Spectroelectrochemical Sensor for Ferrocyanide and Technetium

Design and Development of a New Hybrid Spectroelectrochemical Sensor (54674)

Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone (70010)

Project Goals

- Demonstration of sensor concept with a variety of analytes
- Development of sensor for ferrocyanide with testing on waste tank simulant at the Hanford Site
- Development of sensor for pertechnetate applicable to Vadose Zones and associated subsurface water at Hanford Site

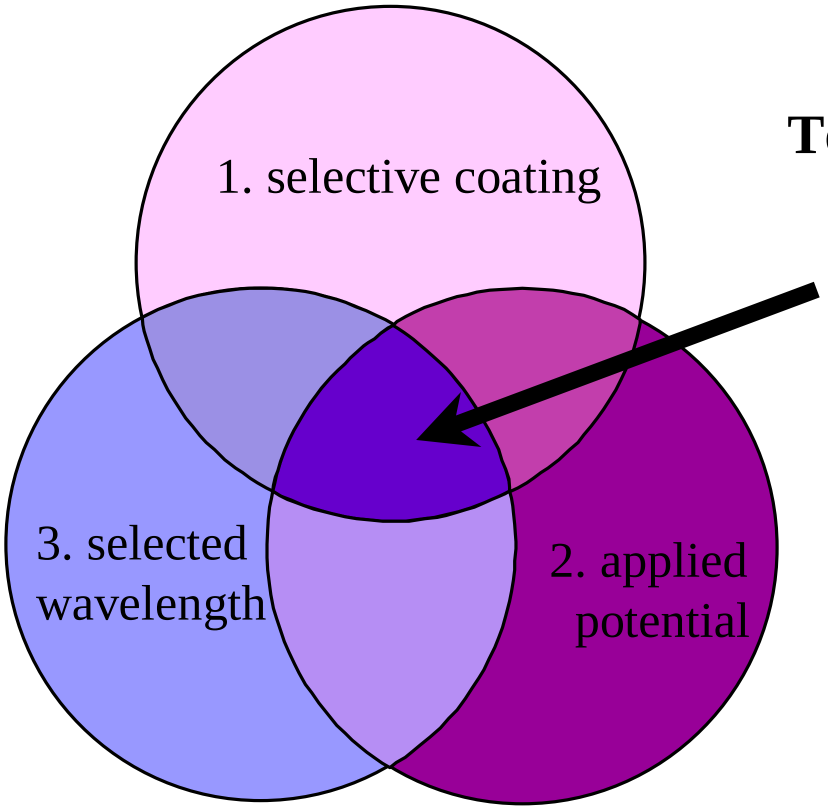
Why a New Sensor

- Many sensors lack the **selectivity** to be useful in real (complex) samples or in harsh environments.

- The **spectroelectrochemical sensor** was developed to overcome these limitations by employing a new concept which incorporates three modes of selectivity.

- To demonstrate the new sensor, **ferrocyanide** (as in some of the nuclear waste tanks at Hanford, WA) was chosen as the target analyte.

Three Modes of Selectivity



To be detected an analyte must:

1. **Partition into the coating**
2. **Undergo electrochemistry at the applied potential**
3. **Absorb light at the chosen wavelength**

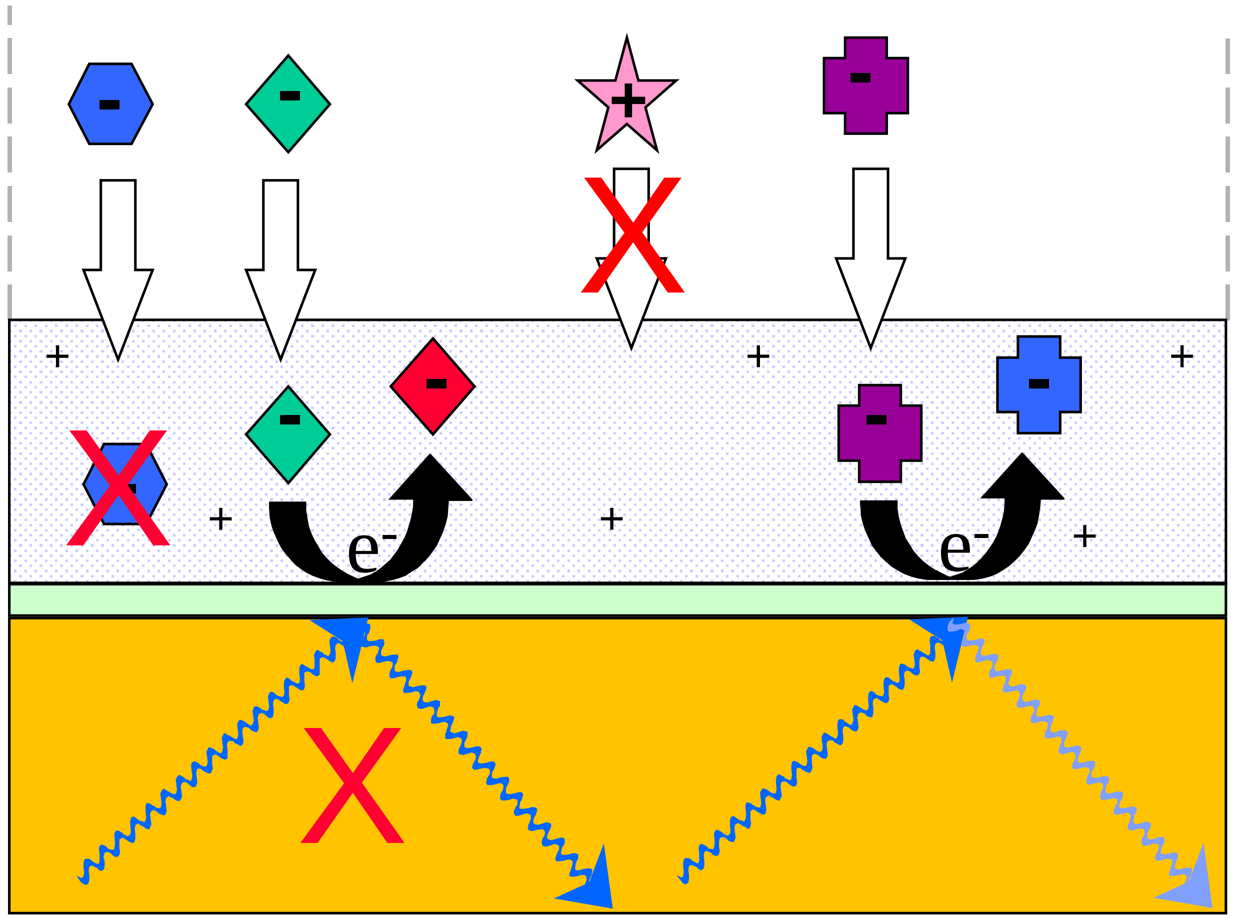
Selectivity Concept

Analyte
in solution MUST

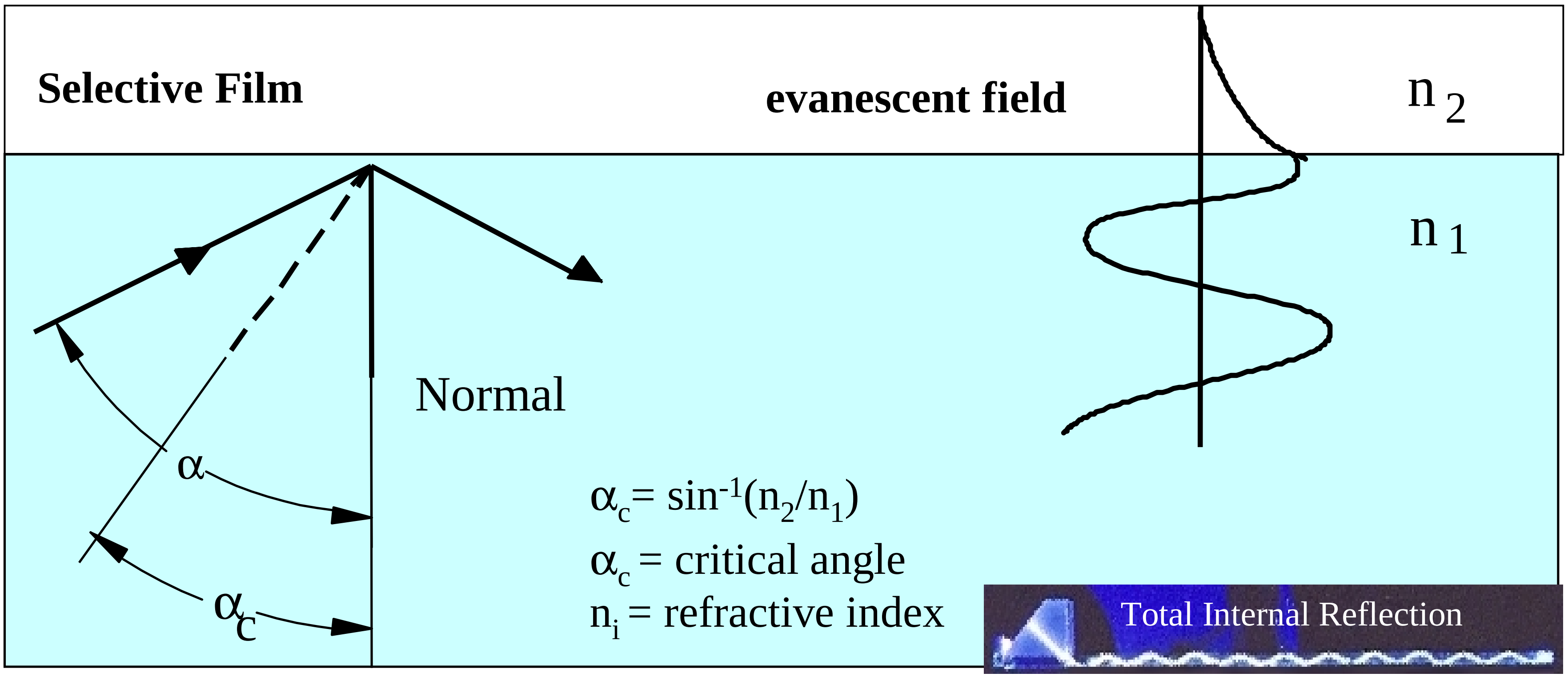
1. Partition into chemically-selective film

2. Electrolyze at chosen potential of electrode

3. Absorb at wavelength of guided light



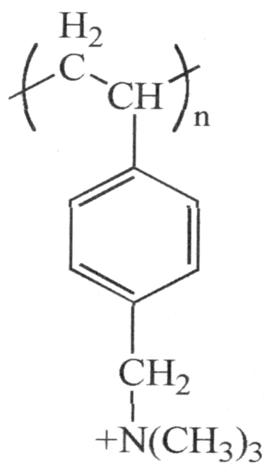
Principle of Evanescent Wave Interaction



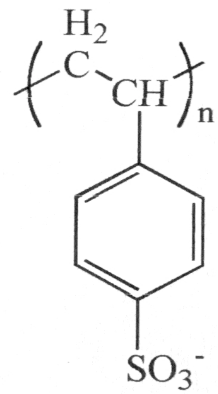
Light under total reflection at an interface establishes an **evanescent field** which penetrates about one wavelength into the film. If an analyte partitions into the film, and if it absorbs at the wavelength propagated in the waveguide, the transmitted light will be attenuated.

Development and Demonstration of Concept

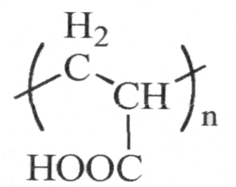
Polyelectrolytes



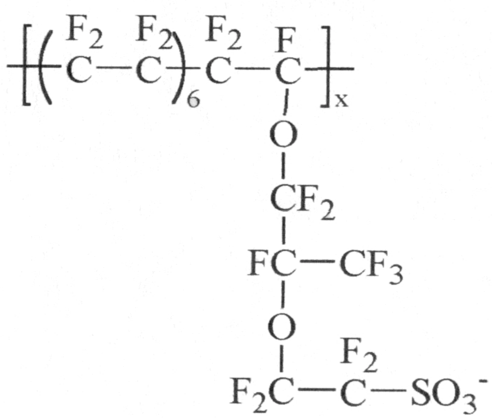
PVTAC



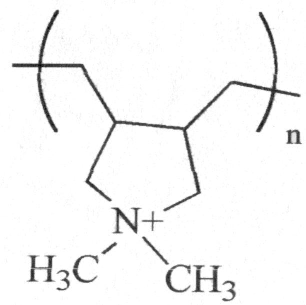
PSS



PAA



Nafion



PDMDAAC

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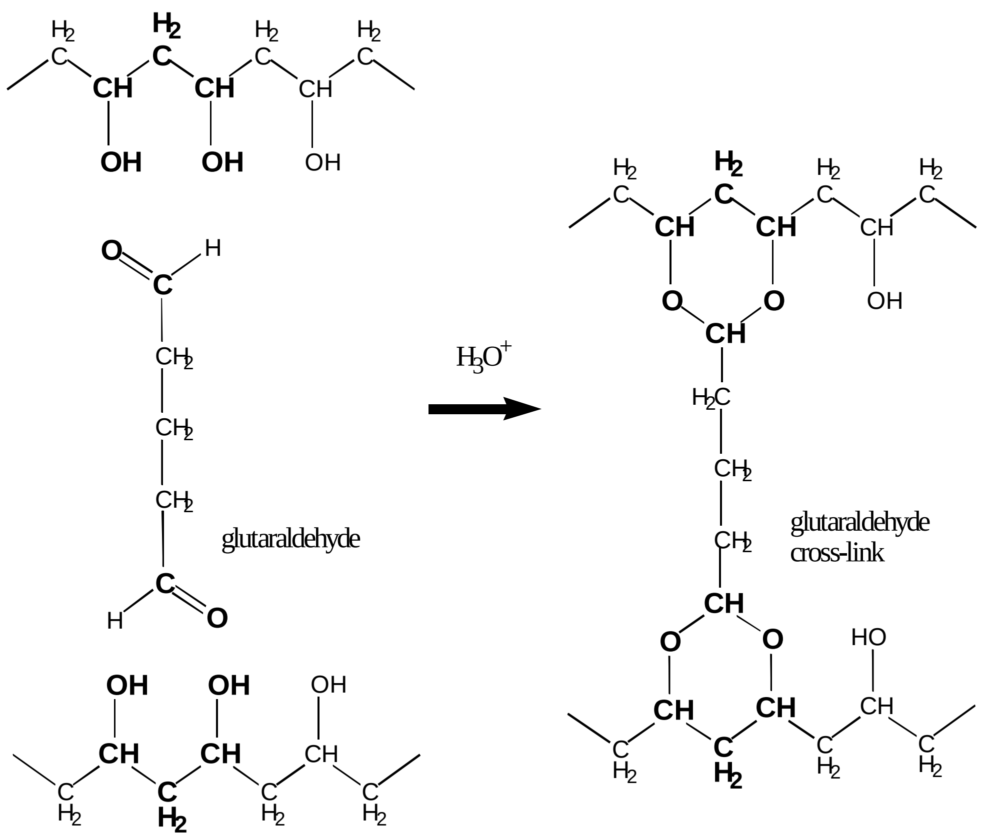
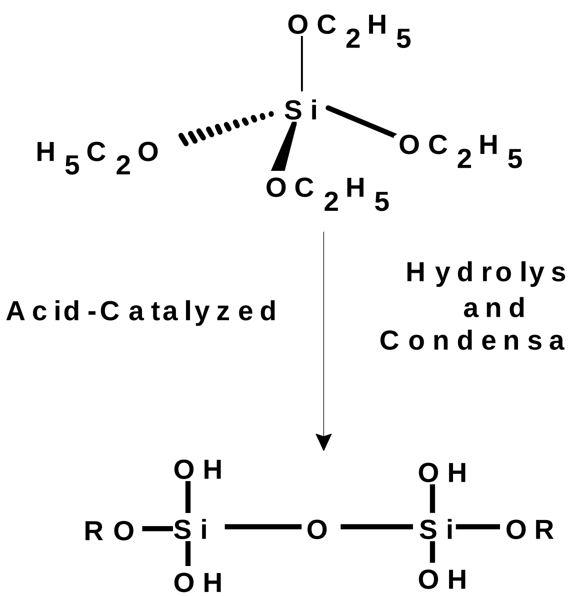
Polyelectrolyte Immobilization

Poly(vinyl alcohol) cross-linked host



Sol-Gel processed silica host



Electrochemical Systems
Polymer Blend Selective Films

Single Analyte:

PAA-PVA **Nafion-PVA** **PVTAC-PVA**

$Ru(BiPy)_3^{2+}$ **$Re(DMPE)_3^{+}$** **$Fe(CN)_6^{3-}$** **$Ru(CN)_6^{4-}$**

Double Analyte:

PAA-PVA **PVTAC-PVA**

$Ru(BiPy)_3^{2+}$ & $Fe(CN)_6^{3-}$ **$Ru(CN)_6^{4-}$ & $Fe(CN)_6^{4-}$**

Electrochemical Systems

Sol-Gel Silica Composite Selective Films

Single Analyte:

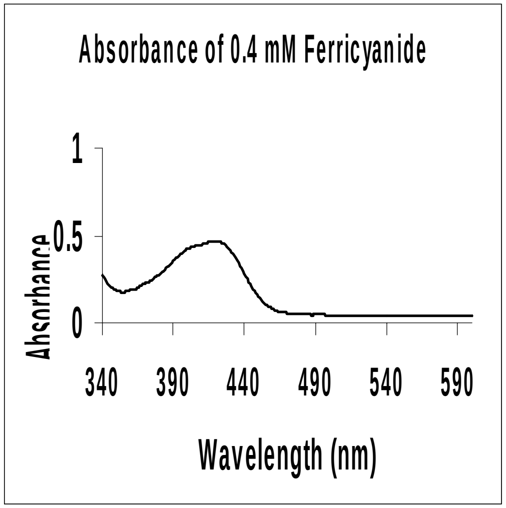
- Nafion-SiO_2
  - Methyl Viologen
  - $Ru(BiPy)_3^{2+}$
  - $Re(DMPE)_3^{+}$
- PDMDAAC-SiO_2
  - $Fe(CN)_6^{3-}$
  - $Ru(CN)_6^{4-}$

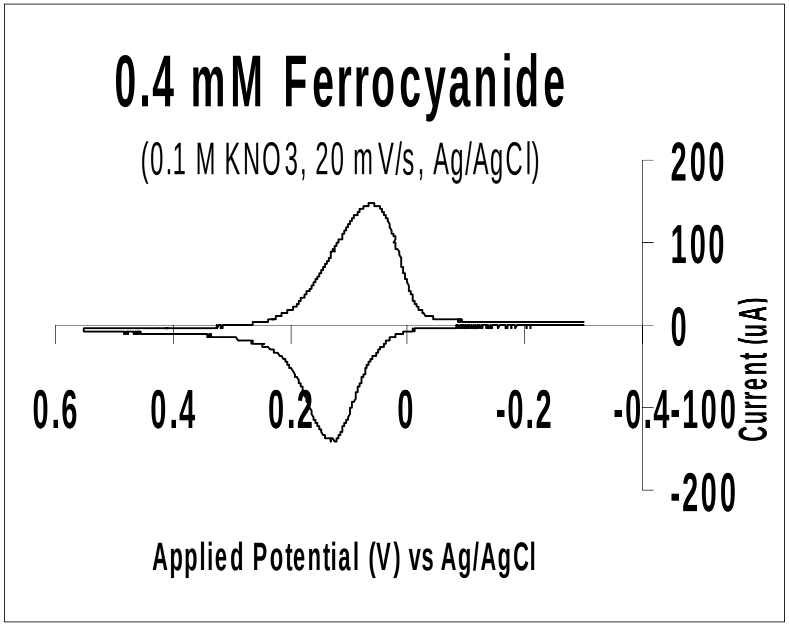
Double Analyte:

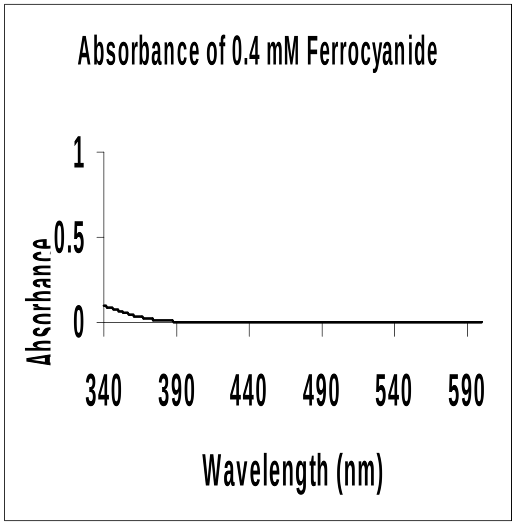
- Nafion-SiO_2
  - $Ru(BiPy)_3^{2+}$ & $Fe(CN)_6^{3-}$
- PDMDAAC-SiO_2
  - $Ru(BiPy)_3^{2+}$ & $Fe(CN)_6^{3-}$
  - $Ru(CN)_6^{4-}$ & $Fe(CN)_6^{4-}$

Spectroelectrochemistry of Ferrocyanide

$$Fe(CN)_6^{3-} + 1e^- \rightleftharpoons Fe(CN)_6^{4-}$$







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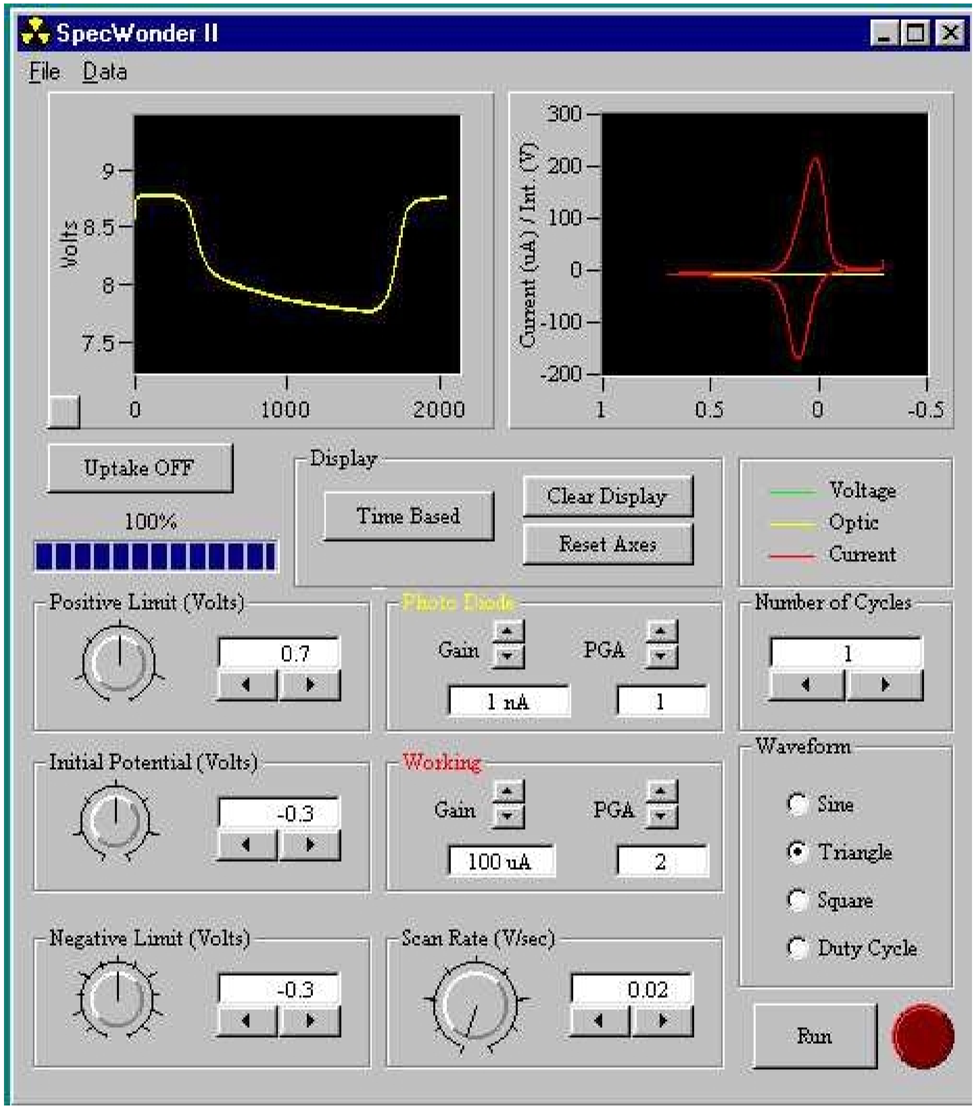
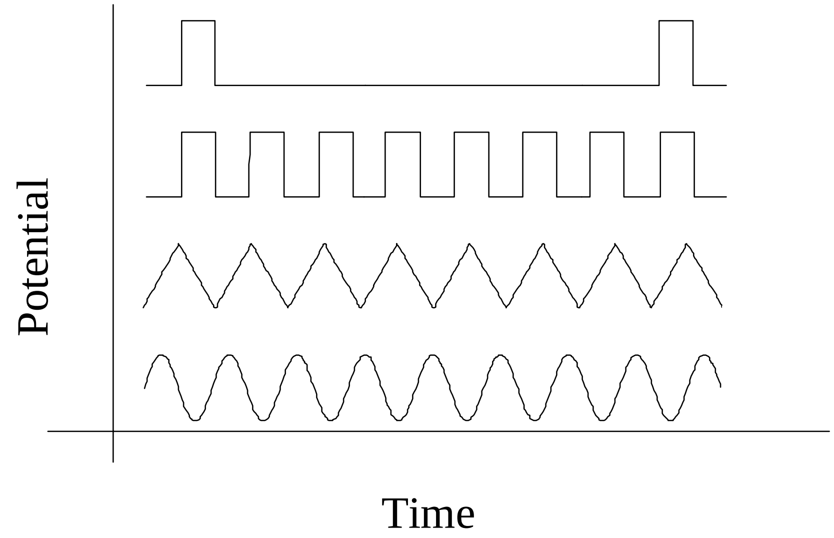
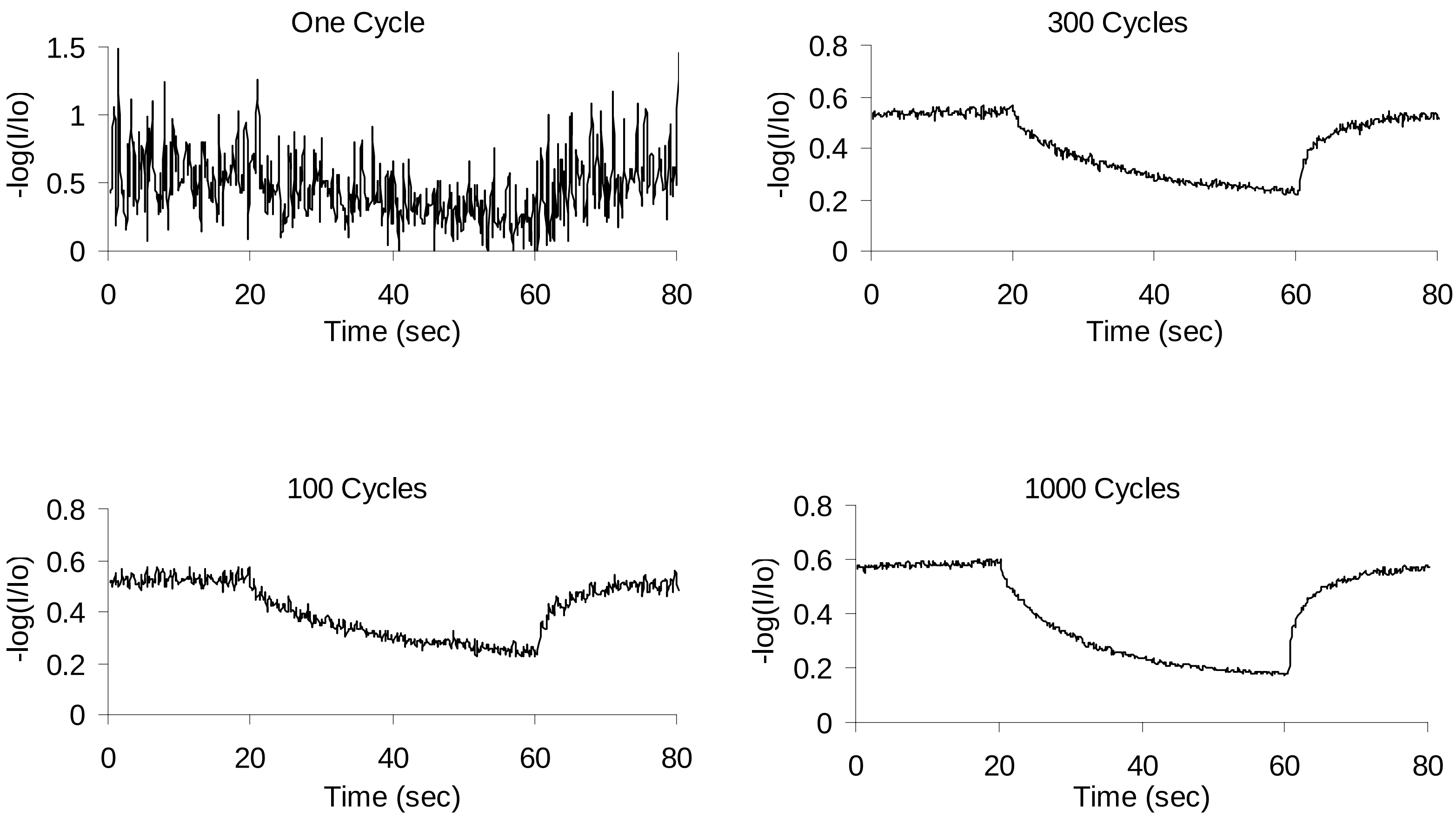
Virtual Software Interface



Excitation potential waveforms



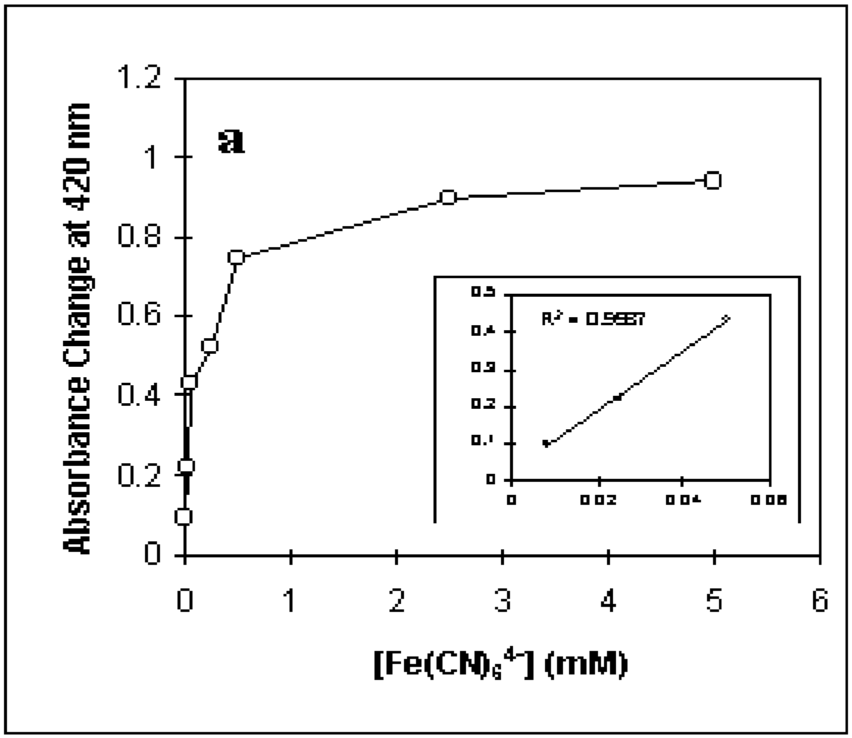
Effect of Signal Averaging on Optical Response

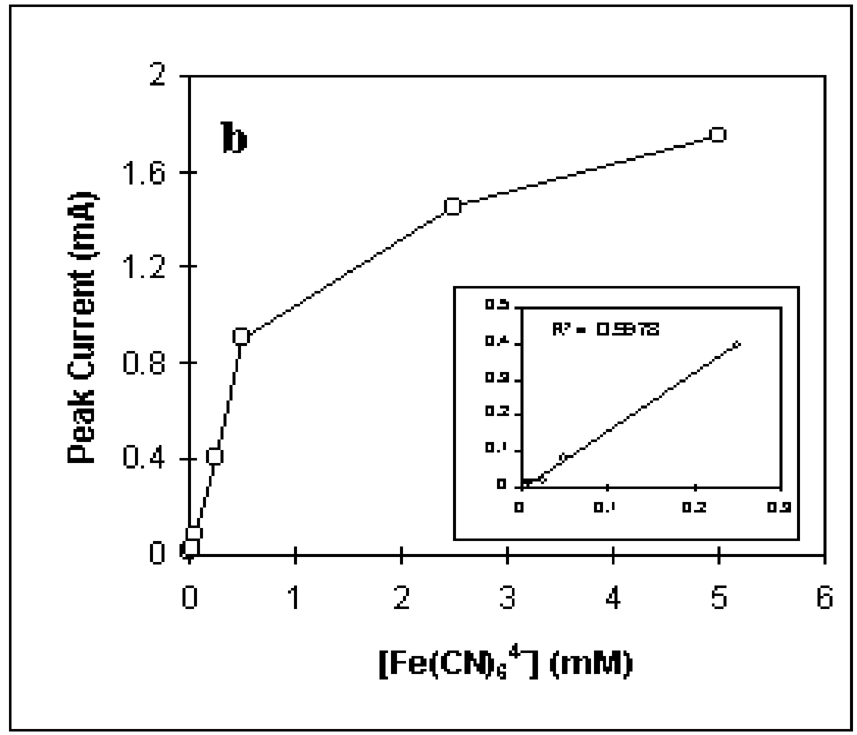


Square wave excitation, tris(2,2'-bipyridyl)ruthenium chloride model analyte, blue LED source, PMT detector

Sensor Calibration Curves:

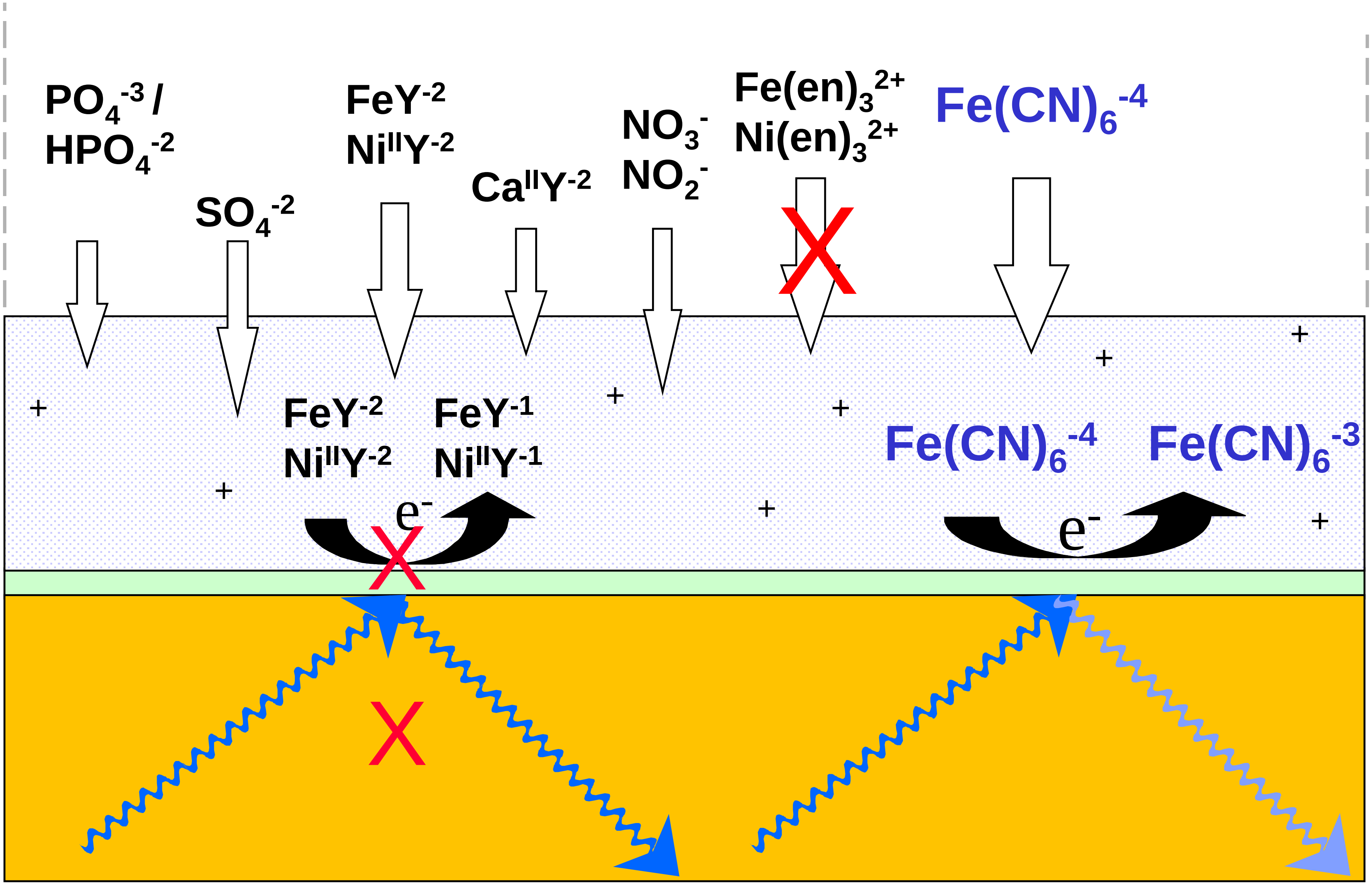
Optical and Electrochemical



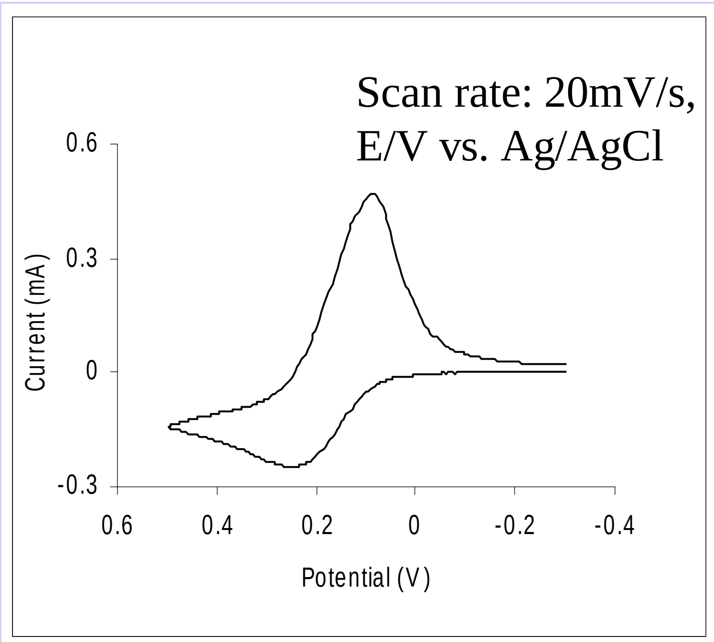


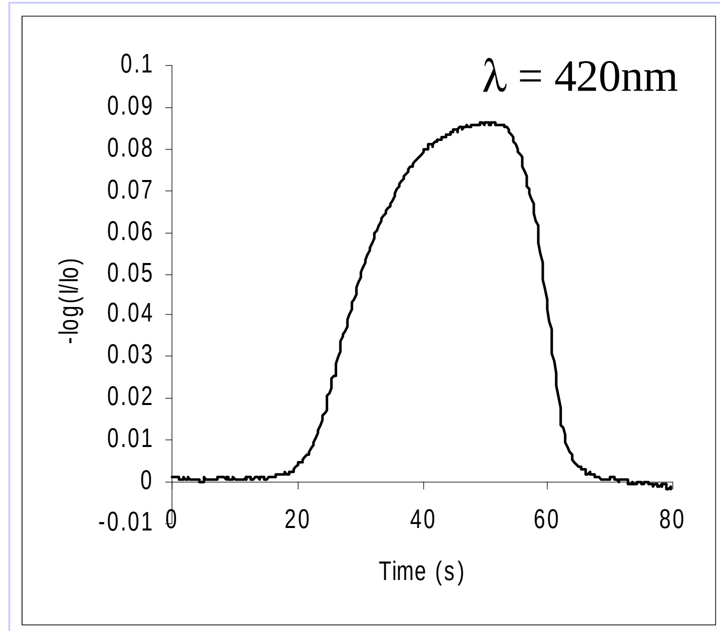
Simulant Solution to Actual Waste Tank Sample

Simulant Solution And Sensor



Sensing of Ferrocyanide in UC-Simulant Solution





cyclic voltammogram

optical response

<u>UC-Simulant Solution:</u>

0.2 M Na_2SO_4

0.005 M $NiSO_4$

0.005 M $K_4[Fe(CN)_6]$

2.8 M $NaNO_3$

0.86 M $NaNO_2$

pH = 11

0.017 M $Fe(NH_4)_2(SO_4)_3$

0.15 M Na_3PO_4

Approximate Composition of the Hanford U-Plant-2 Simulant Sludge

Species	*Weight Percent*
Na^+	8.33
NO_3^-	**13.18**
NO_2^-	**3.25**
SO_4^{2-}	4.55
SO_3^{2-}	0.21
PO_4^{3-}	2.50
NH_4^+	0.10
Ca^{2+}	0.88
Ni^{2+}	0.41
Fe^{2+}	0.39
Fe^{3+}	1.34
CN^-	1.08
H_2O	65

Simulant Sludge

↓

Dilute with 5% EDTA / 5% En

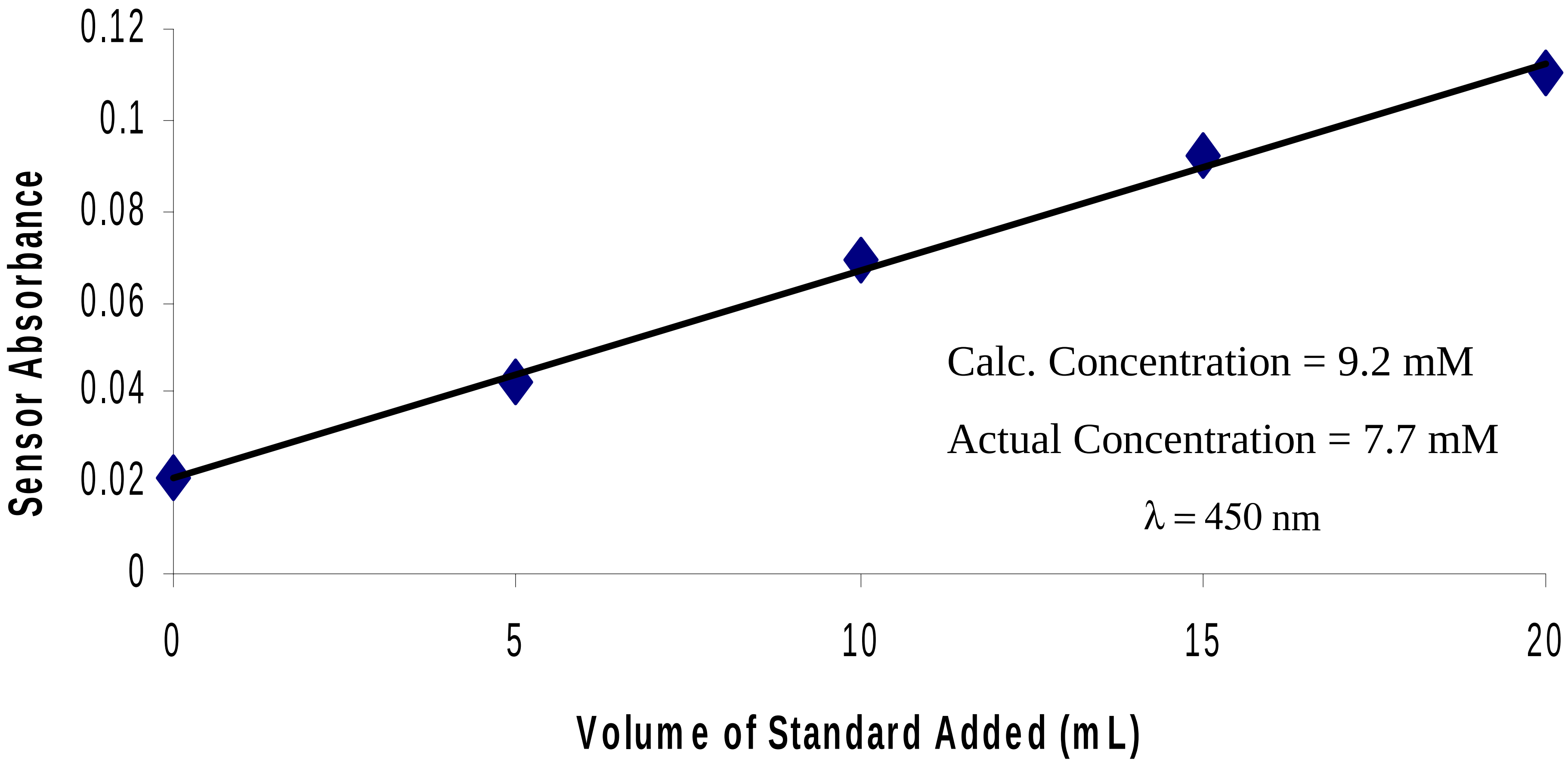
↓

Simulant Solution

U-Plant-2 Simulant Solution

Species	Weight %	M (mol/L)
Na^{+}	0.78	0.41
NO_3^{-}	1.23	0.24
NO_2^{-}	0.30	0.079
SO_4^{-2}	0.42	0.053
SO_3^{2-}	0.02	0.03
PO_4^{3-}	0.23	0.029
NH_4^{+}	0.01	0.007
Ca^{2+}	0.08	0.024
Ni^{2+}	0.04	0.008
Fe^{2+}	0.014	0.009
Fe^{3+}	0.12	0.026
CN^{-}	0.106	0.0077
en	4.54	0.92
EDTA	4.54	0.19
H_2O	87	---

Ferrocyanide Determination in U-Plant-2 Simulant Solution



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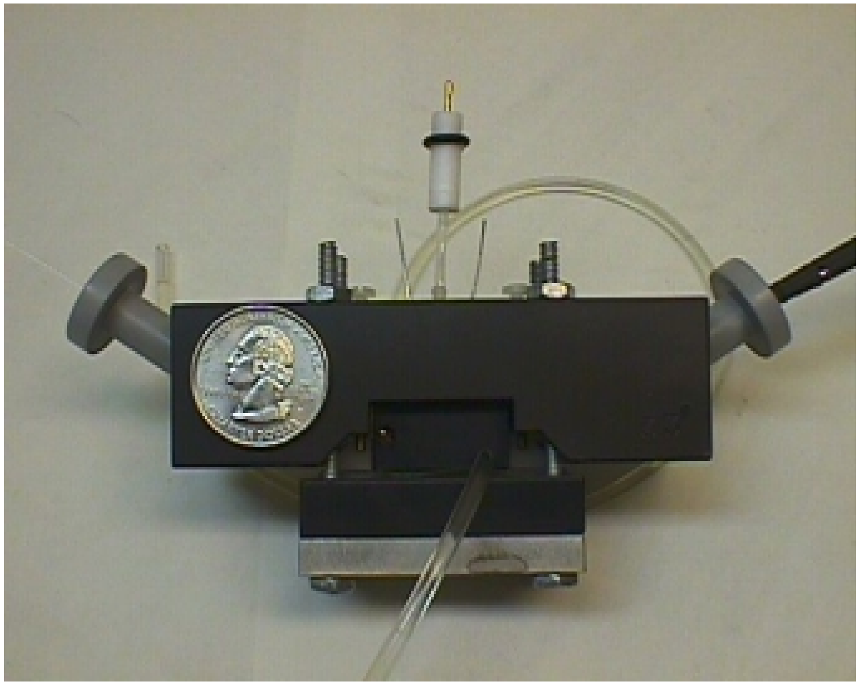
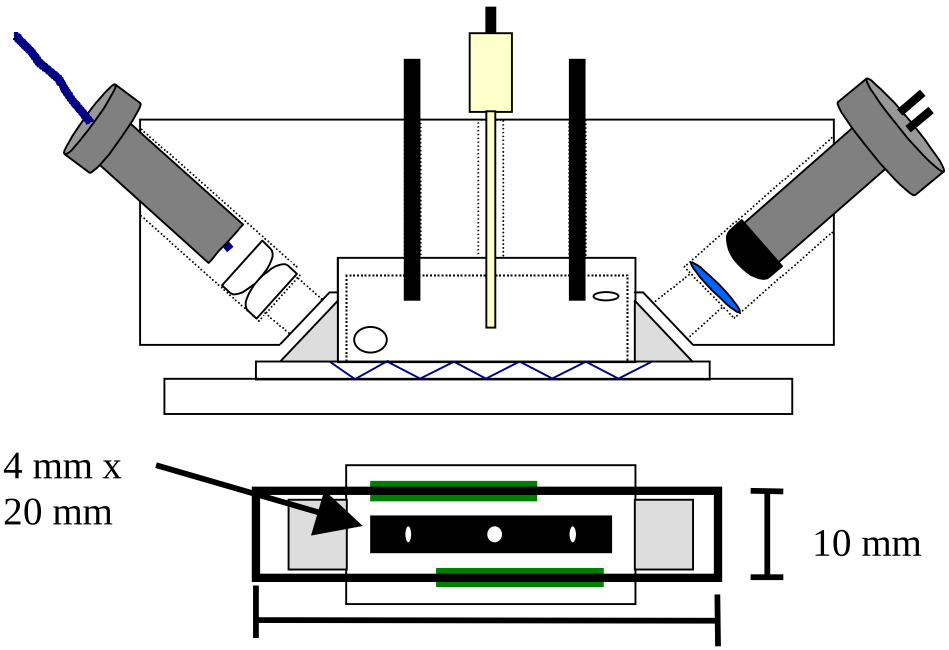
General Design of Prototype Sensor

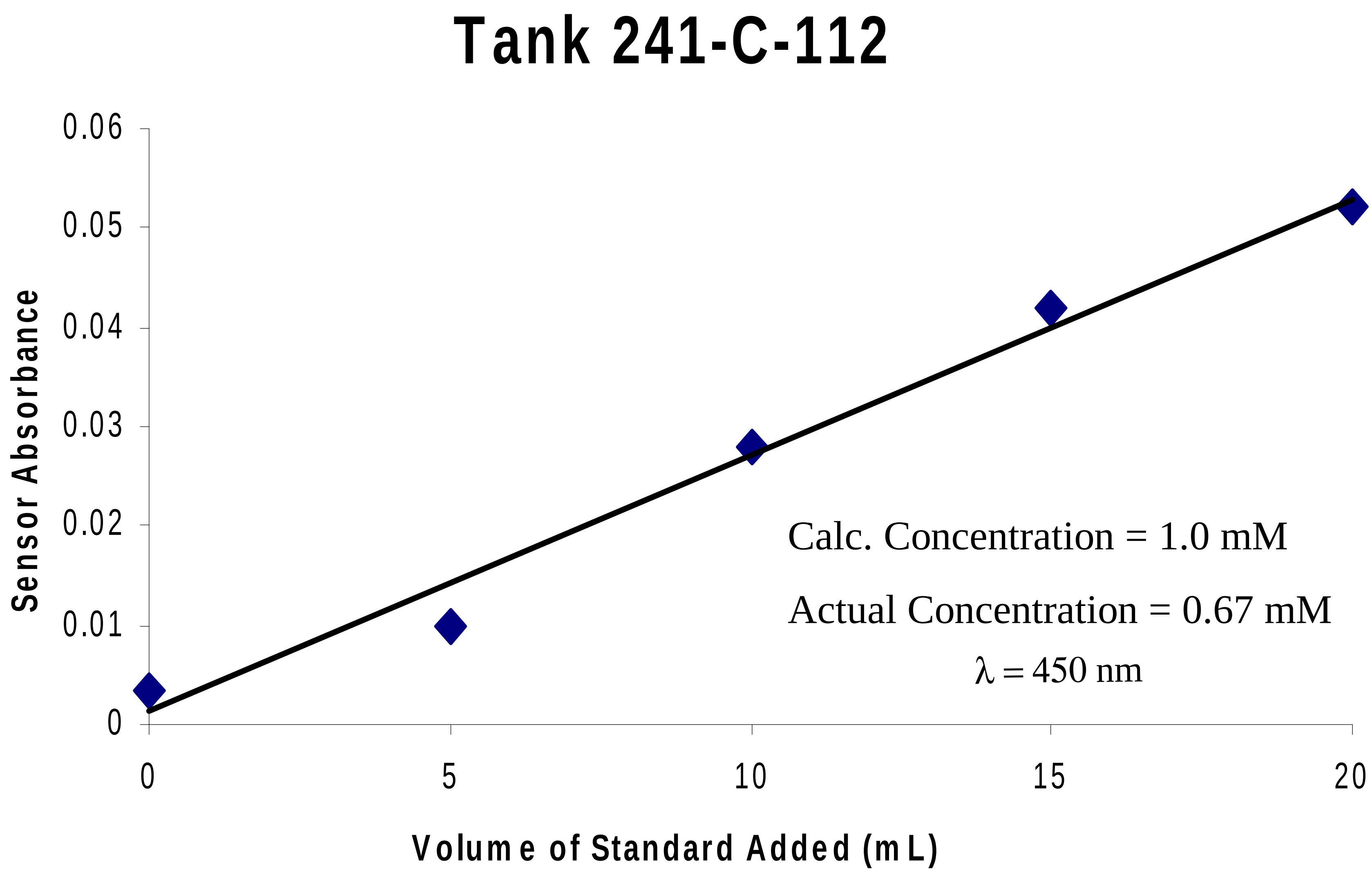




- Material - Delrin, PVC
- Volume - 800 μL
- Light Source - Blue LED
- Detector -Blue enhanced photodiode

On-Site Testing of Actual Waste Tank Sample at PNNL / Hanford

Standard Addition of Waste Tank Sample



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Accomplishments

- Concept demonstrated with detection of $Fe(CN)_6^{4-}$, $Re(DMPE)_3^{+}$, $Ru(bipy)_3^{2+}$, and methyl viologen
- Selectivity against direct interference's demonstrated
- Signal averaging to achieve lower detection limits demonstrated
- Prototype instrumentation package to control electrochemical modulation and optical readout developed
- Sensor for detection of ferrocyanide in Hanford U-Plant 2 simulant solution demonstrated
- Sensor package (microcell and instrumentation) for demonstration on $Fe(CN)_6^{4-}$ in waste tank sample at Hanford developed

Future and Pertechnetate

Extension of Sensor Concept

Addition of Different Classes of Analytes:

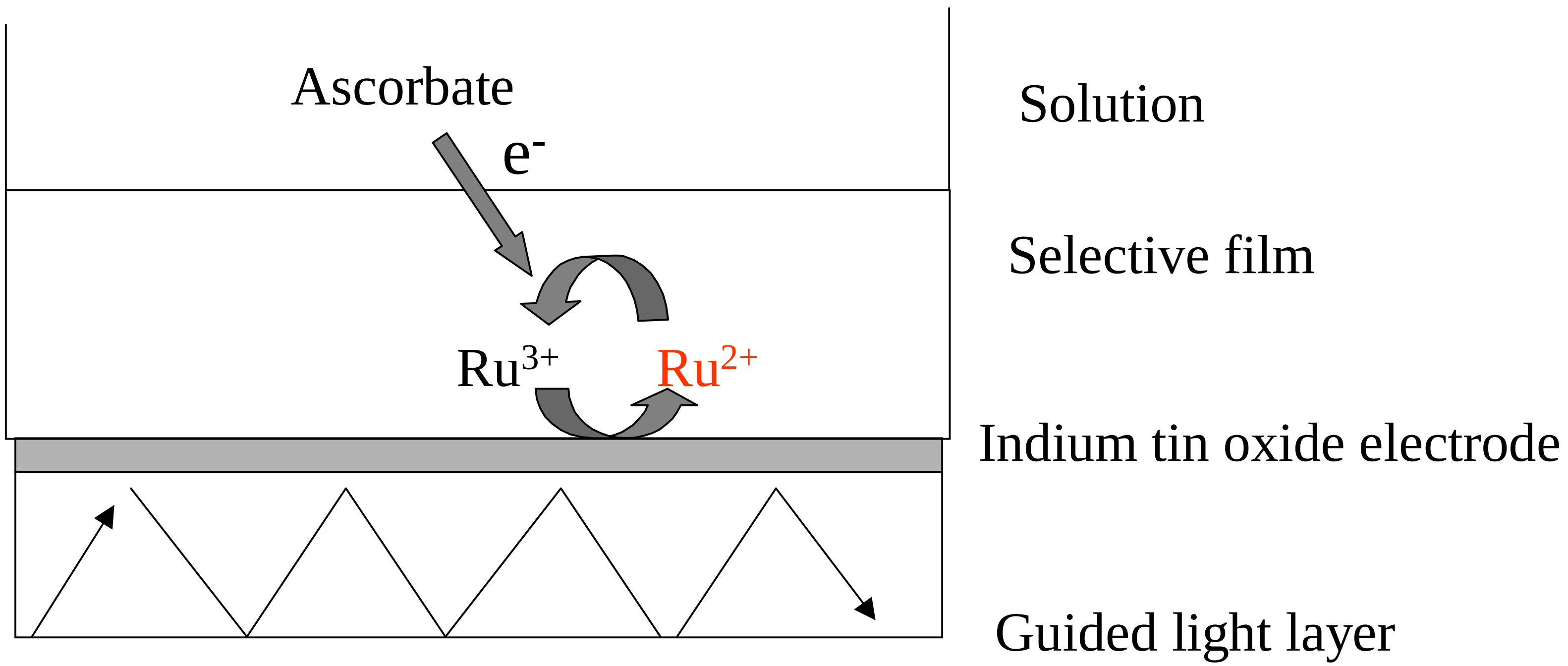
- Detection of analytes that do not exhibit a measurable optical change associated with its electrolysis
- Neutral Analytes
- Complex Redox Couples

Waveguides:

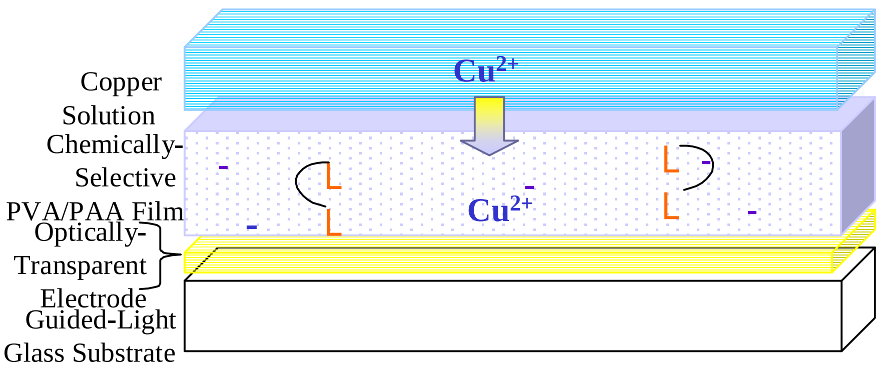
- Increased Sensitivity
- Miniaturization

Mediated detection of ascorbate using $Ru(bipy)_3^{2+/3}$

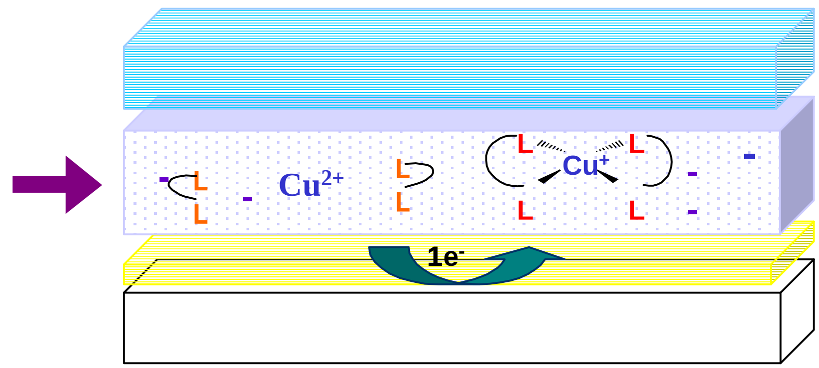
In order for ascorbate to be detected it must (1) transfer e^- to the mediator, (2) the mediator must undergo spectroelectro-chemical modulation in response to the analyte.



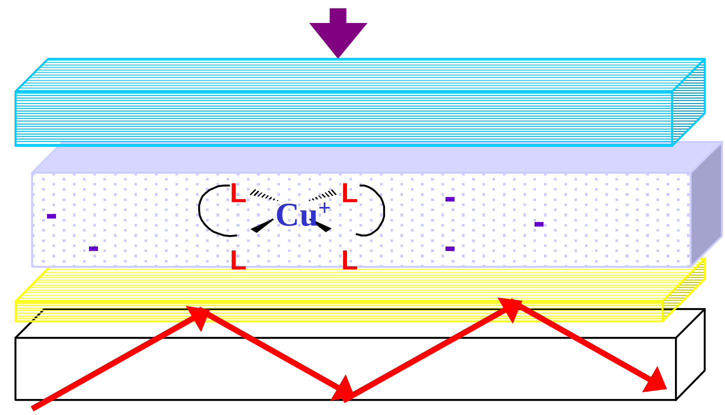
Detection of Cu^{2+}



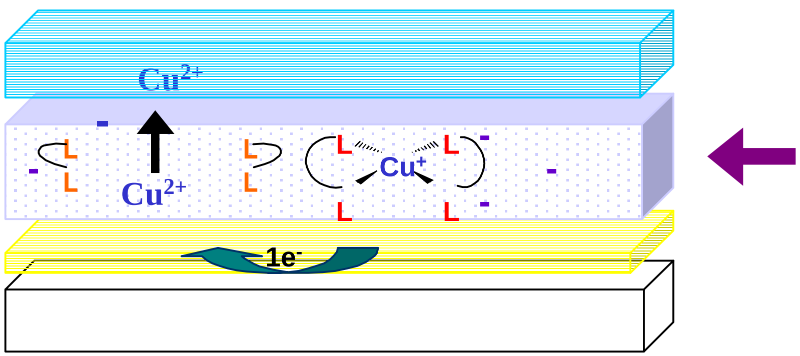
1. Copper Uptake into Chemically - Selective Film



2. Electrochemical Reduction/ Trapping of Cu^{2+} by L (Ligand)



3. Optical Detection of CuL_2^+



4. Release of Cu^{2+} by Oxidation of CuL_2^+

Where, ⟨L L is 2, 9-dimethyl-1, 10-phenantroline

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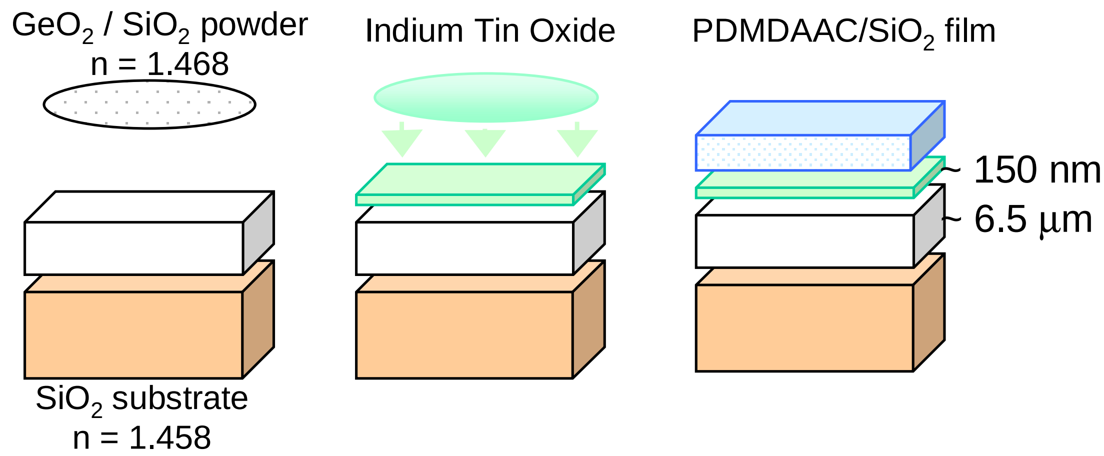
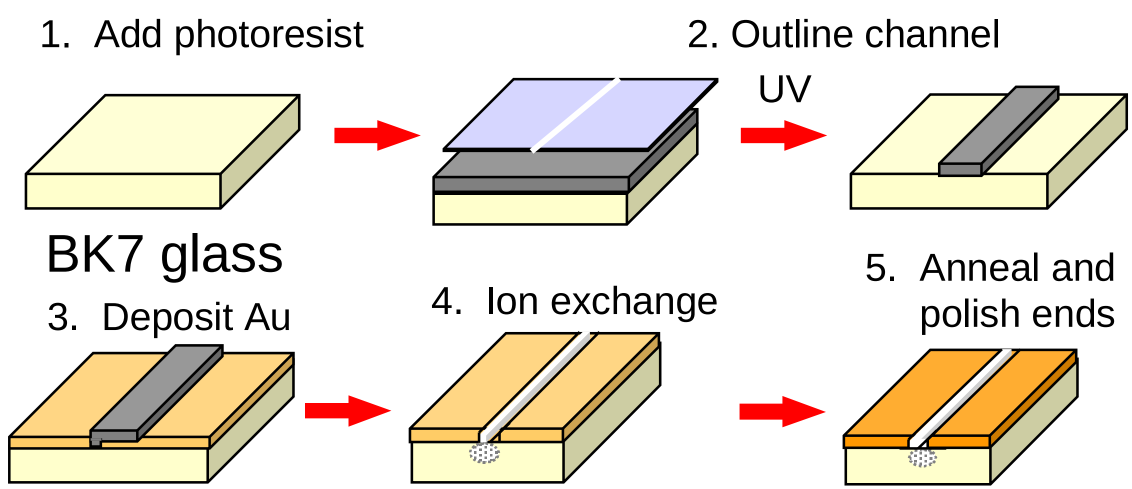
Waveguide Fabrication

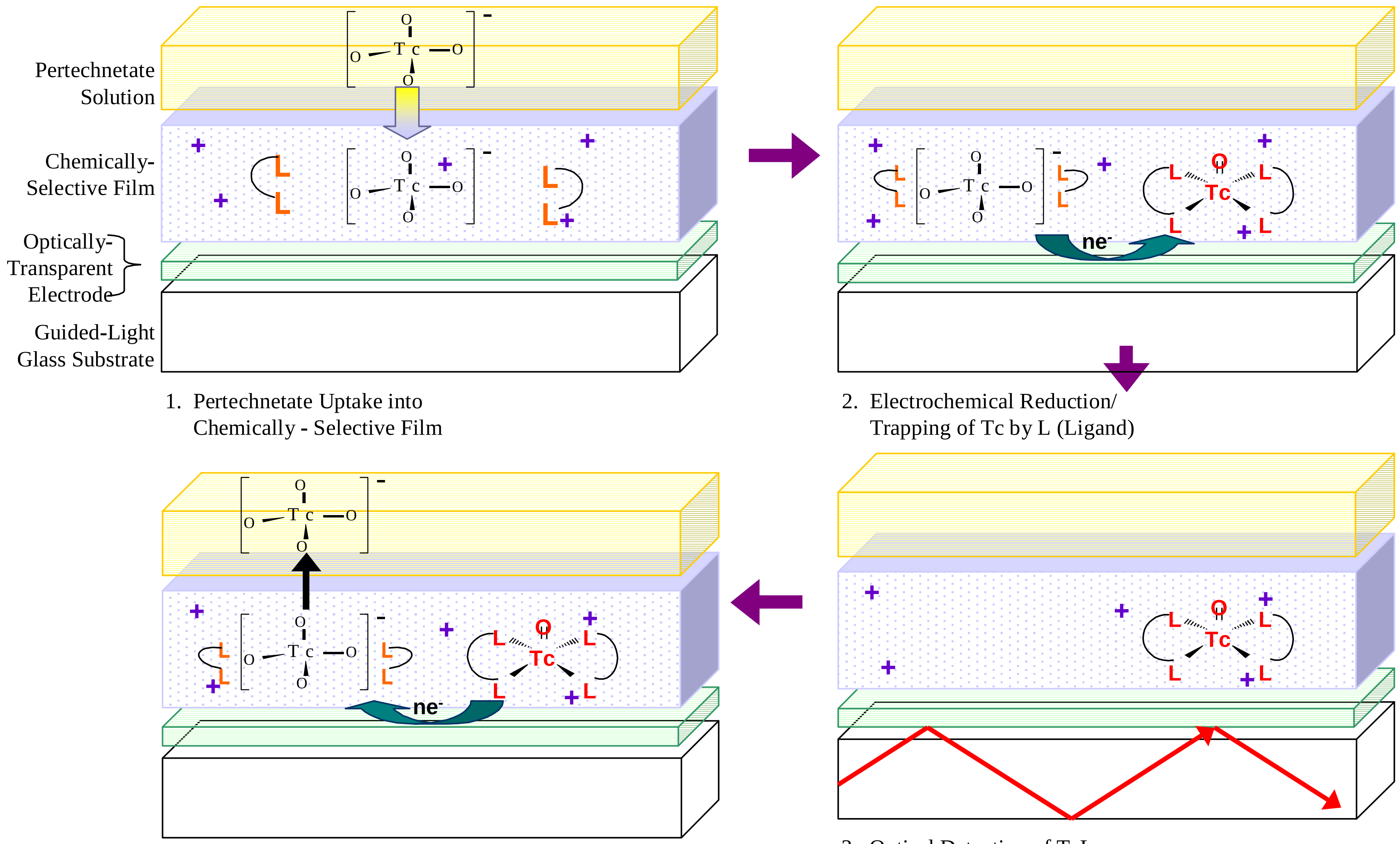
1. Slab



2. Channel



Detection of Pertechnetate



1. Pertechnetate Uptake into Chemically - Selective Film
2. Electrochemical Reduction/ Trapping of Tc by L (Ligand)
3. Optical Detection of TcL
4. Release of Tc by Oxidation of TcL to TcO_4^-

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Ligands Evaluated for Pertechnetate

- Diphosphonates (Methylene diphosphonate, hydroxyethylidene diphosphonate)
- O- donor (gluconate, tartrate, citrate)
- S-donor (dimercapto succinic acid)

Graduate Students

Yining Shi*
Andrew Slaterbeck*
Letian Gao*
Zhongmin Hu*
Mila Maizels
Michael Clager
Susan Ross
Saroj Aryal*
Jennifer DiVirgilio-Thomas
Michael Stegemiller
Mark Wanamaker
Karin Renner (Univ. Bonn)
Tanya Rarog
Imants Zudans
Sean Conklin
Debi Verhoff
Dave Monk

Principle Investigators

William R. Heineman (UC)

Carl J. Seliskar (UC)

Thomas H. Ridgway (UC)

Samuel A. Bryan (PNNL)

Timothy L. Hubler (PNNL)

Undergraduate Students:

Ian Rodway*
Ryan Steinmetz*

Collaborators:

Joseph H. Nevin (Elec. Eng.)
Eberhard Steckan (Univ. Bonn)

* Graduated

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Department of Chemistry

University of Cincinnati

Cincinnati, OH 45221-0172