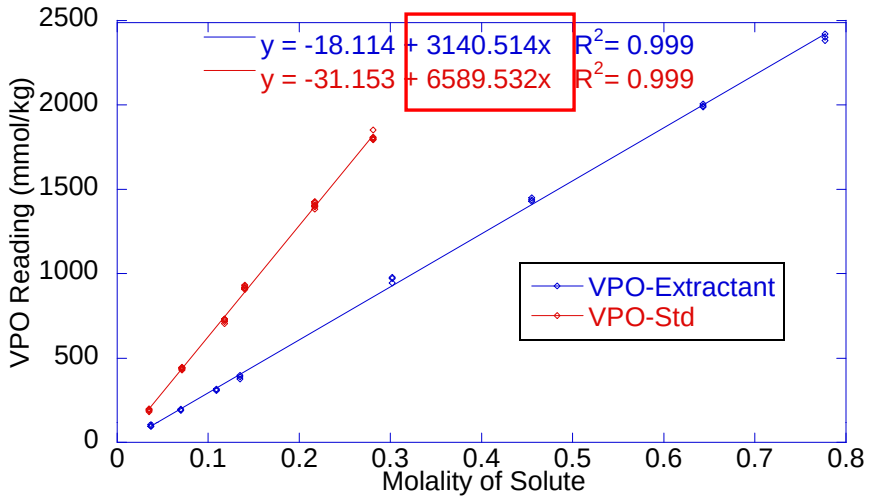
- **Actinide speciation data set is varied and incomplete**
  - Determination of thermodynamic quantities
  - Modeling and experiment
- **Titrations**
  - Competitive titrations to determine the stability constants of the UO_2^{2+}-NO_3^- system
  - Spectrophotometric titrations
- **UV-Visible spectroscopy**
  - Used for chemistry-based safeguards
    - Online monitoring of SNM
    - Real time *Material Control* and *Accountability*
    - Process/chemistry control
  - Development of a robust method for simultaneous, online determination of nitrate and uranium in a reprocessing plant
  - Adaptation of bench scale work (1 cm pathlength) to waveguide based (1 m pathlength) experiments for reduced higher actinide load
- **Laser induced fluorescence of Curium for trace level determinations**

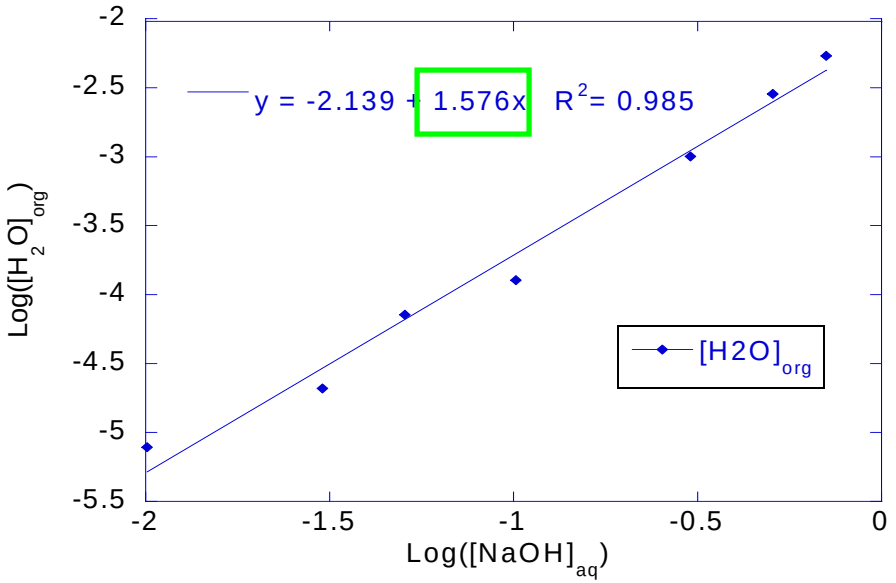
Solvent Extraction Fundamental Chemistry

- **Extractant Aggregation**
  - Vapor Pressure Osmometry
- **Water Extraction**
  - Karl Fischer Titration
- **Stability Constant Titration**
  - Spectrophotometric
  - Potentiometric

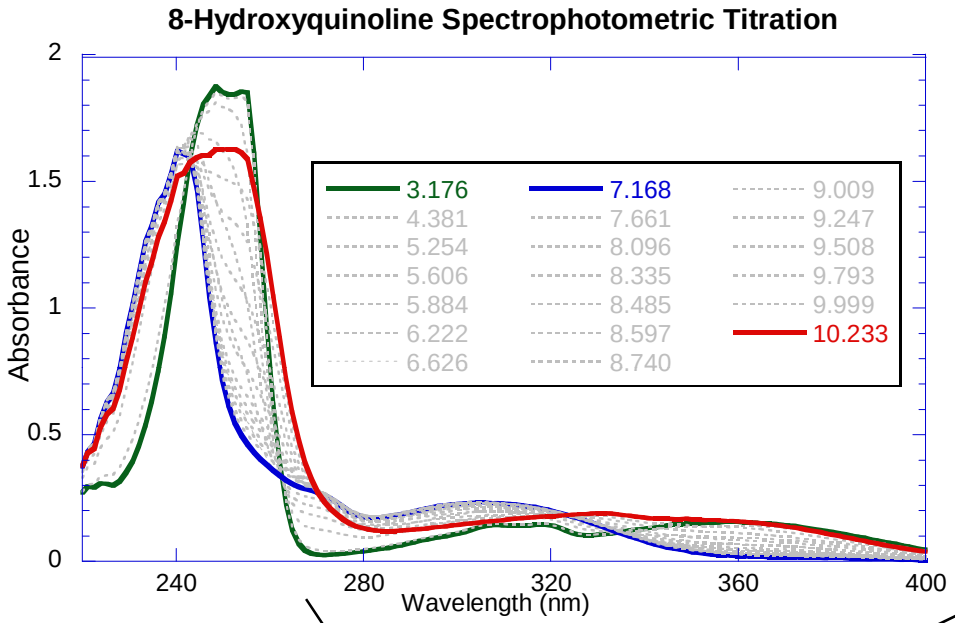
$$n_{agg} = \frac{6589}{3140} = 2.08 \pm 0.04$$

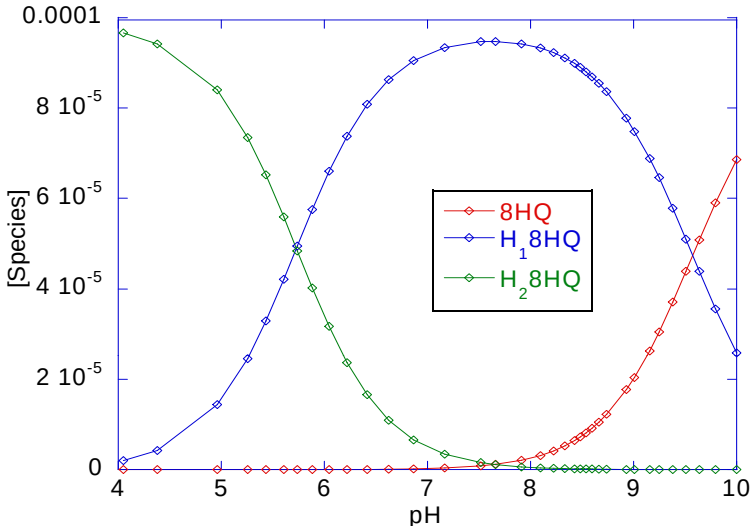
$$\frac{H_2O}{Ligand} = \frac{1.576}{1}$$



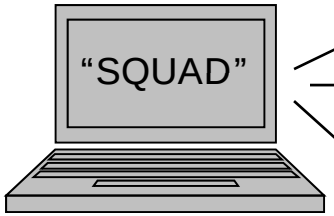


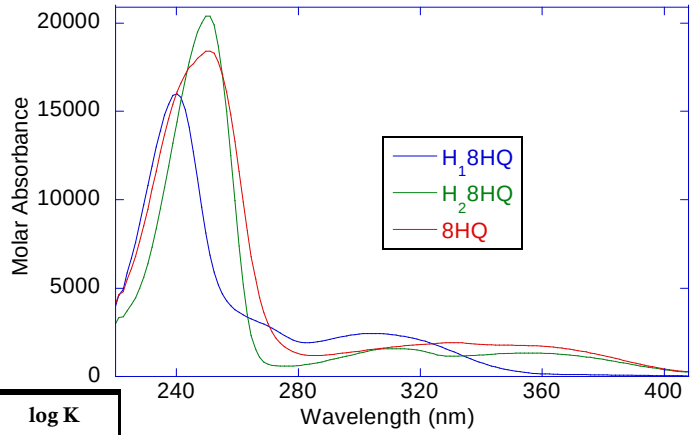
Stability Constant Modeling





Stability Quotients from Absorbance Data





T=0.3°C	log β	log K
$H_2(Q)^+$	15.38±0.01	5.30
H(Q)	10.08±0.01	10.08

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Fundamentals

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Radiochemistry Program – Fall 2009