Field Portable Electrochemical Sensors for Uranium and Other Species in Aqueous Samples

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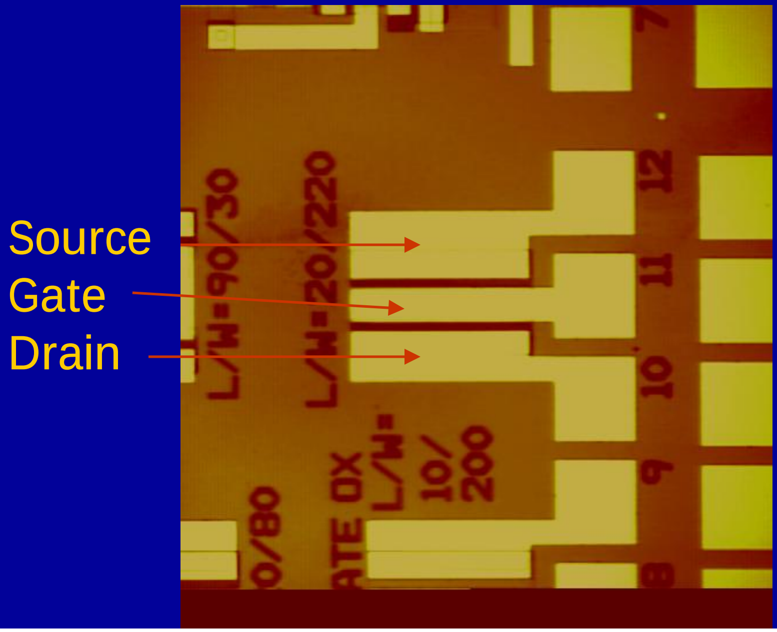
Handheld Portable Sensors Developed in our Lab

- Uranium, plutonium, thorium (actinides)
- Other heavy metals, e.g. mercury, cesium
- VOCs: benzene, toluene
- Biologicals: catechols and catechol amines
- Two operating modes:
  - FET type
  - Potential sweep type (cyclic voltammetry)



Uranium Sensor Project Goals
A Paradigm Case

- Detection of Actinide species in water
- Detection in the field
  - Hand held
  - Autonomous operation w/ data logging
- Non-Proliferation treaty compliance: clandestine deployment
- Highly selective to minimize false signals
- Analytical parameters: real time signal, robust, dynamic range, low detection limit, selective, sensitive

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Remediation Applications for Uranium Detection in Water

- Detection in waste holding tanks, containers
- Process streams
- At a distance from the source: run-off
- Detection in saturated soil
- Monitoring fate and transport in surface and ground waters.

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Existing Methods of Uranium Analysis

- ICP-AAS, x-ray, and fluorescence spectroscopies
- Portable laser ablation method (PNNL)
  - Field portable by heavy vehicle
  - Requires solid sample
- Stripping analysis incl. MEMS device (Wang, ASU)
- Radiochemical methods

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Capability Shortfall in Actinide Detection in Aqueous Media

- These isotopes are alpha-emitters: ^{209}Ac through ^{225}Ac; $^{226}Th \rightarrow\ ^{230}Th$; $^{222}U \rightarrow\ ^{238}U$ (except ^{237}U); most Pu.
- Alpha radiation is low energy; low penetration
- Water quenches alpha signal; alpha emitters are not detected in water by their radiochemical signatures.
- Other current methods rely on lab-based or large, truck “portable” methods
- True hand-held or clandestine methods do not exist
- Only ICP-AA and stripping methods detect U directly in the aqueous medium.
- Other methods require sample de-solvation.

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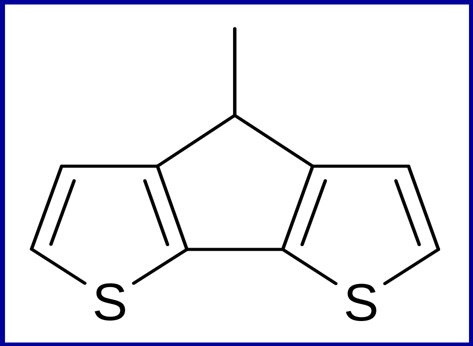
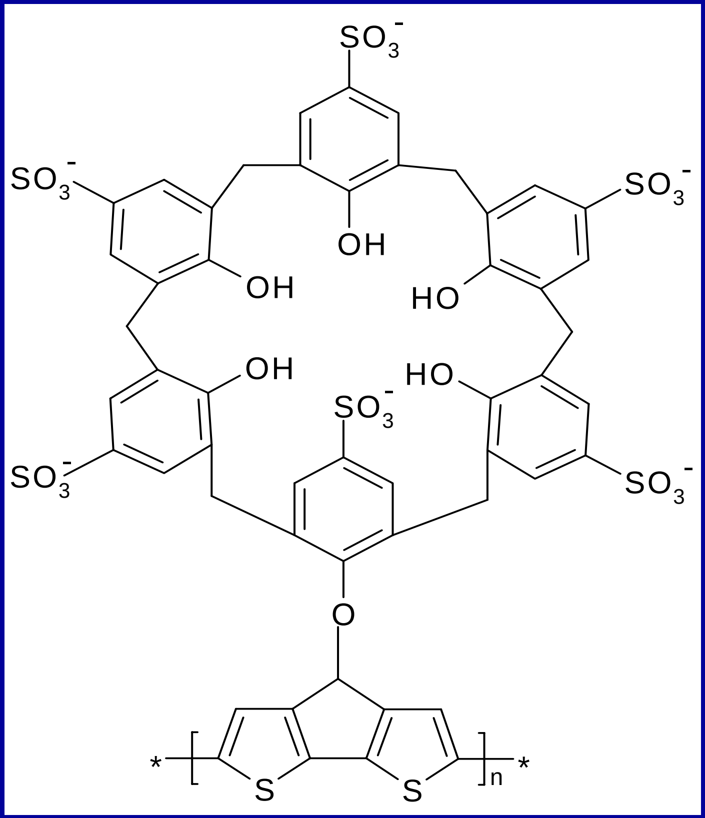
Sensor Concept

- Metal substrate coated with sensing polymer
- Polymer is derivatized
  - Chelating ring for metals
  - MIPs for polyatomic species
- Target analyte binds to polymer
- Electronic or electrochemical property of polymer or target analyte changes.
- Changes are concentration dependent





Advantages of this Sensor

- Treat uranium and other actinides like any other redox active metal
- Detection based on redox and complexation chemistries, not radiochemical signature.
- Direct chemical-to-electronic signal transduction.
- No moving parts.
- Small sensor, simple, robust, inexpensive; hand-held or autonomous operation is possible.
- Both our chem-FET and CV sensors are much less complex than MEMs stripping method.

A Thiophene-Based Chelating Polymer

- Selective receptor sites for target analyte
- Electrochemically polymerized
  – Film thickness can be varied over wide range
- Non-hygroscopic: Thiophene does not hydrogen-bond
  – Polymer does not swell or change morphology in aqueous or humid environments
  – Polymer does not de-laminate in water
- Semiconducting polymer
  – Direct chemical-to-electronic transduction of signal
  – Does not require photon or particle detection
- Mechanically and chemically robust
  – Inert to strong mineral acids, bases and most organic solvents
  – Has to be burned off of platinum substrate!

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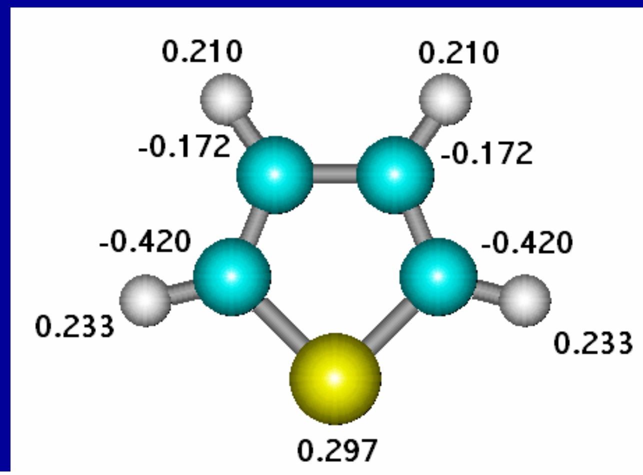
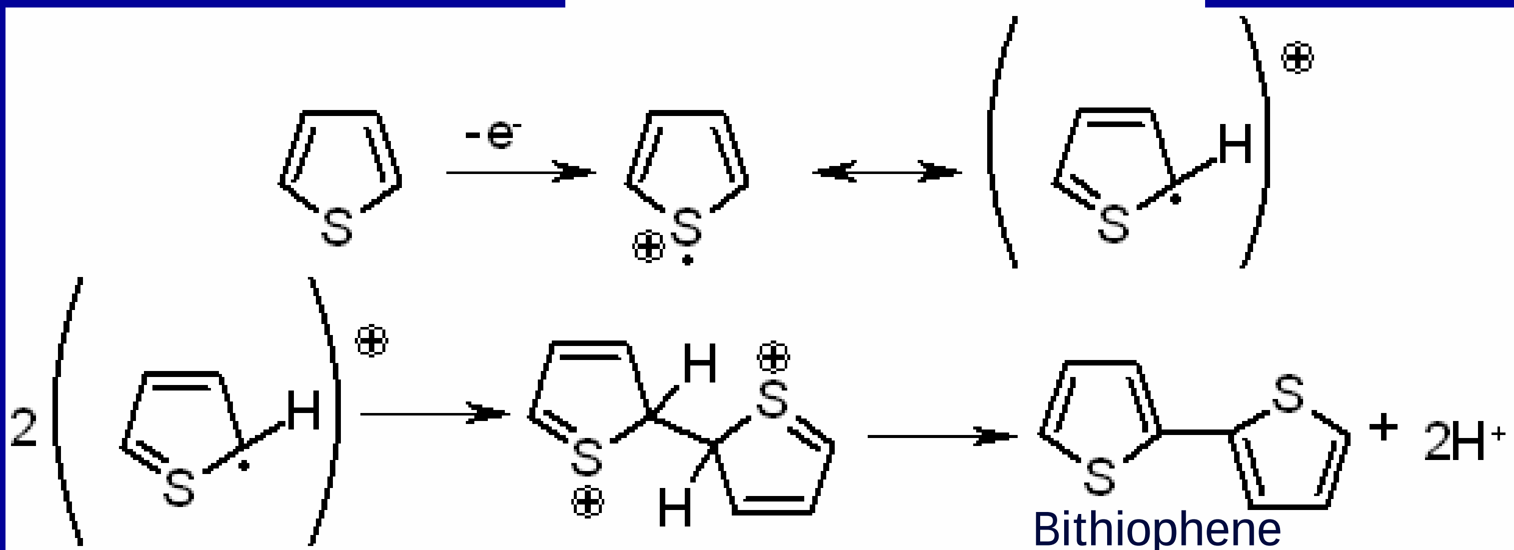
Thiophene Polymerization

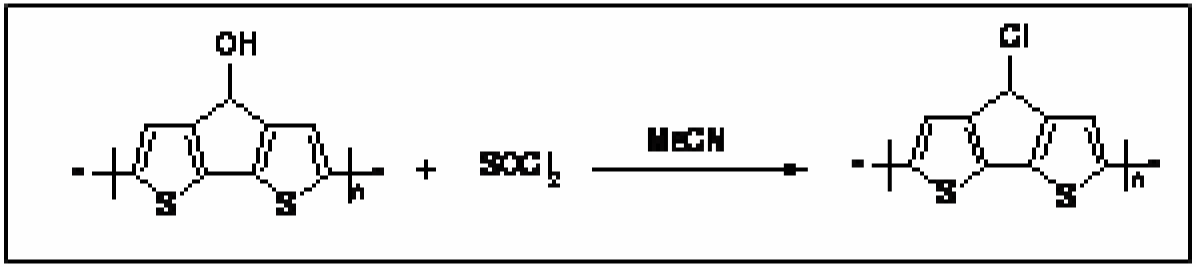




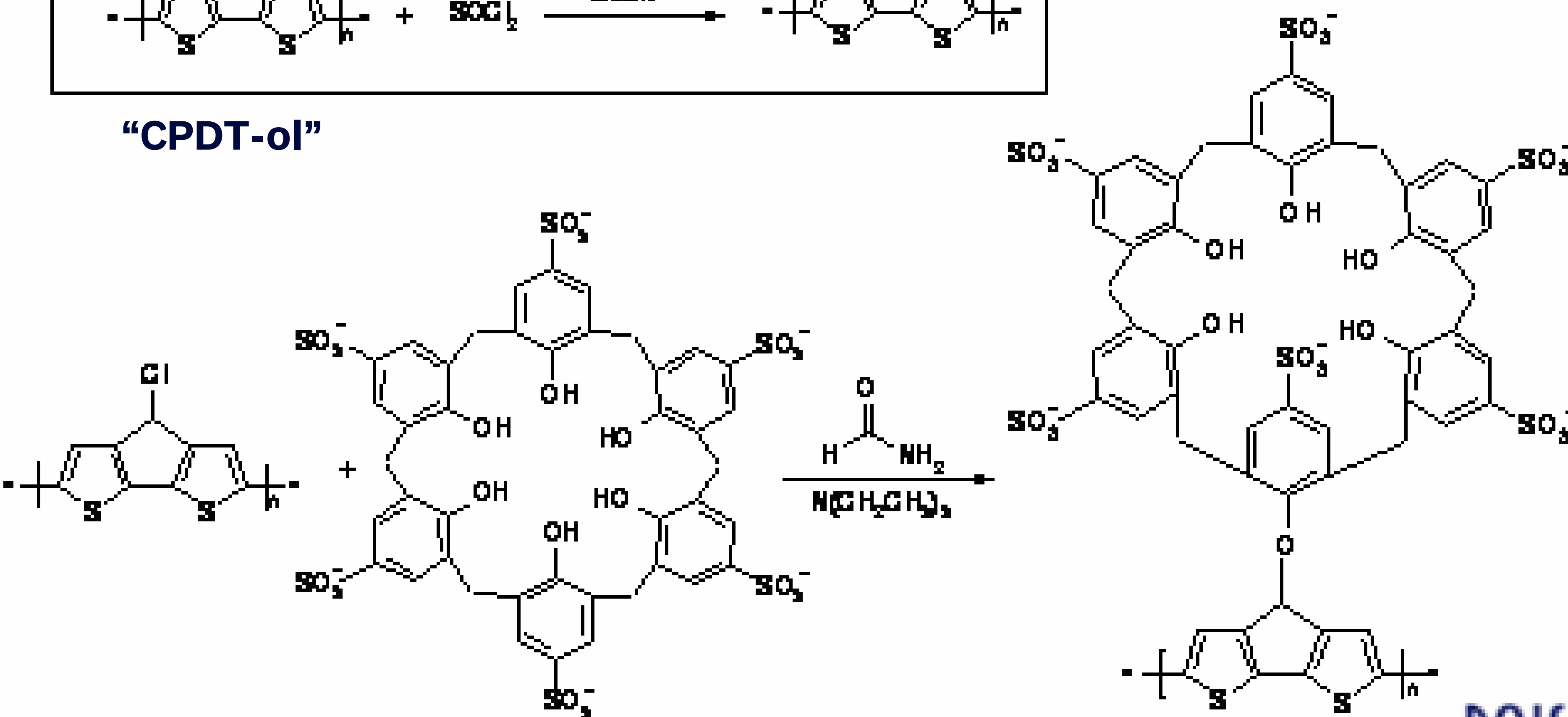
Advantages of Chelating Polymer

- Polymer is conductive: direct chemical-to-electronic signal transduction
- Binding site is covalently attached
  - Does not readily diffuse away
  - Signal is stable with time
- Binding site selectivity minimizes chemical interferences.
- Analyte is preconcentrated on surface
  - Lower detection limits
  - Greater sensitivity

Synthesizing the Chelating Polymer



“CPDT-ol”

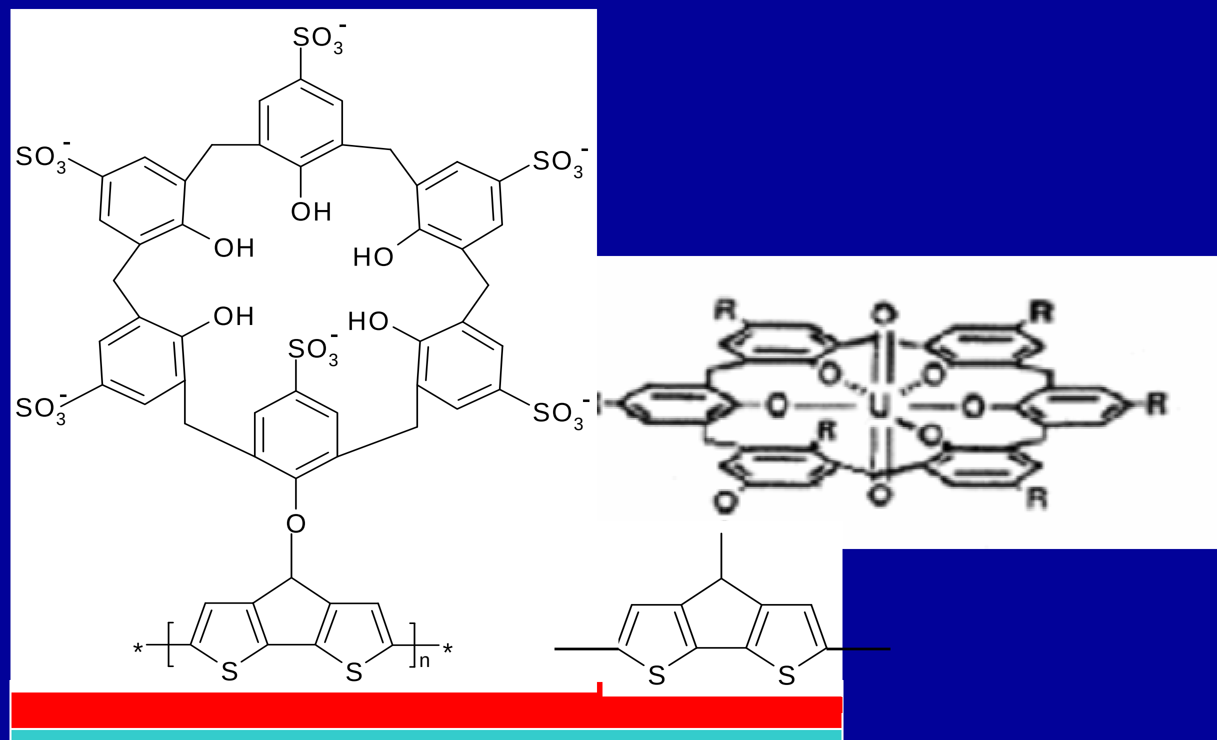


4-sulfonic calix[6]arene

The Polymer Coated Electrode Surface

Chelating ring shown free, and with a uranyl ion bound

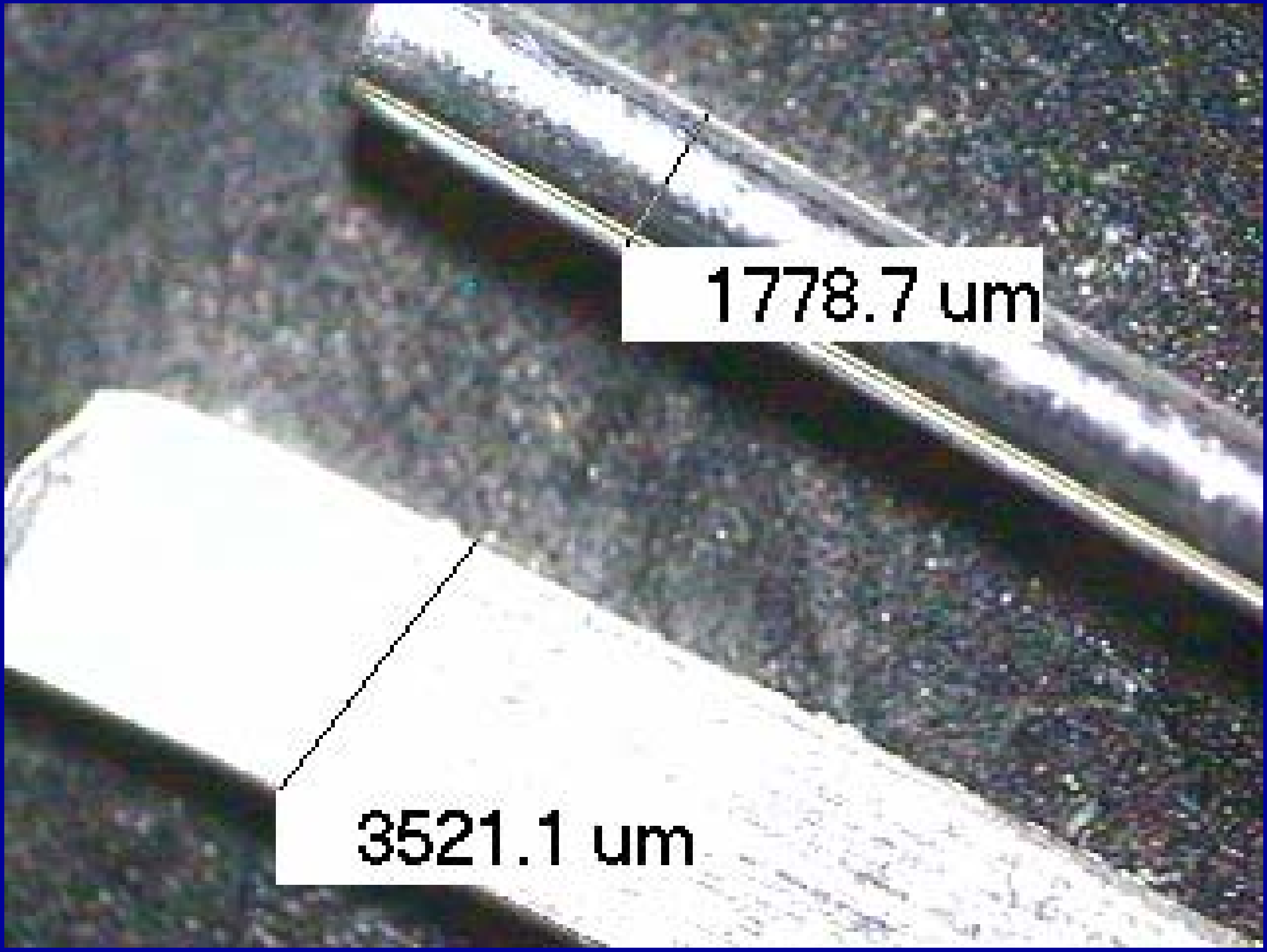
K_f with $UO_2^{2+} = 10^{26}$



Electrode Surface

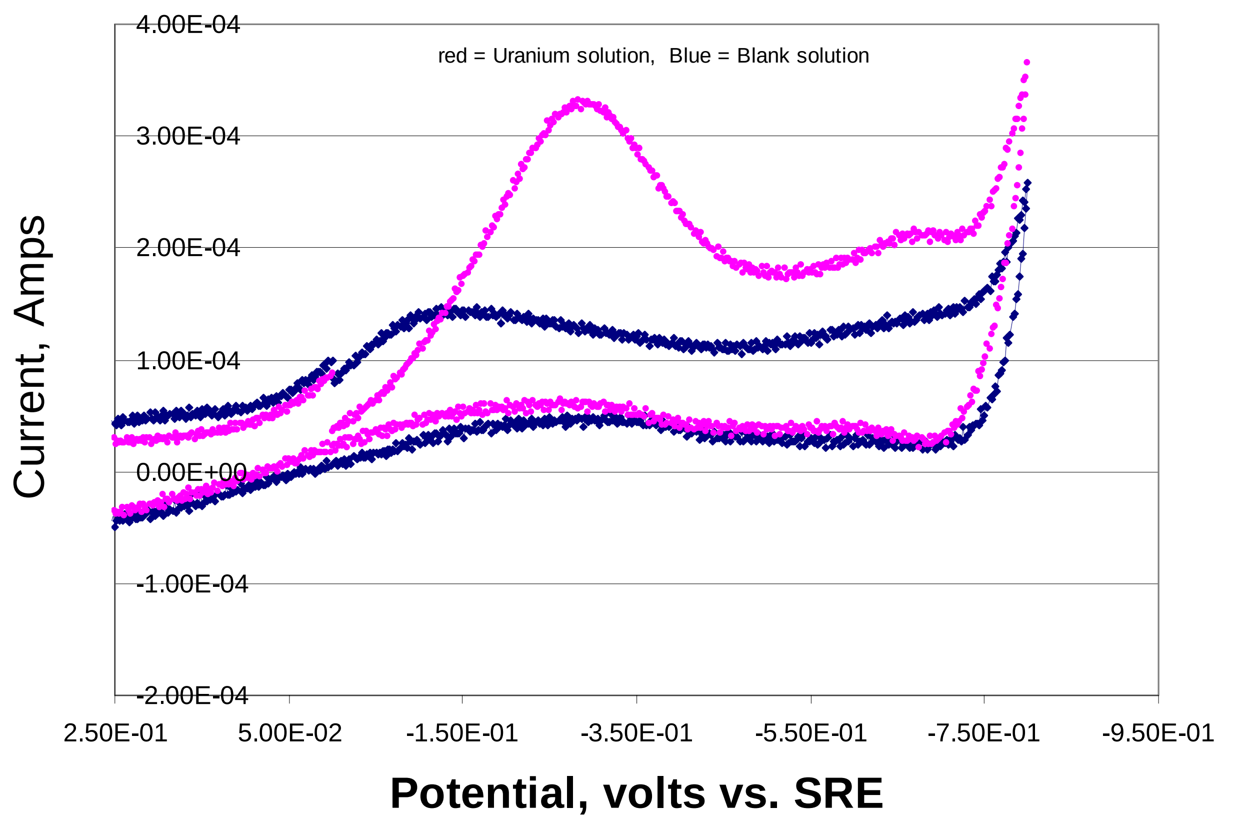
Bulk polymer, poly(2,2’-bithiophene)

Pressed Wire Electrode Blank for CV Mode Sensors

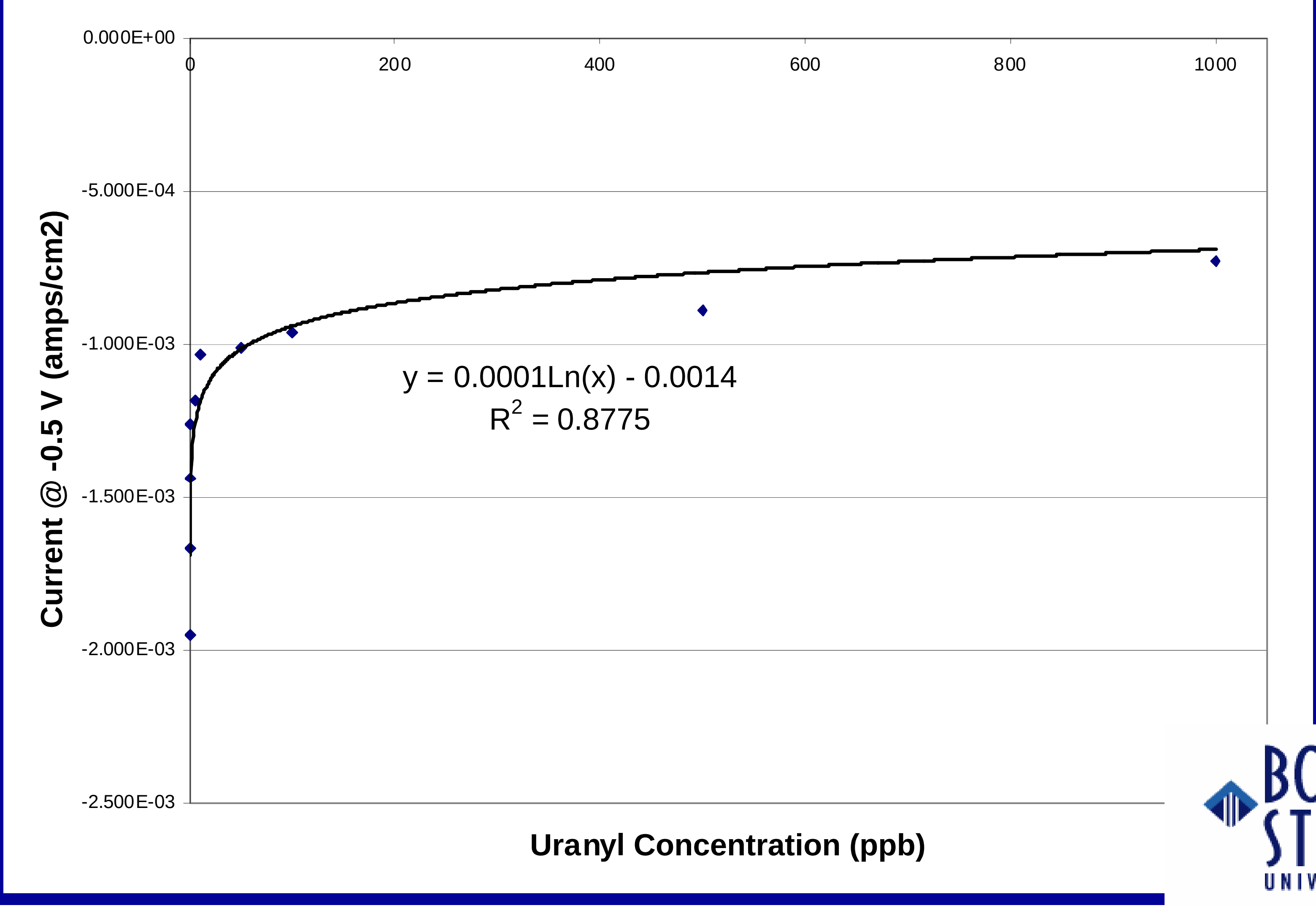


Polymer Coated Electrodes for CV Mode Sensors

Cyclic Voltammogram of UO_2^{2+} Response of Chelating Uranium Sensor



Response of Uranium Sensor with varying concentration of UO_2^{2+}



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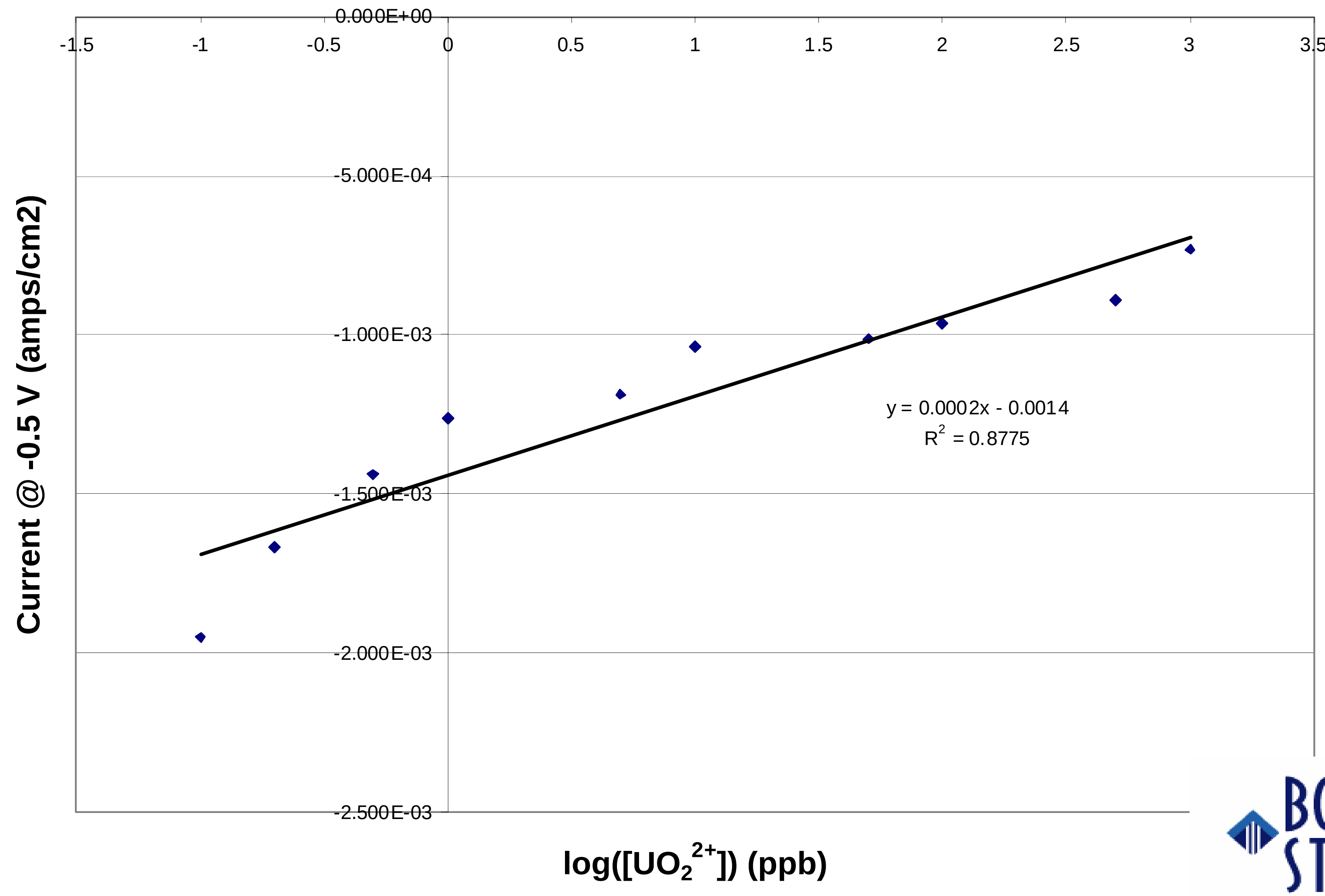
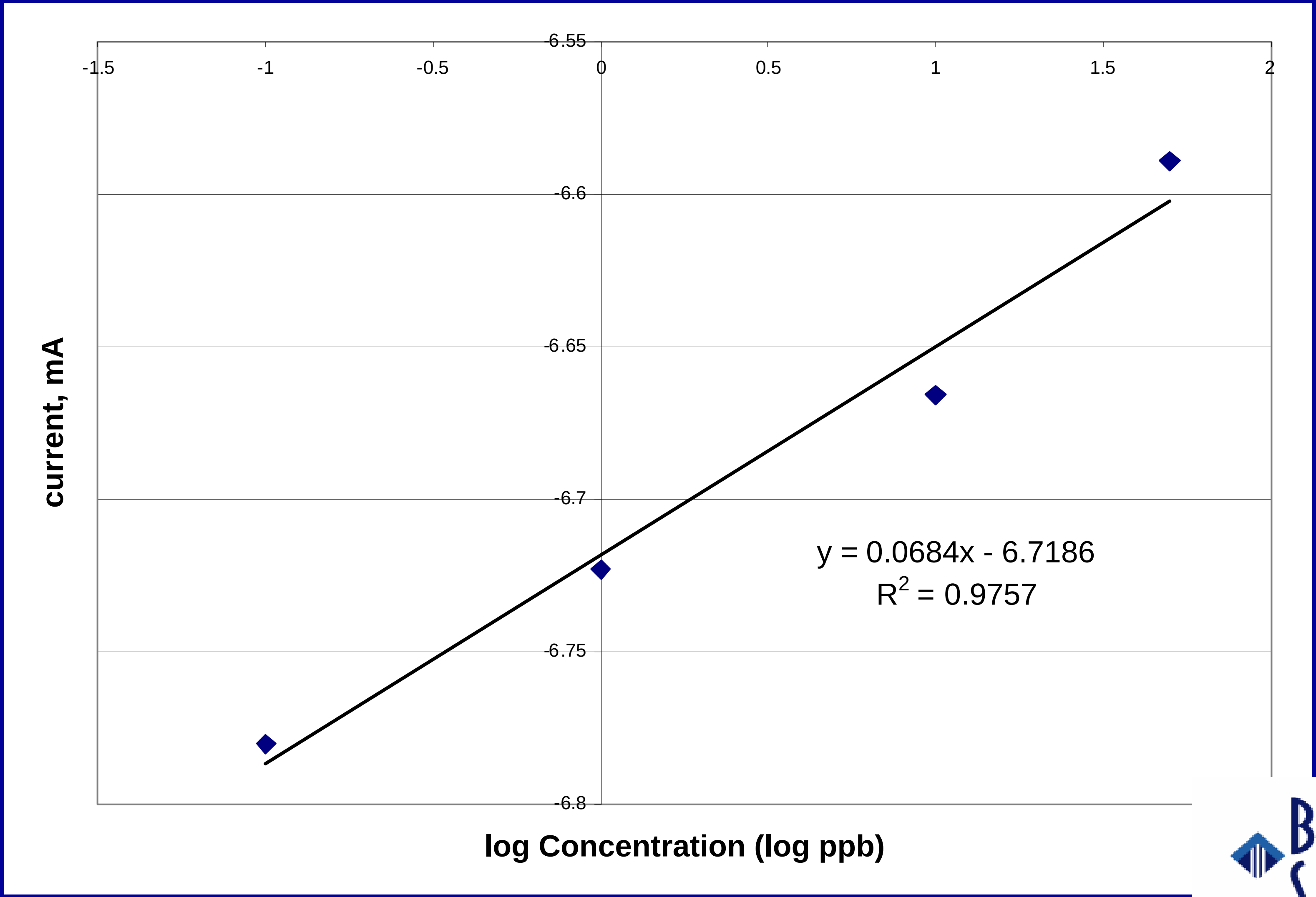
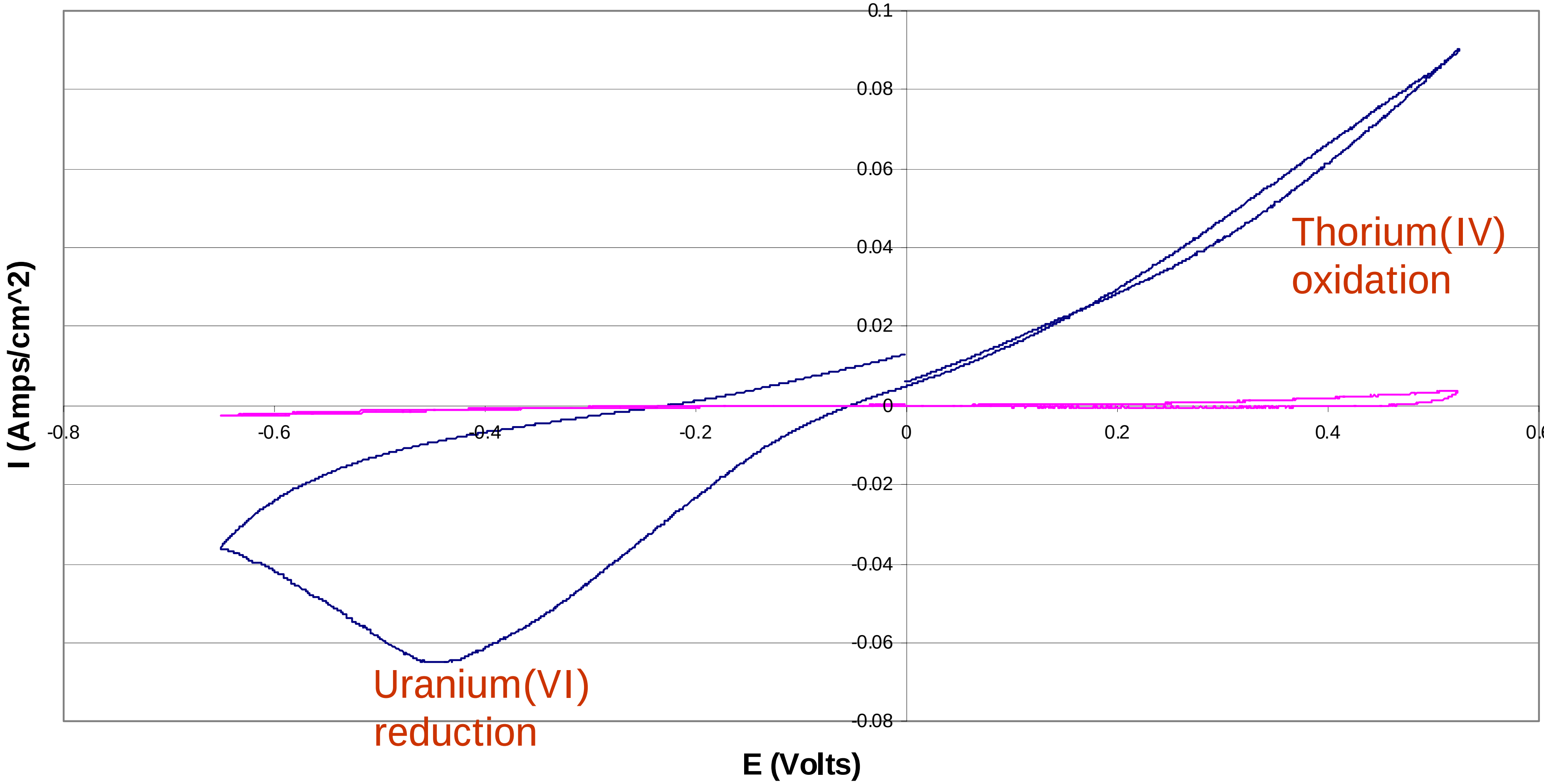
Current Response as Function of Concentration



Thorium Reduction Current vs. Concentration



50 ppb ThO_2^{+} with 50 ppb UO_2^{2+} and H_20 Baseline



Actinide Sensor Detection Limits

By direct measurement of standards

Uranium detection limit = 0.1 ppb

Thorium detection limit = 0.1 ppb

By 3σ calculation of noise analysis

Detection limit on the order of 0.01 ppb

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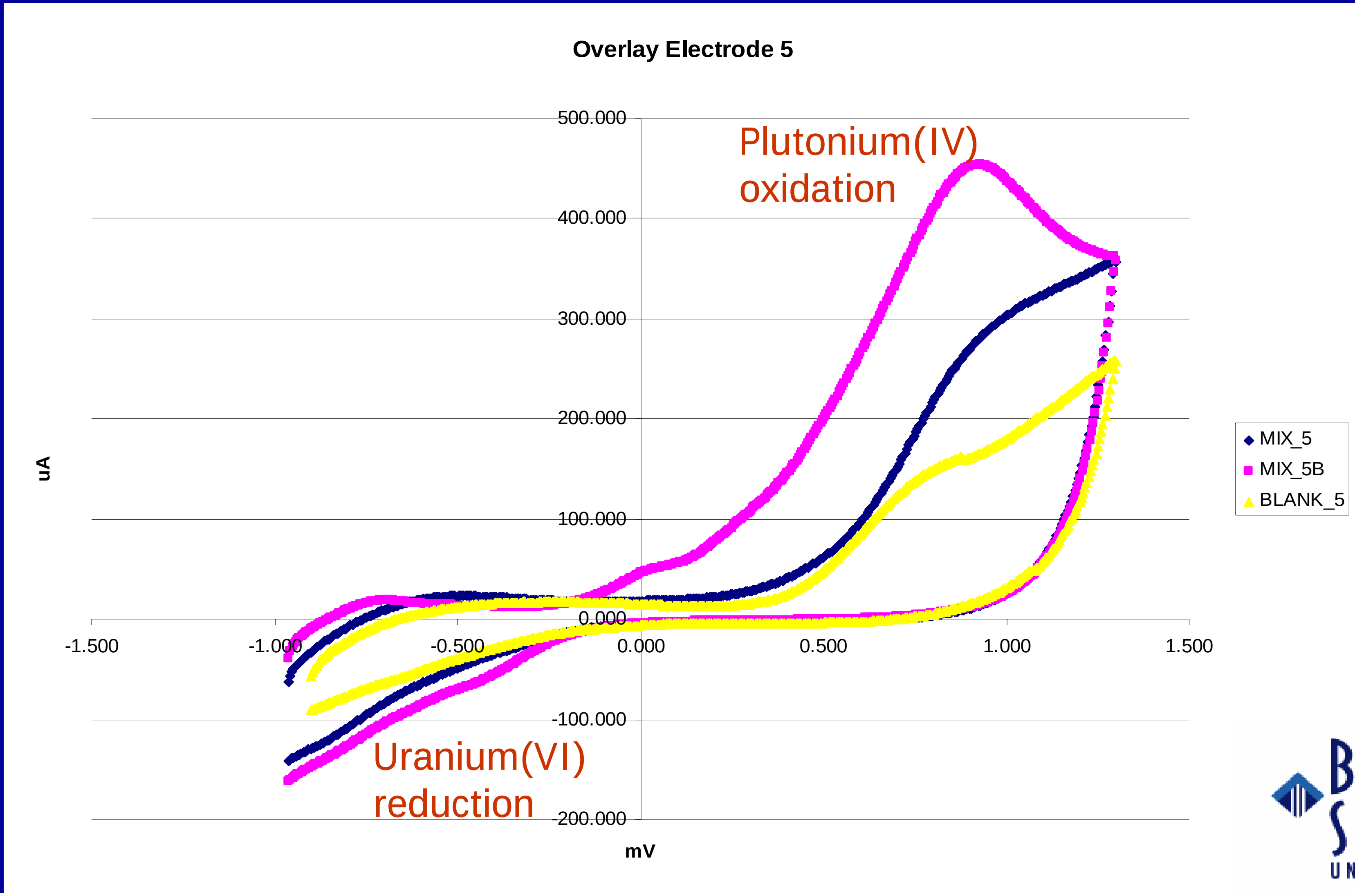
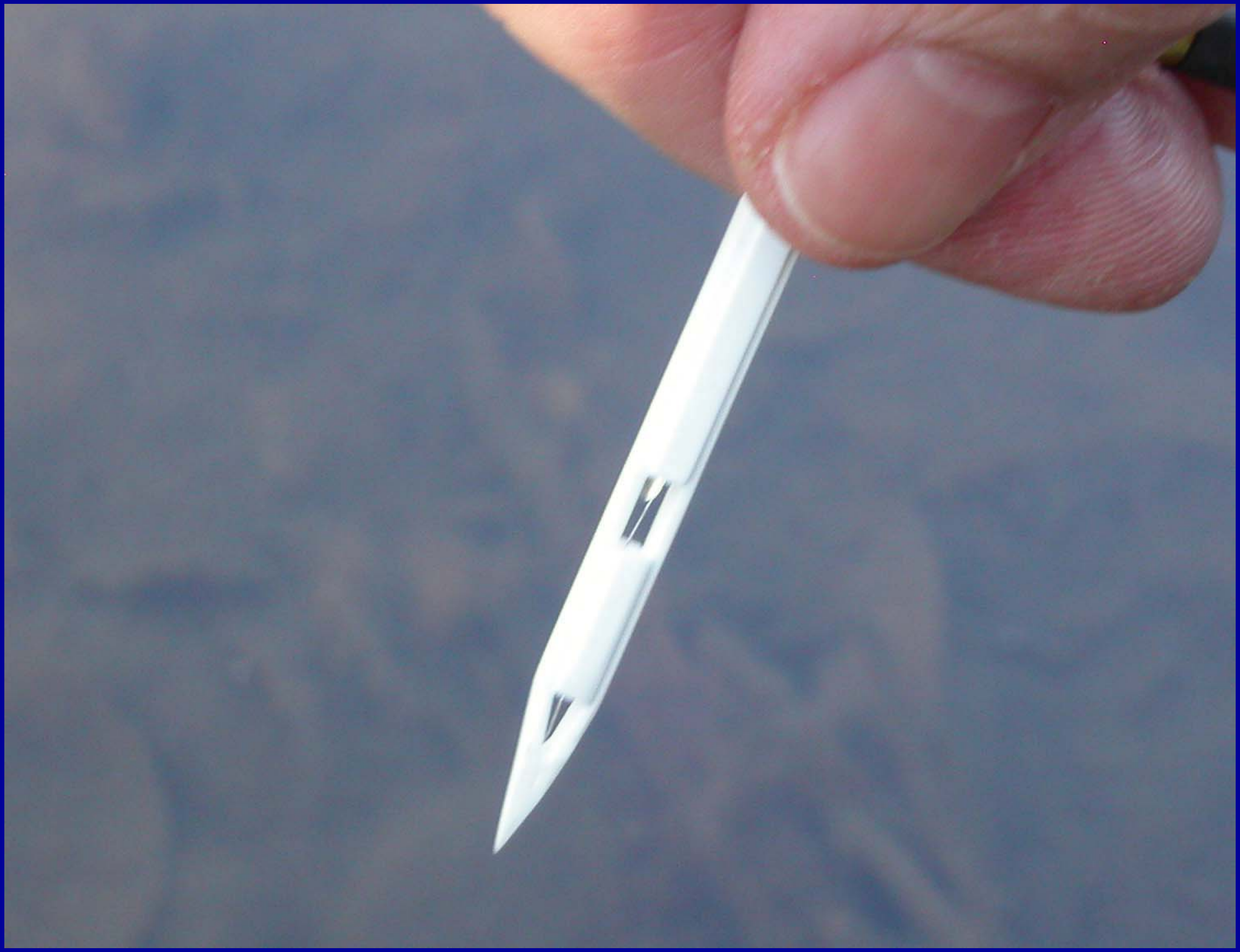
Plutonium Detection
Field test at DOE-NV test site



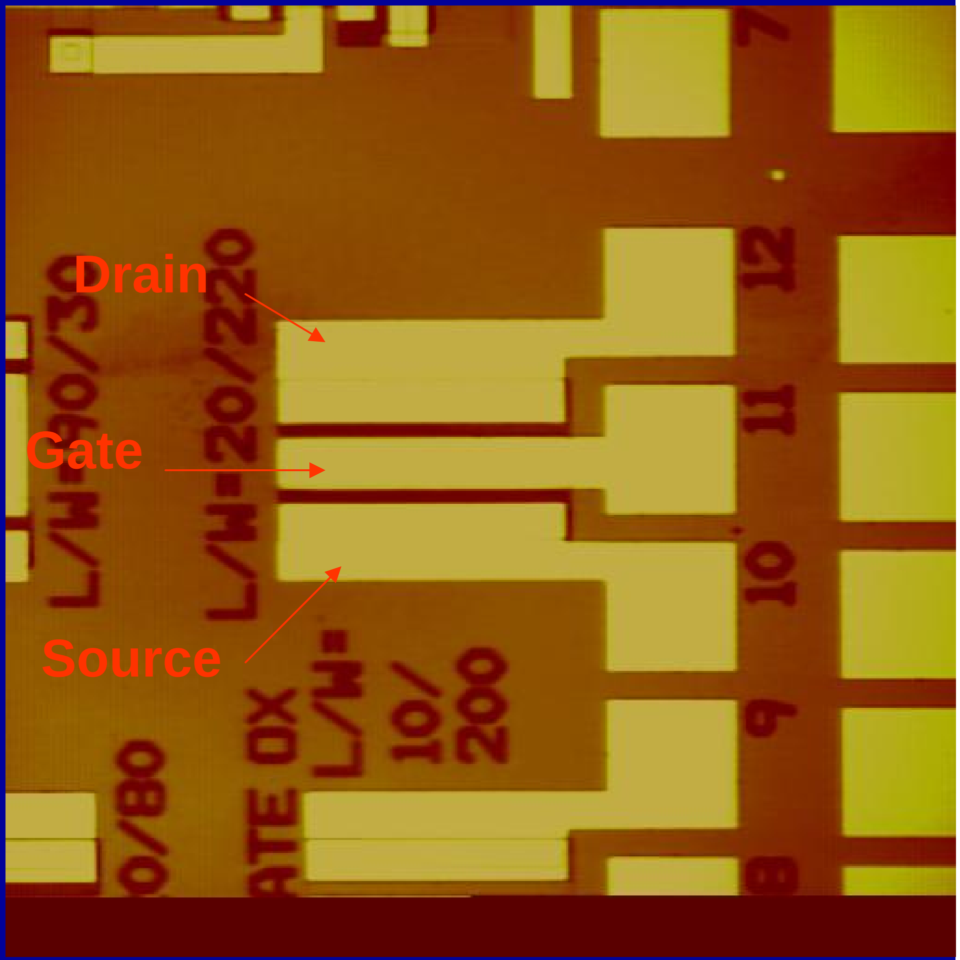
A Demonstrated Field Portable System
Potentiostatic Mode of Operation

3-Electrode Uranium Sensor Tip With Sliding Protective Window



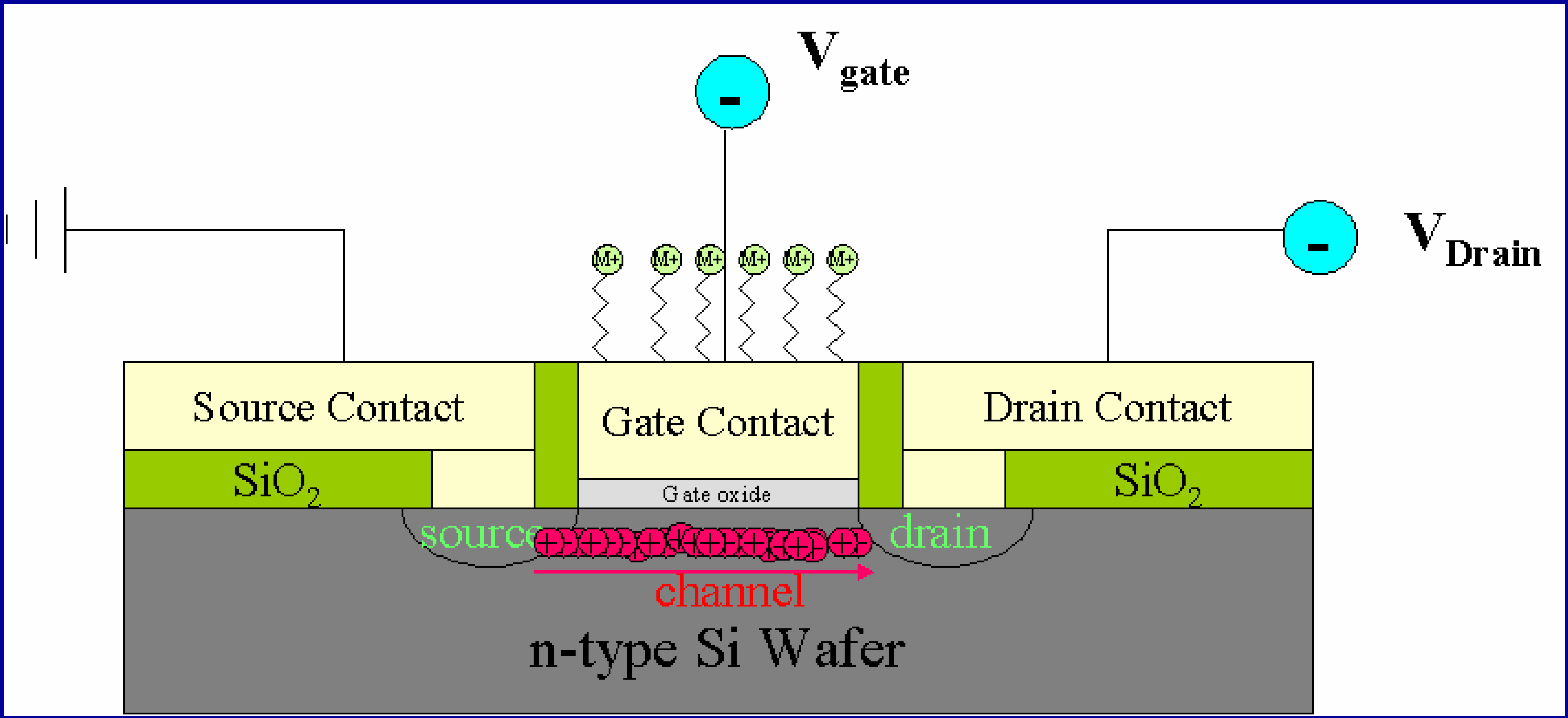
A Field Effect Transistor

- **An optical micrograph showing the gate, source, and drain on a pMOSFET device.**
- **The Scale is L/W 20μm/220μm**



Courtesy of W.B. Knowlton, Ph.D. Dept of Electrical and Computer Engr. BSU

A Field Effect Transistor



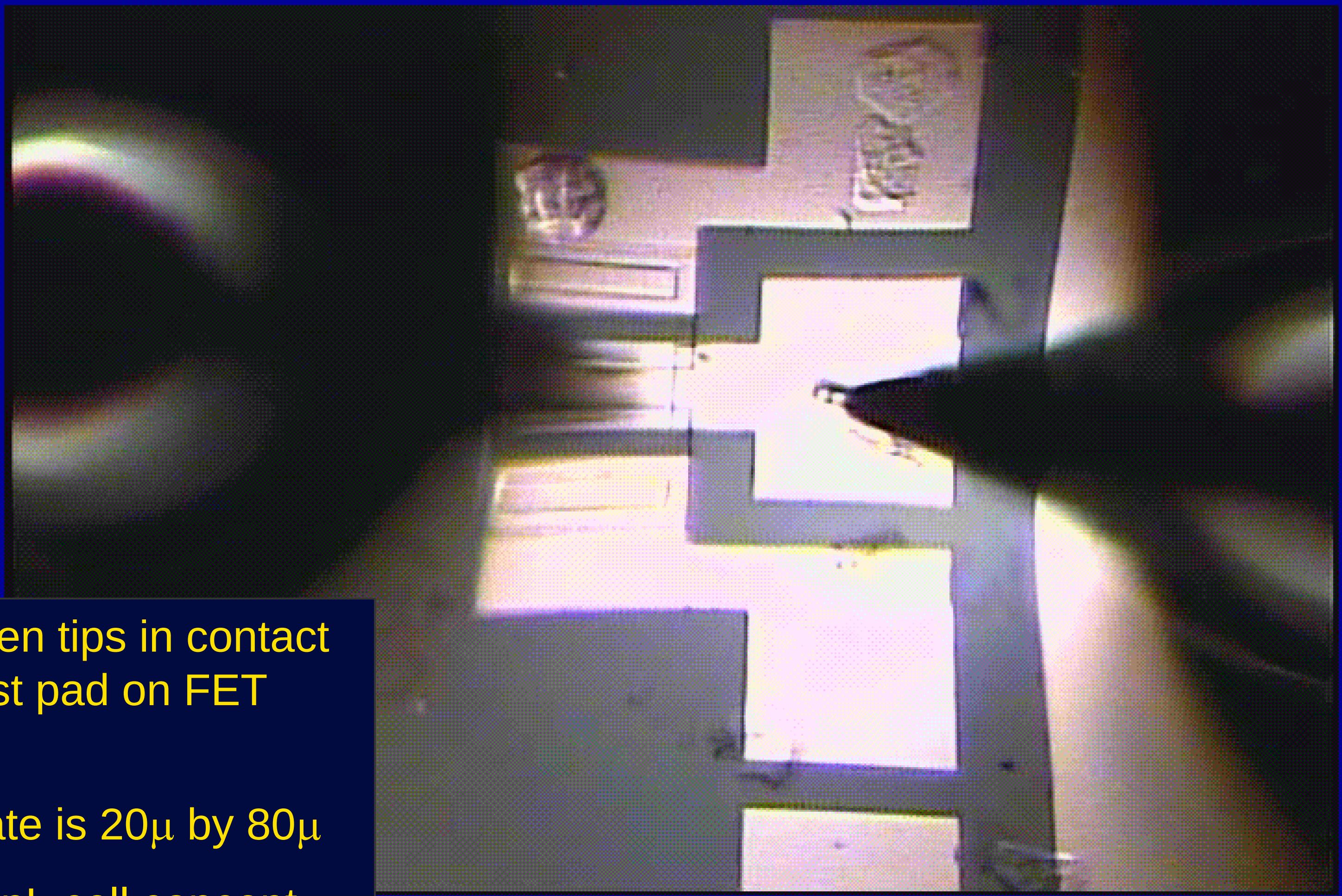
Courtesy of W.B. Knowlton, Ph.D. Dept of Electrical and Computer Engr. BSU

Nanoliter Deposition Technique

(Patent Pending)

- 400 nL droplet on gate
- Polymer coats only surfaces in electrical contact with microprobe.
- No masking or photolithography required.
- Different sensing polymers could be applied to different devices on same wafer
- Quick, easily automated.
- Low cost, minimal waste, eco-friendly

Electrodeposition of Uranium Sensing Polymer



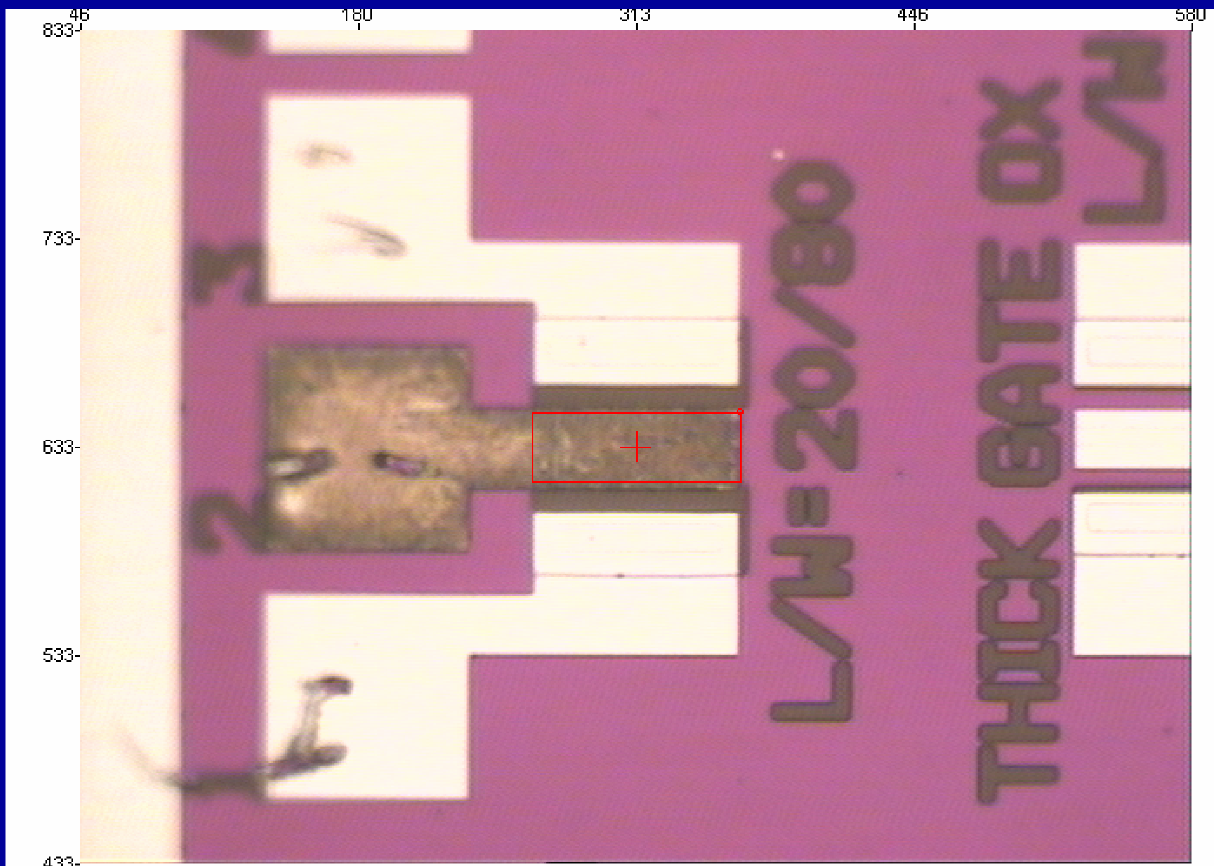
Tungsten tips in contact with test pad on FET device

This gate is 20μ by 80μ

Use of nL cell concept

Courtesy of W.B. Knowlton, Ph.D. Dept of Electrical and Computer Engr. BSU

Micrograph of Coated FET Sensor

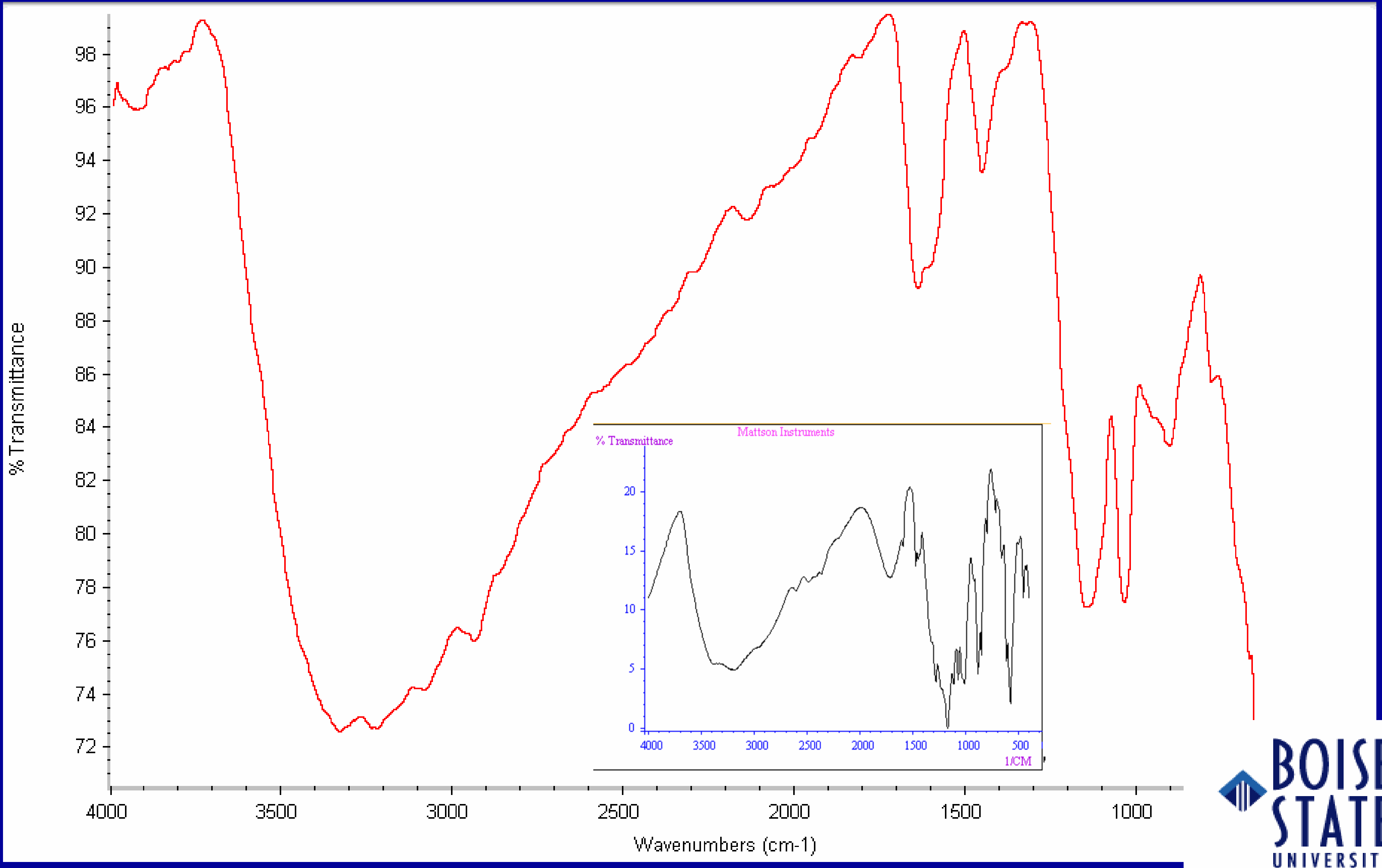


20 µM by 80µM gate metal

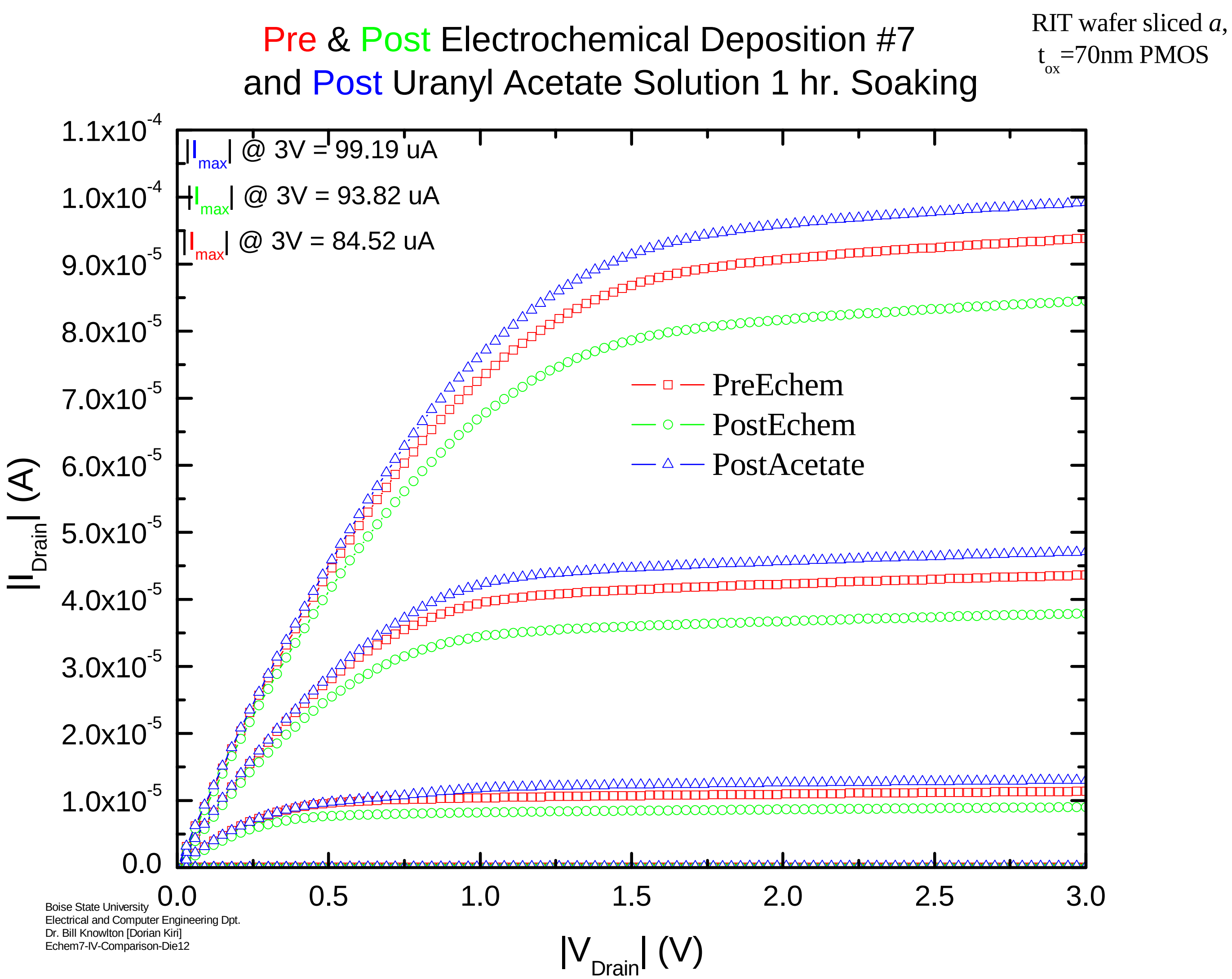
Image Taken on IR-microscope

Courtesy of W.B. Knowlton, Ph.D. Dept of Electrical and Computer Engr. BSU

FTIR of Calix[6]arene on FET gate



FET Response: I_D vs. V_D Curves



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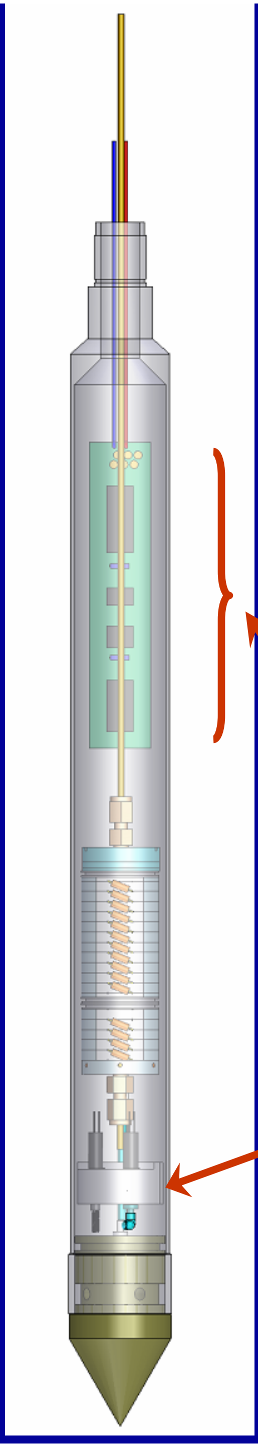
Cone Penetrometer



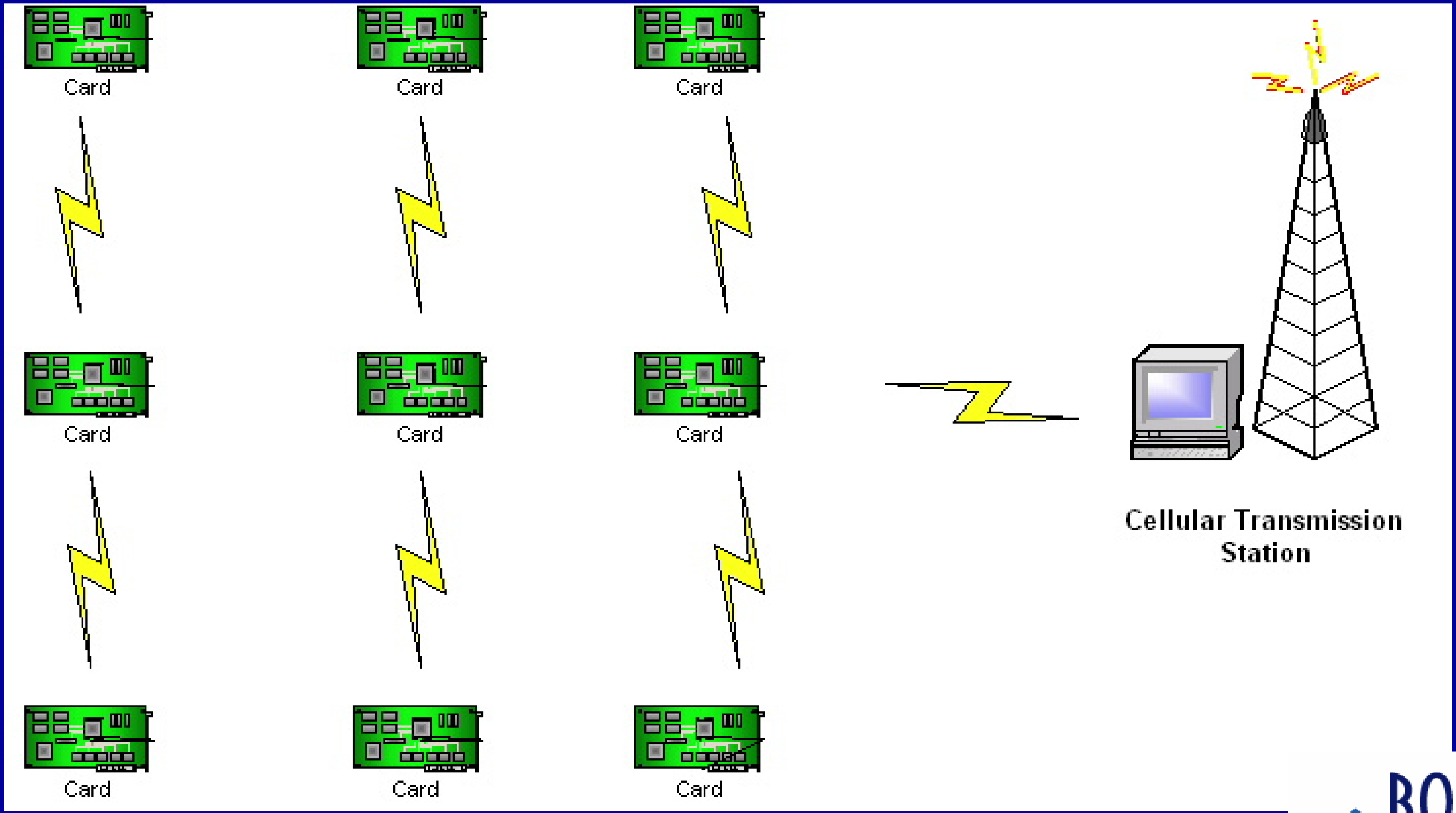
Push probe for shallow geologic subsurface

Power supply
Data handling and
Data transmission units

Both FET and potentiostatic mode sensors in housing

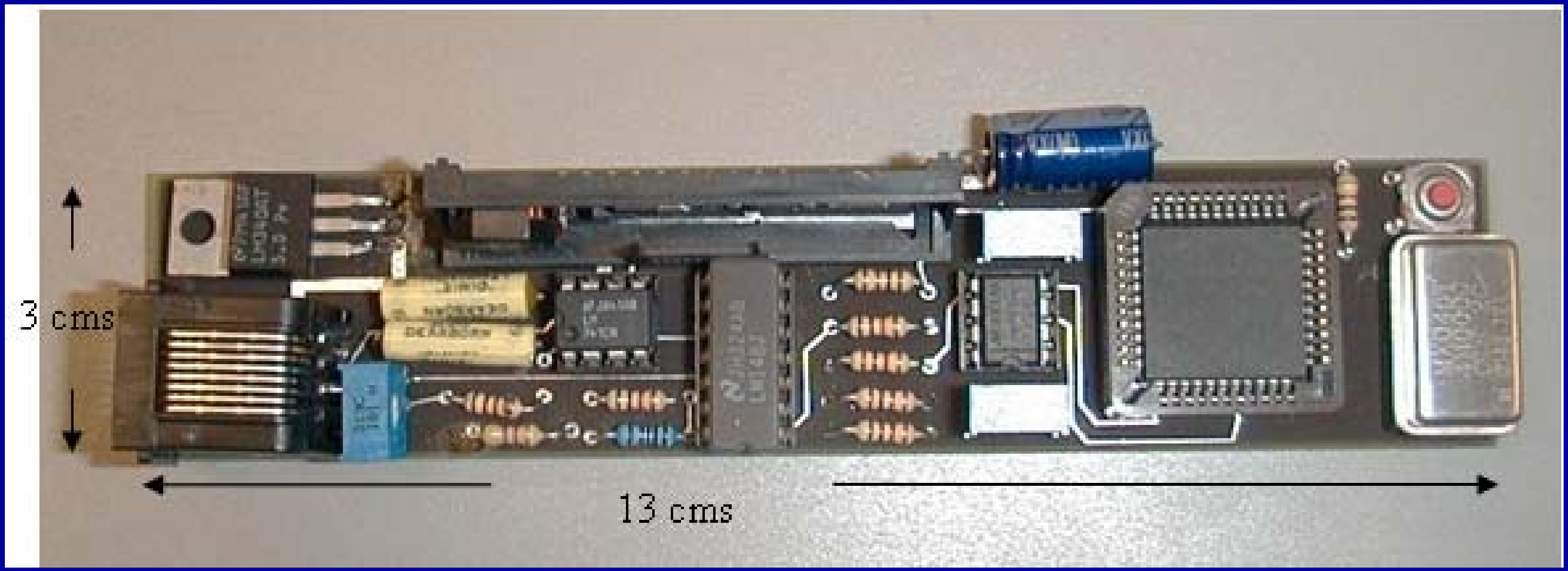
Courtesy of Molly Gribb, Ph.D. Dept. Civil Engr. Boise State Univ

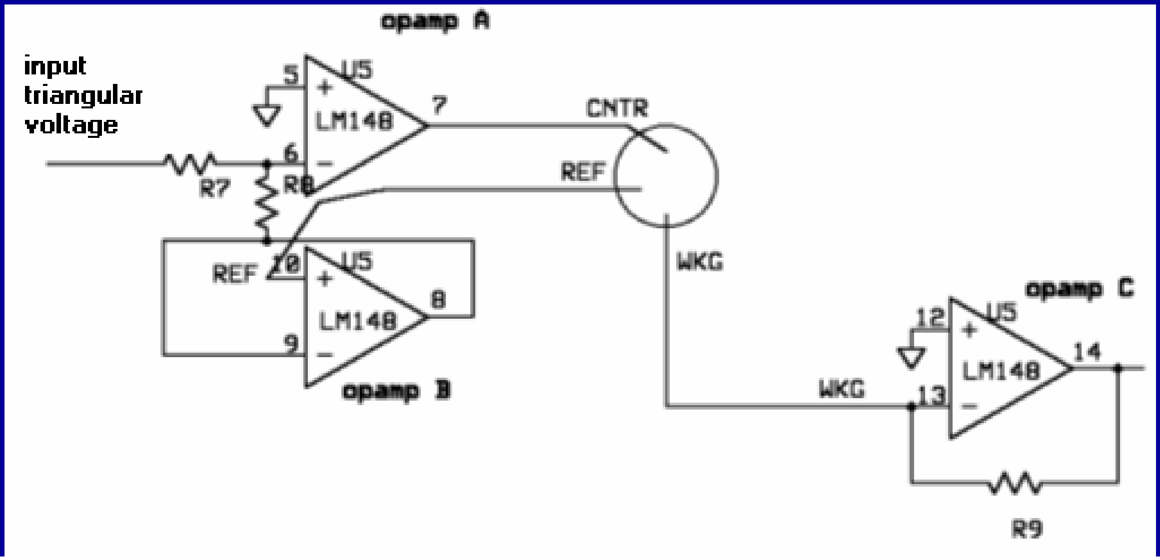
Possible Sensing Array Scenario



Courtesy of Dr. Joe Hartman, Dept. Electrical and Computer Engr., BSU

Breadboard Potentiostat



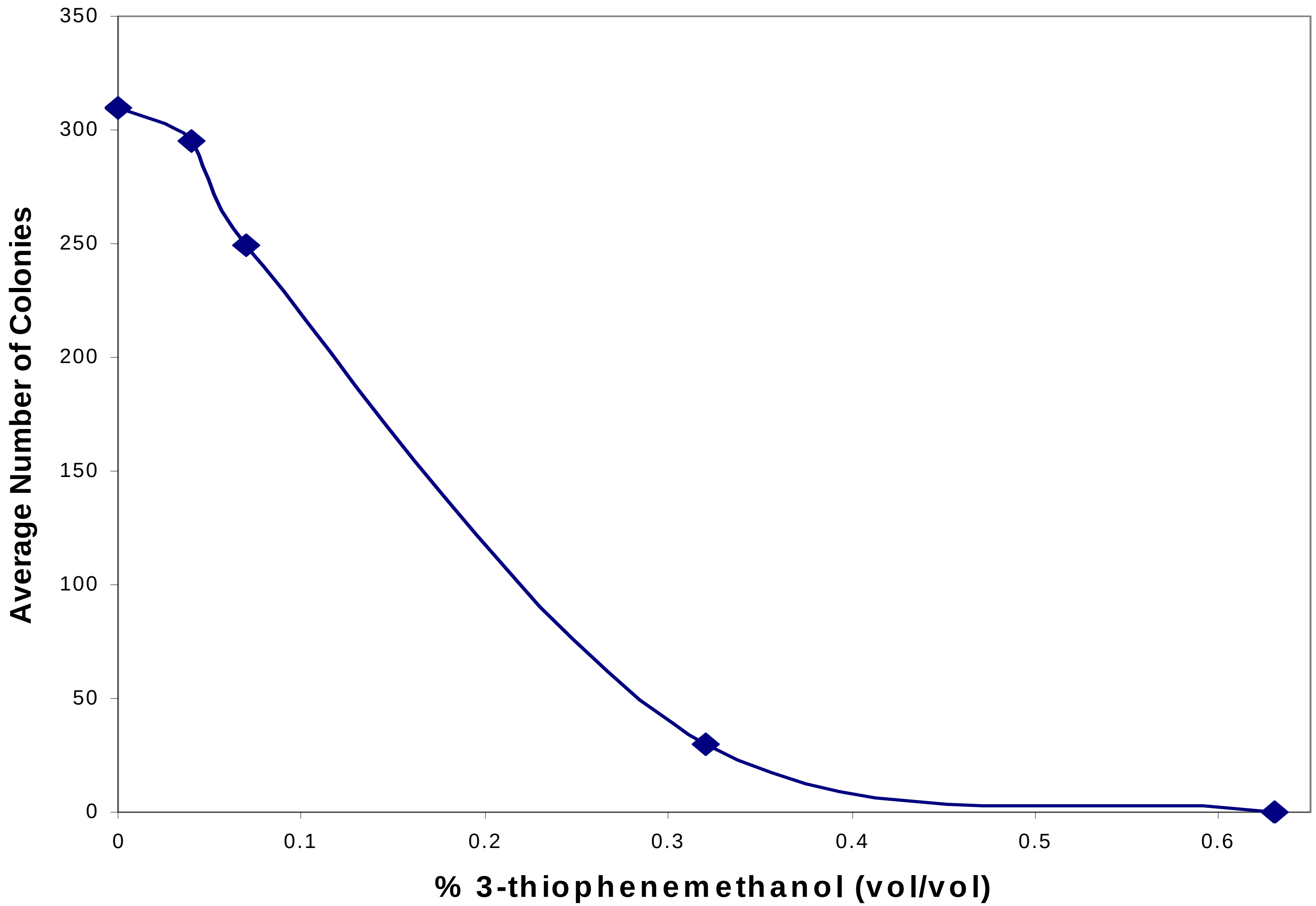


Designed by
A.V. Gopinath
MS thesis

Features of the Breadboard Potentiostat

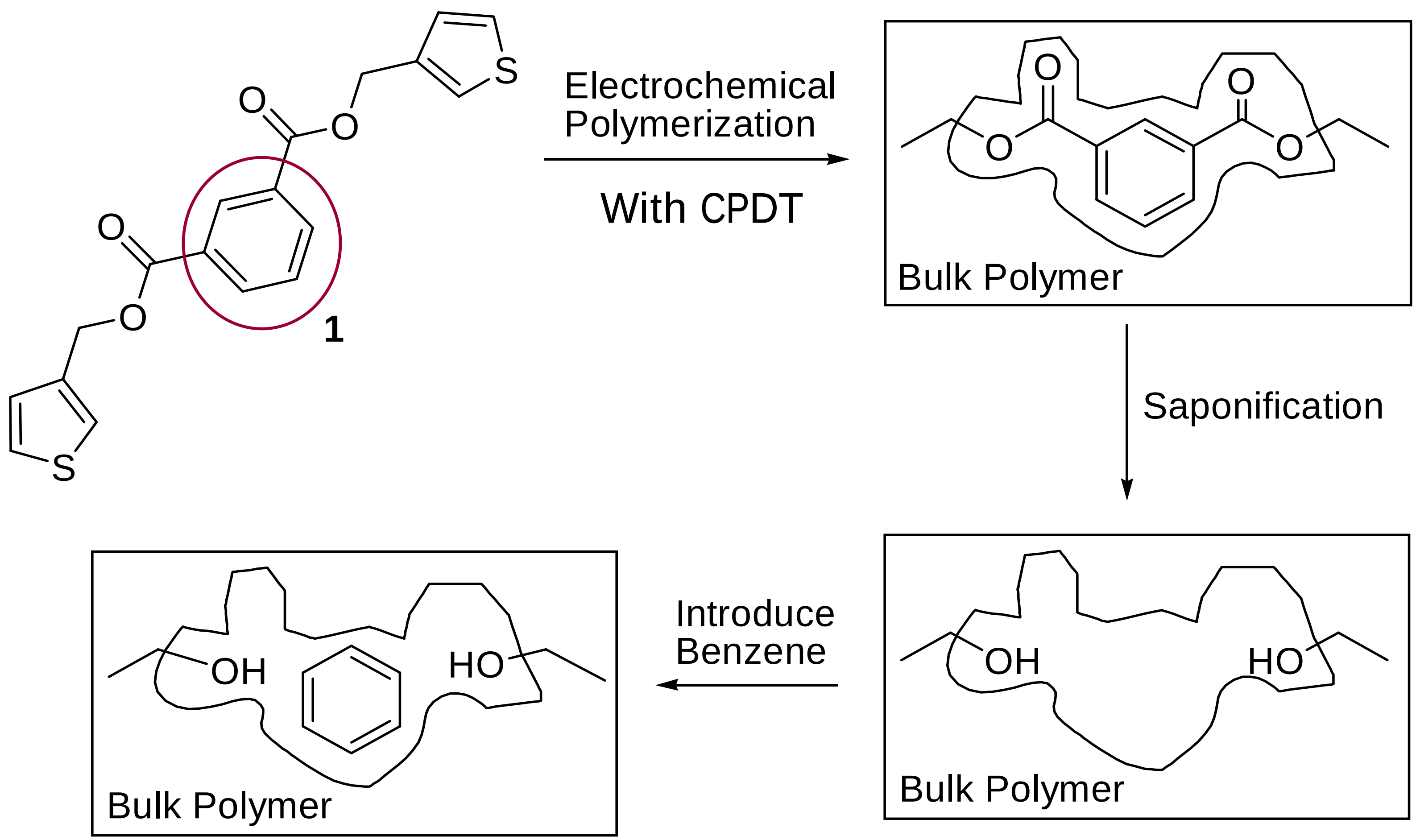
- Remote activation pulse initiates data cycle
- Rugged, solid state experimental control
- Data smoothing and other signal processing
- Peak detection and baseline correction
- Analytical current computation
- Data compression to minimize transmission power requirement
- Interface to data transmission system.

Effect of 3-Thiophenemethanol on Soil Micro-organisms



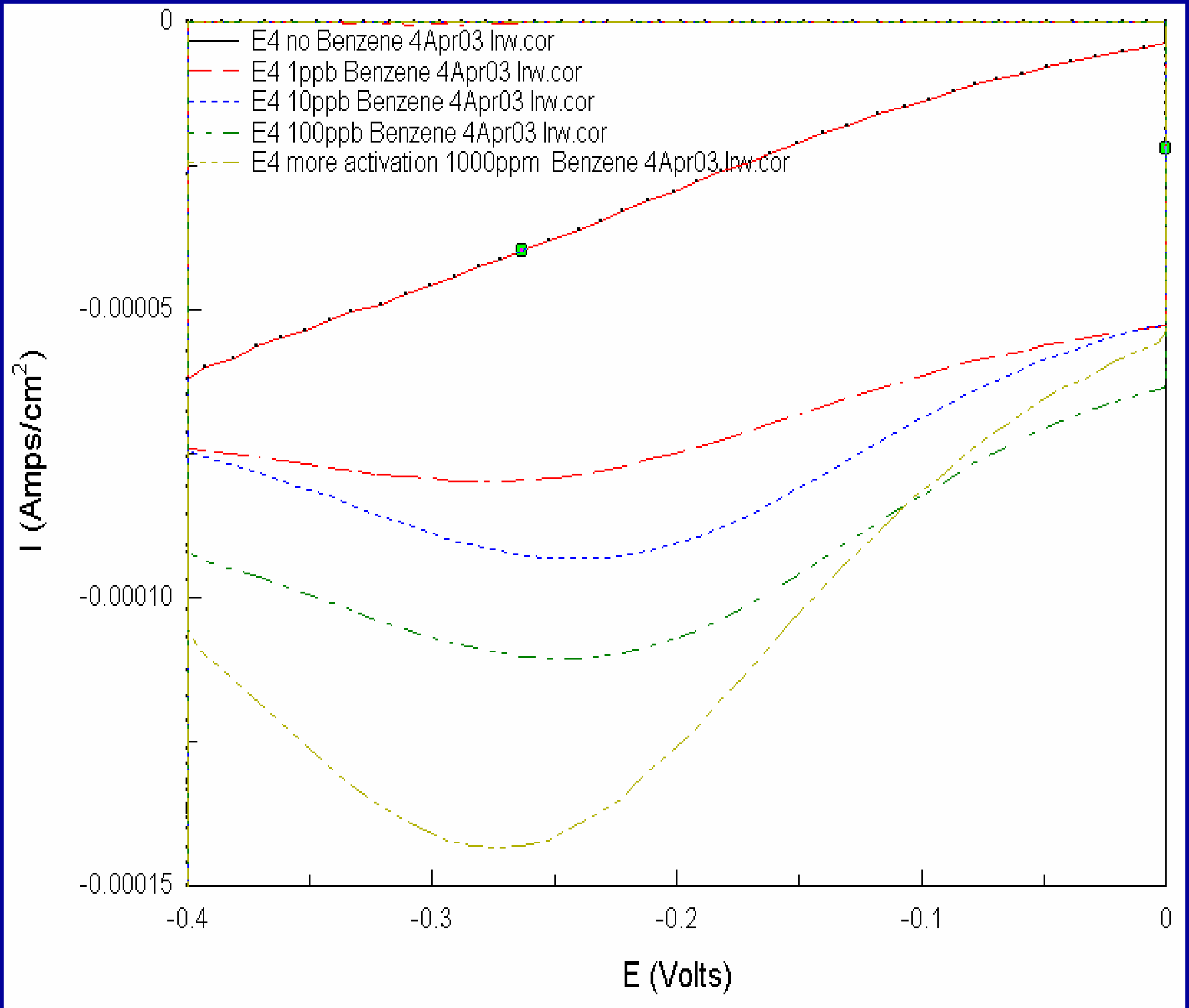
Sensors for Polyatomic Species:
Molecularly Imprinted Polymers: MIPs

- Target analyte attached to monomer by reversible reaction: “templated monomer”
- Templated monomer copolymerized with simple monomer, e.g. CPDT
- Template molecules removed from bulk polymer by reversing the binding reaction
- Vacancies left behind are complementary in geometry and electrostatics to the analyte
- Surface will re-bind the templating molecule
- Selectivity of the vacancies can be “tuned”

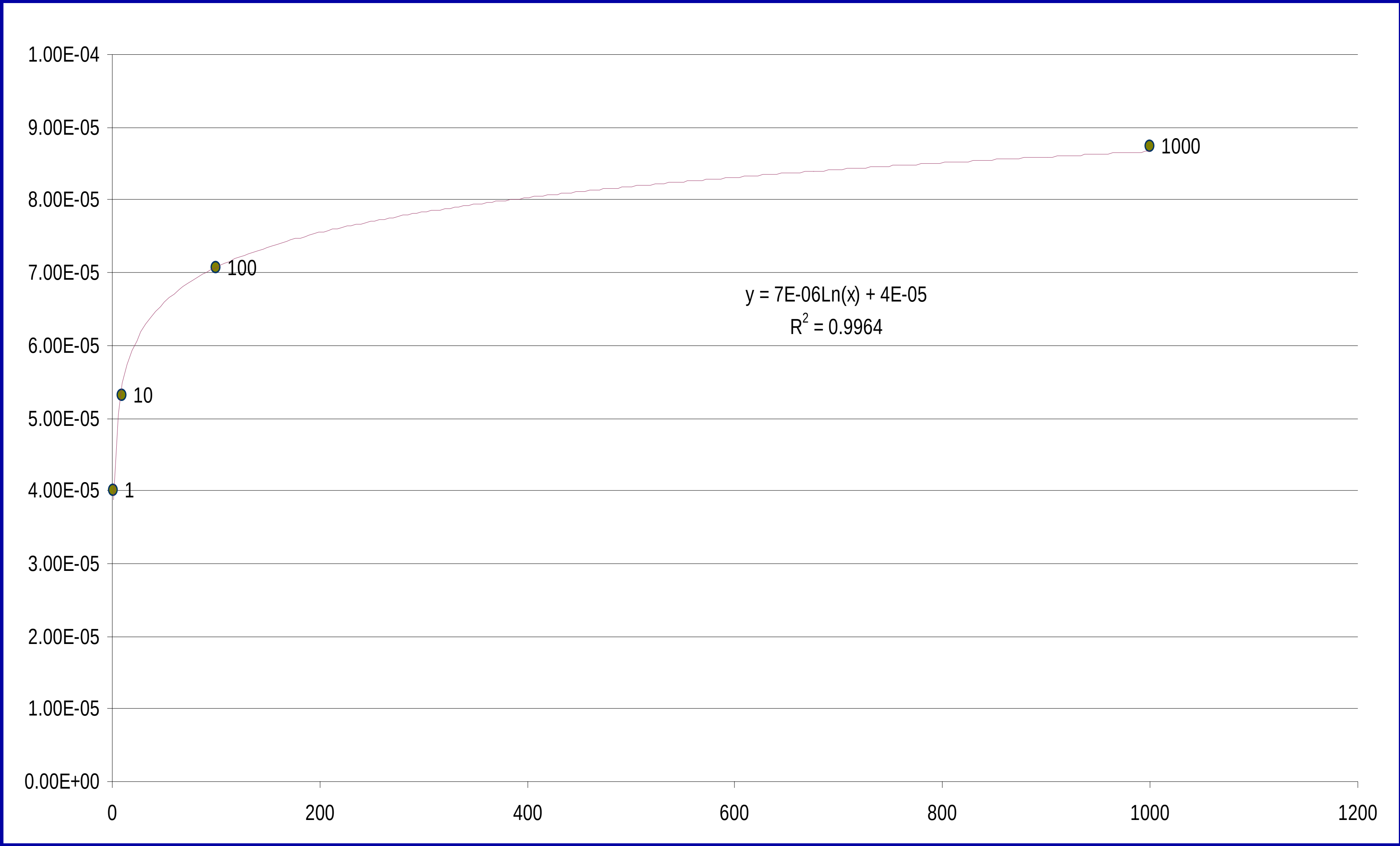


Representation of MIP Preparation For Benzene/Toluene/Catechol Sensor

CV response of Benzene Sensor

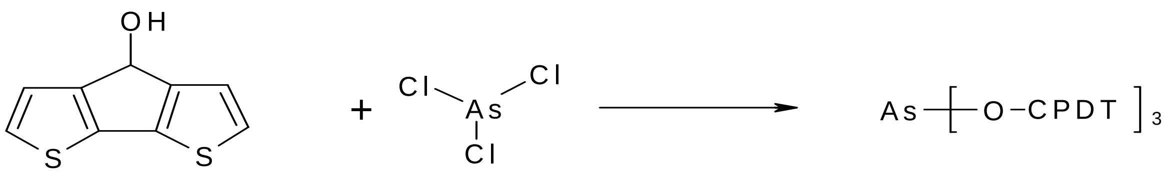


Benzene Sensor Calibration Data



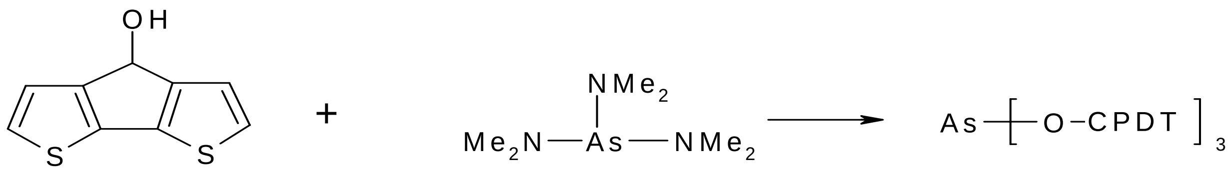
Synthesis of MIPs for Arsenic Species

1.



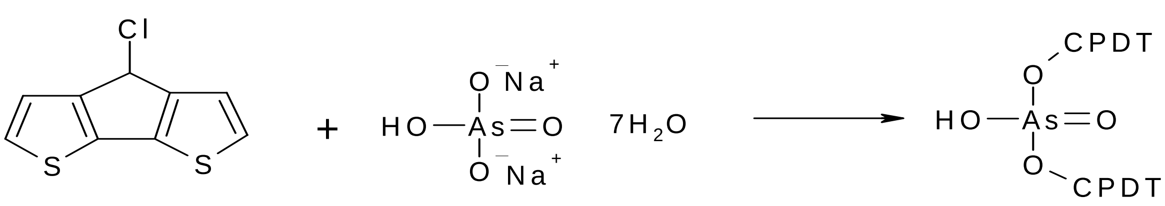
CPDT(alcohol) Arsenic (III) chloride

2.



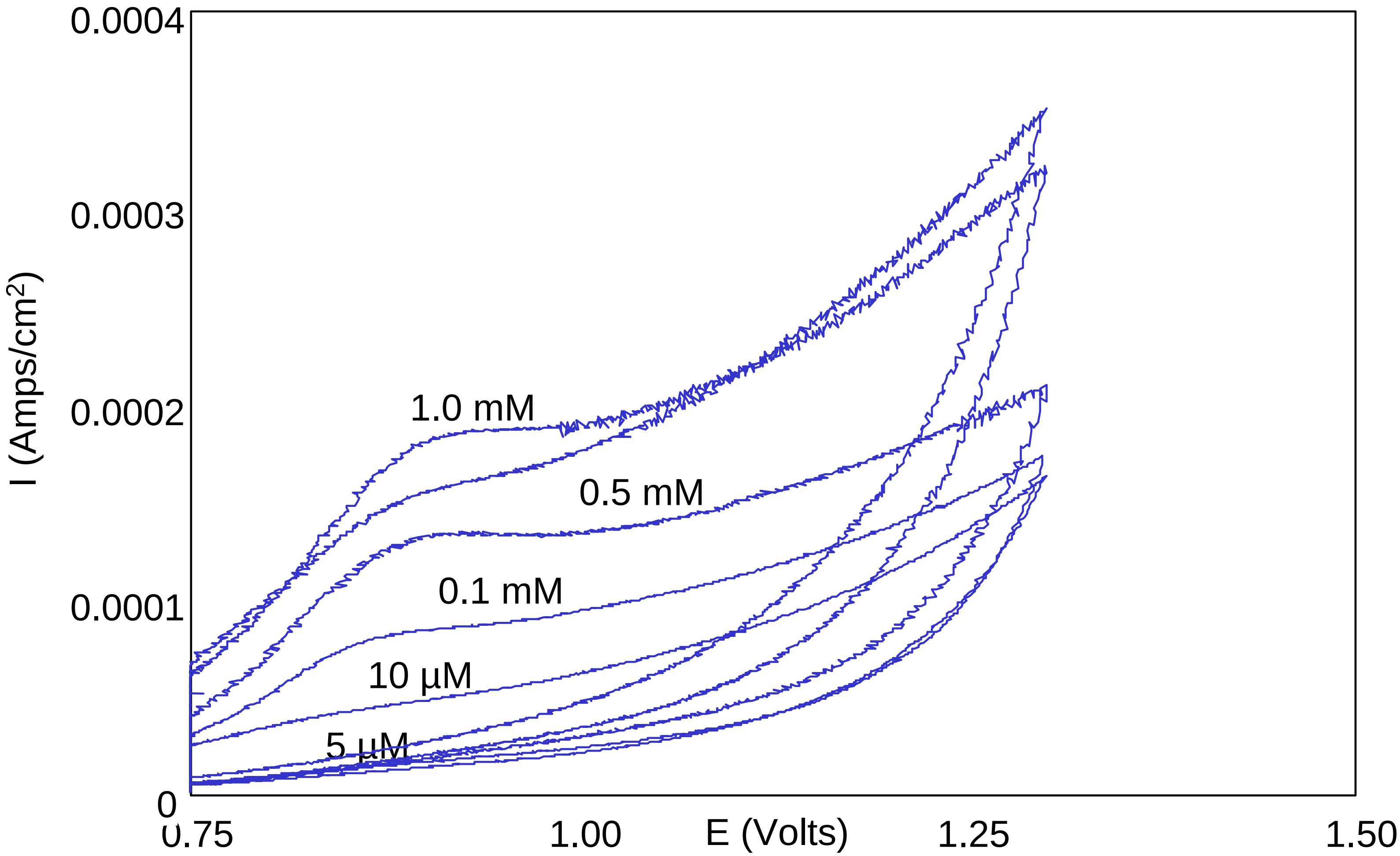
CPDT (alcohol) Tris(dimethylamino)arsine

3.

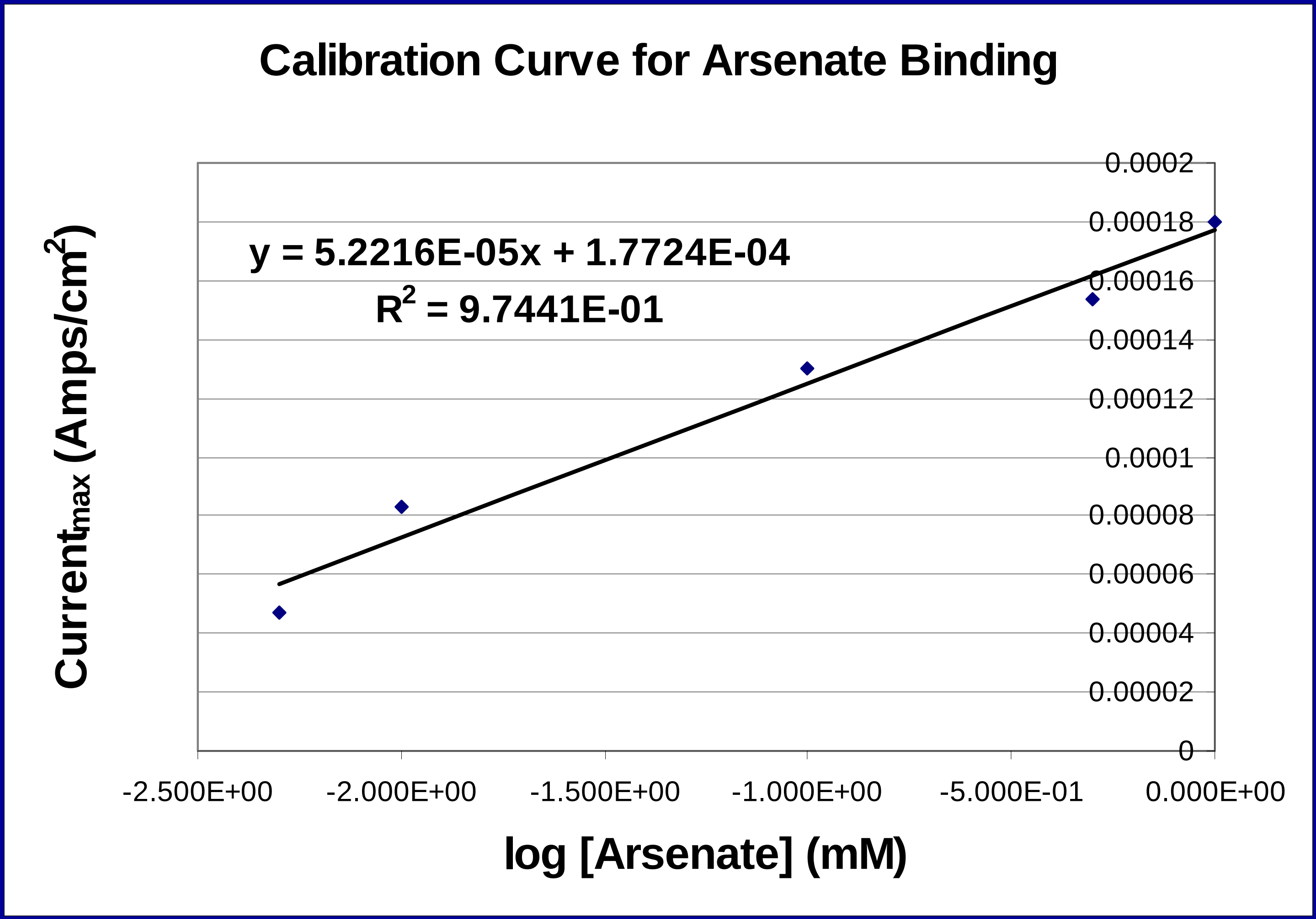


CPDT (chloride) Sodium arsenate dibasic heptahydrate

Current Response of Arsenate Sensor with Varying Concentration



Response of Arsenic MIP Sensor



Summary and Conclusions

- Selective, field portable sensors have been demonstrated with rapid sub ppb-detection
- Detection in water is shown
- Wide dynamic ranges and good selectivity for target analytes
- Field portable system demonstrated
- FET and CV modes of operation
  - FET gives total change in gate potential, e.g. all actinides
  - CV differentiates species based on redox potential
- More optimization and characterization is neede

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  - Lisa Warner
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  - Dr. Michael Hill
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  - Dr. Susan Burkett, EE
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  - Dr. Joe Hartman, EE

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