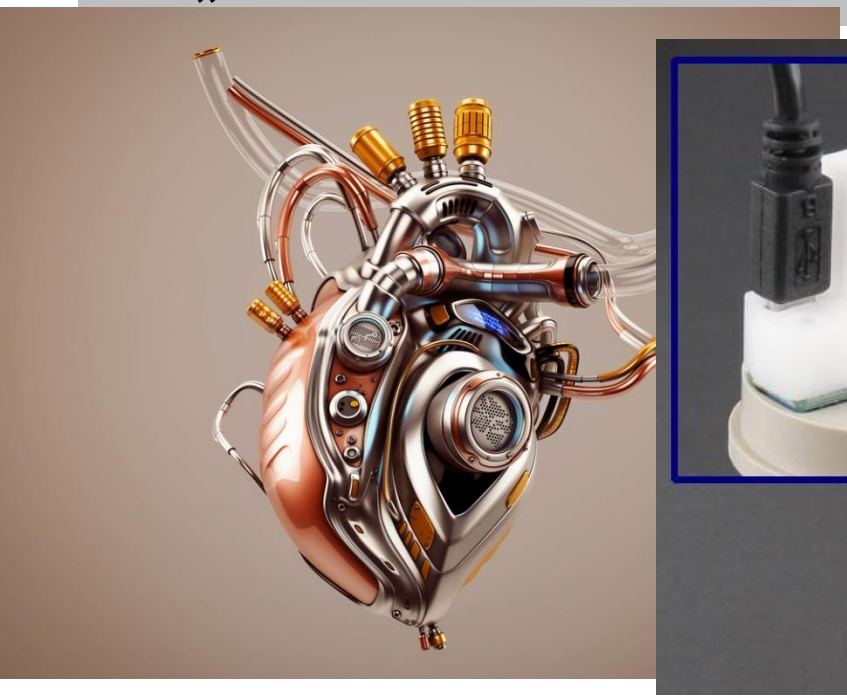
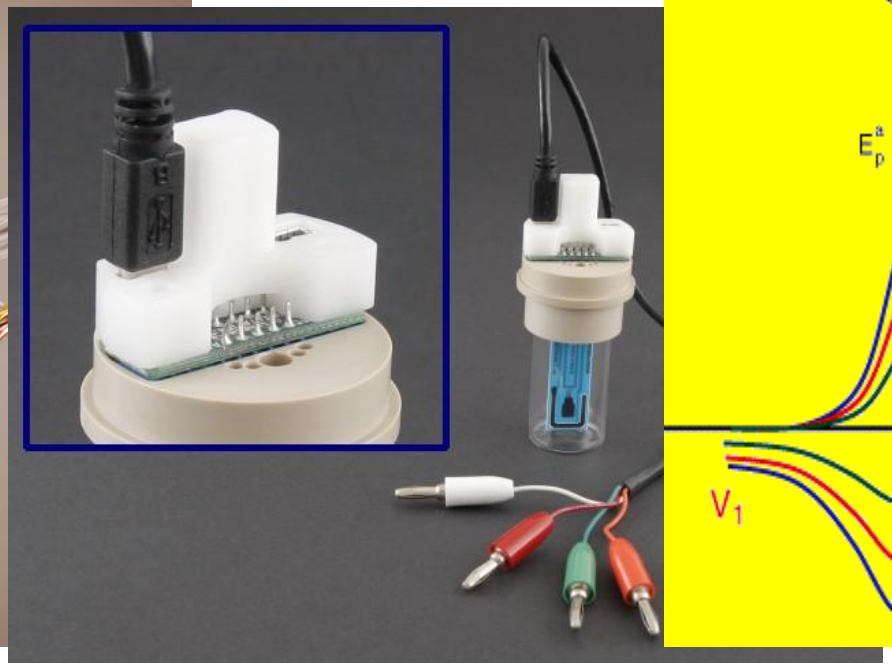
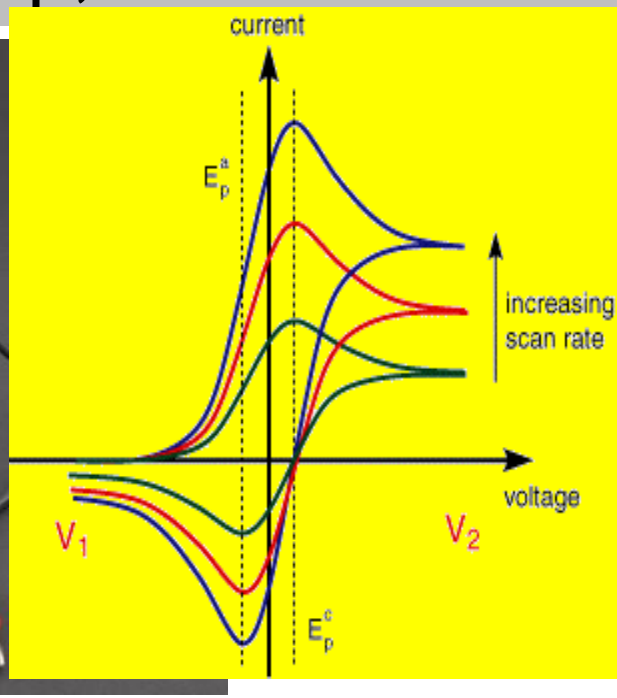
VOLTAMMETRY OF MEDICAL BIOMATERIALS

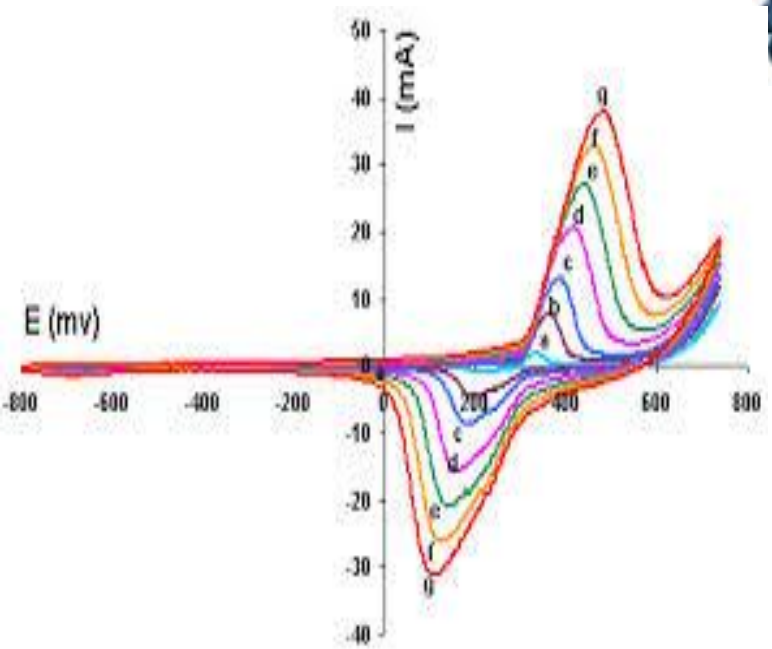
RUBIN GULABOSKI;
VELO MARKOVSKI
„GOCE DELCEV“ University, Stip, Macedonia

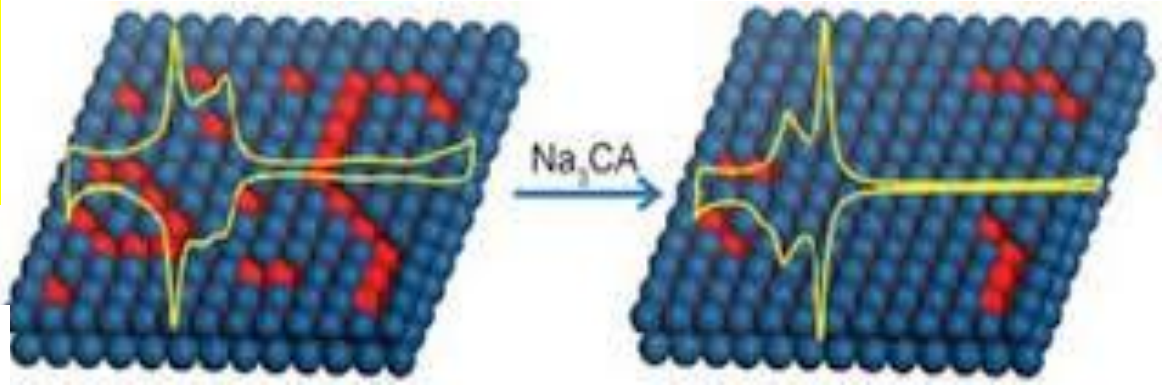


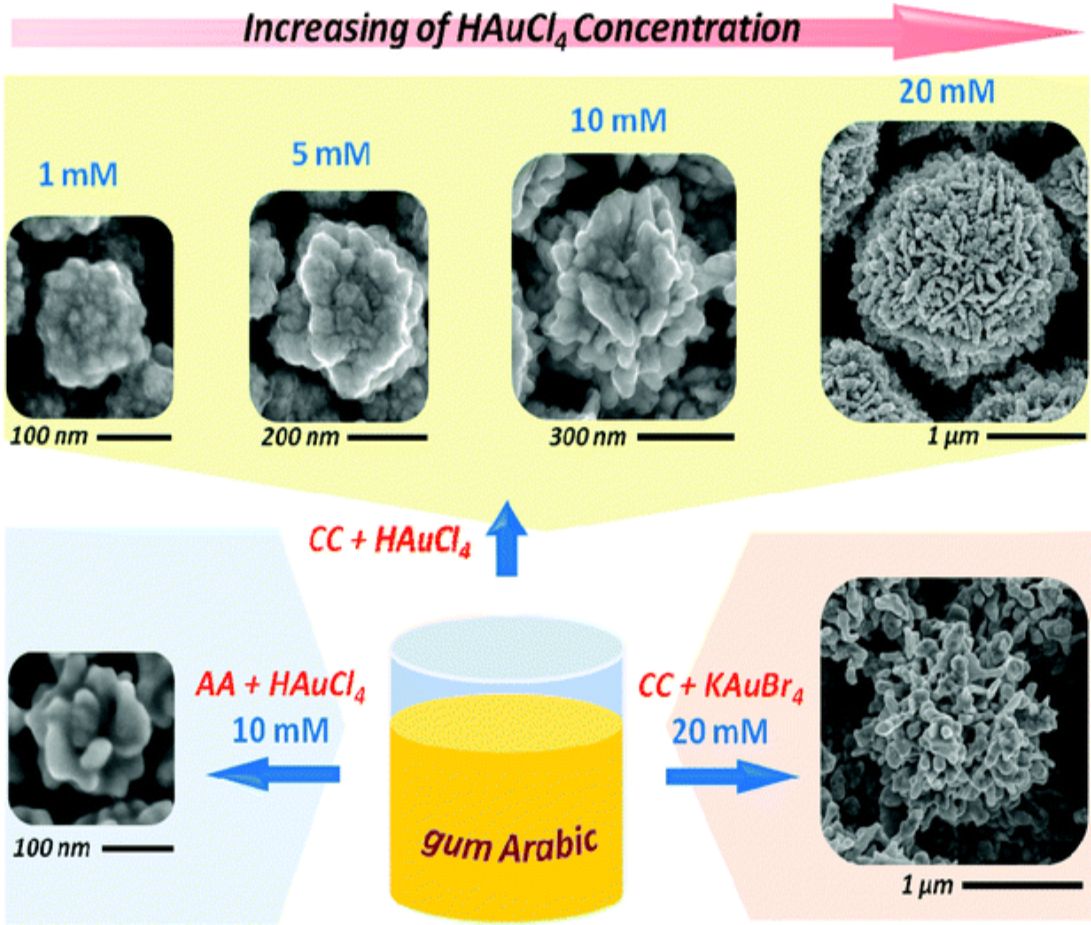




Voltammetry in Nano-Science



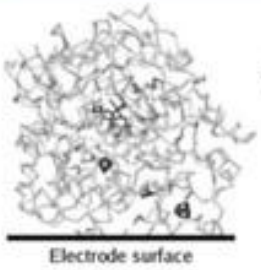


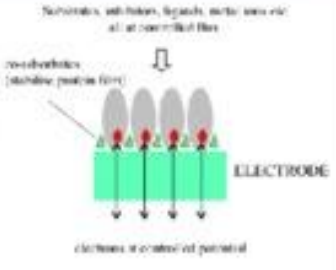


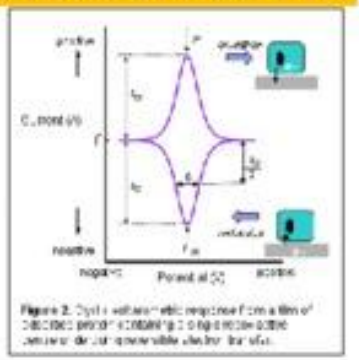
Protein-film Voltammetry

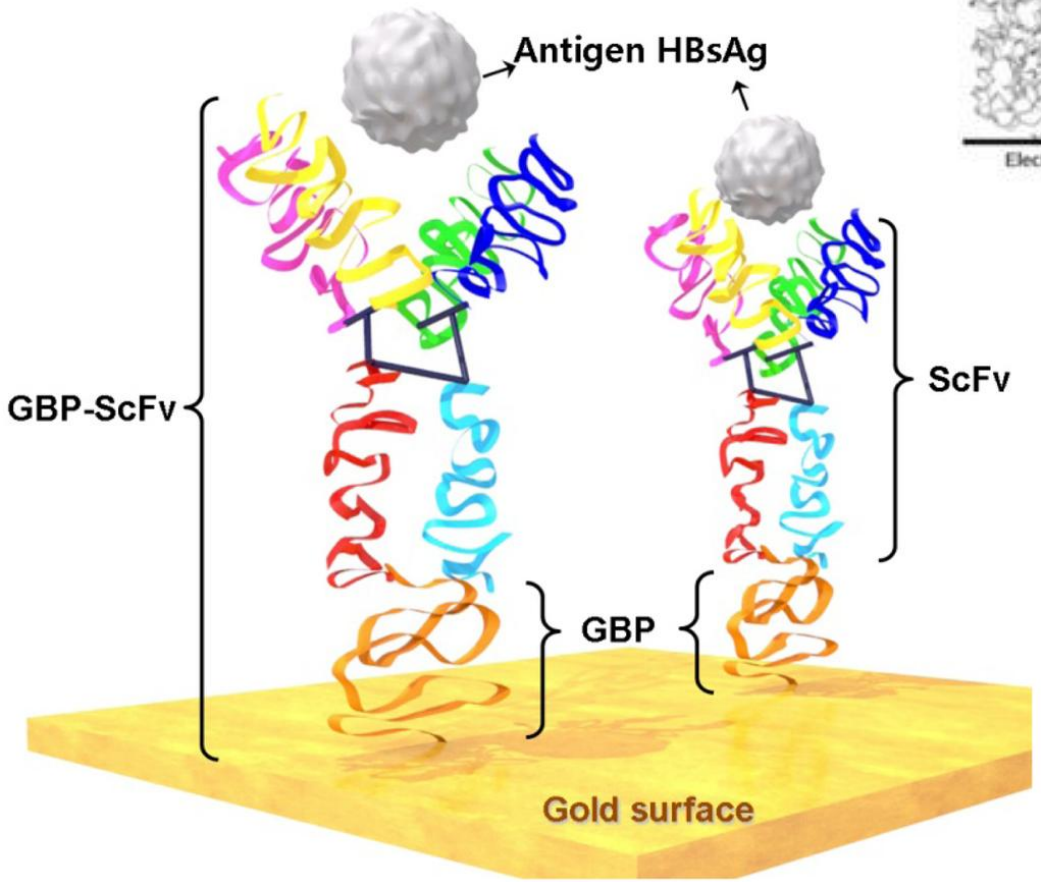
PROTEIN-FILM VOLTAMMETRY-ELECTROCHEMICAL SPECTROSCOPY FOR PROBING THE REDOX FEATURES OF BIOCATALYSTS

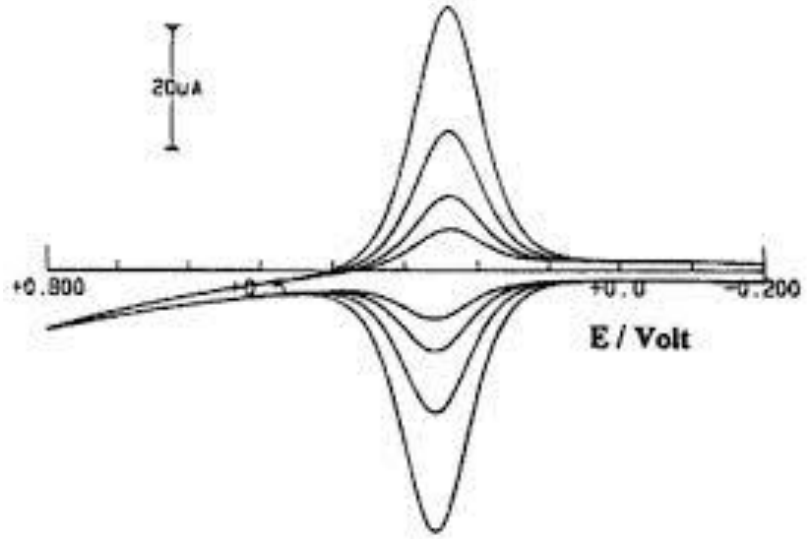
RUBIN GULABOSKI, GOCE DELCEV UNIVERSITY-STIP, MACEDONIA





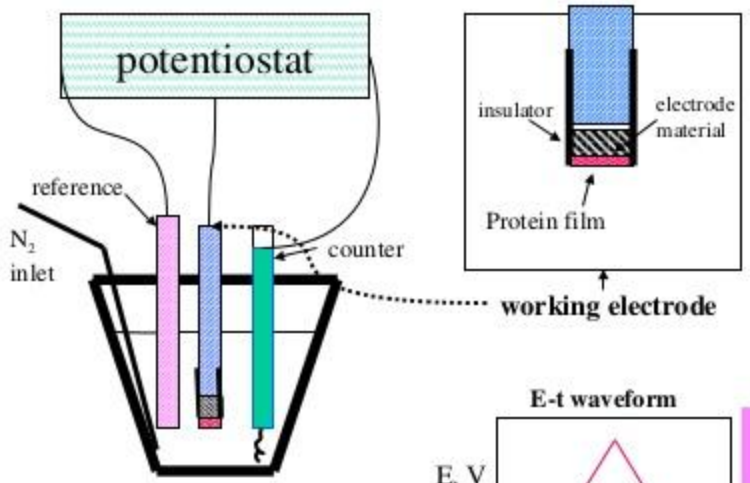


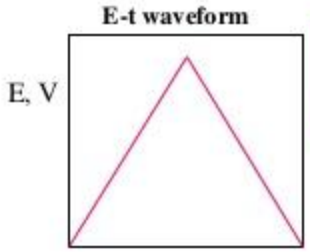




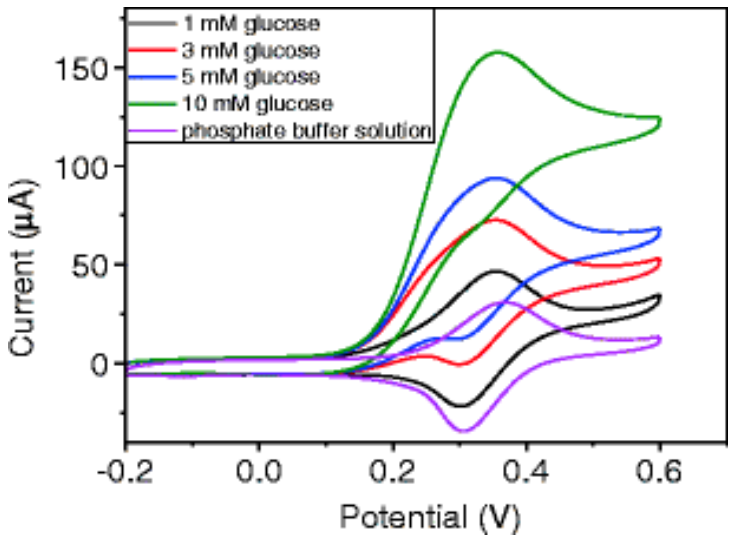
Voltammetry-Biosensors

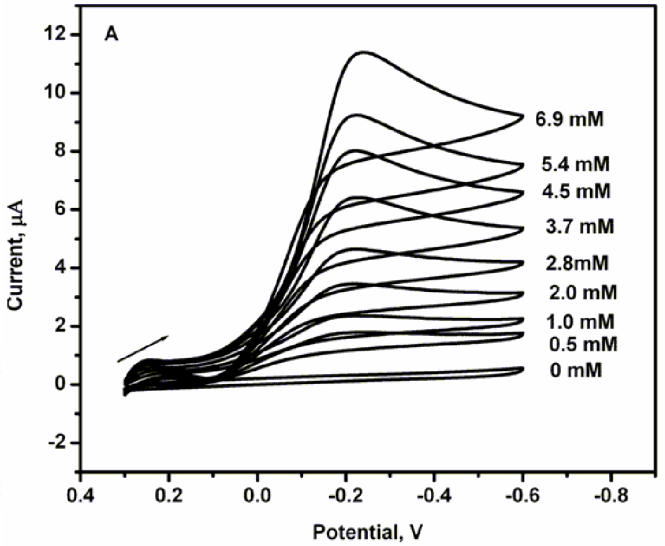
Equipment for developing electrochemical biosensors

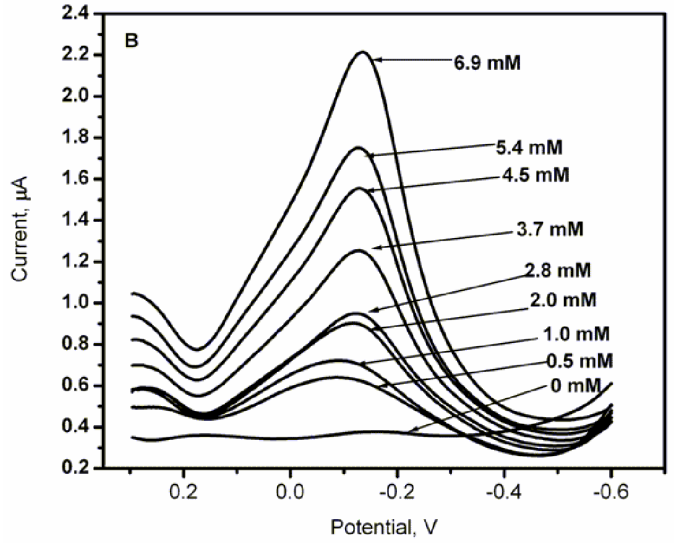




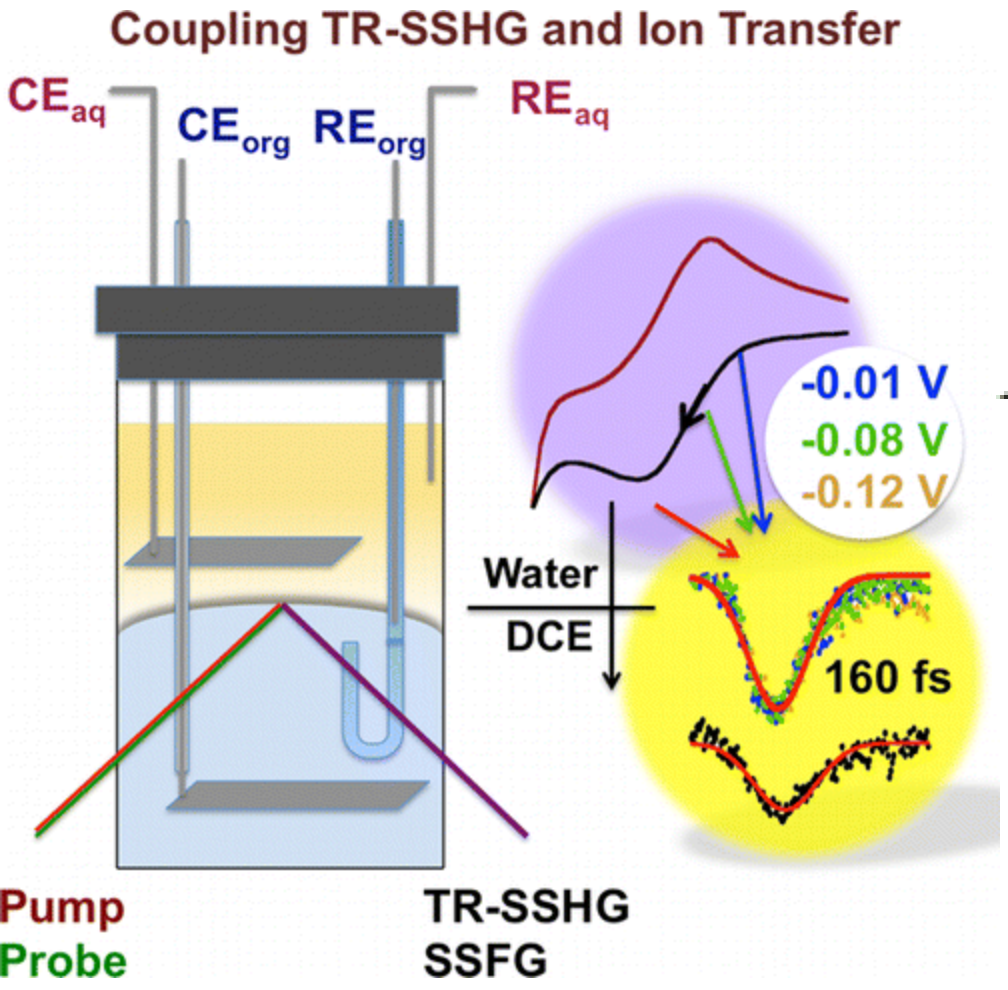
Cyclic voltammetry

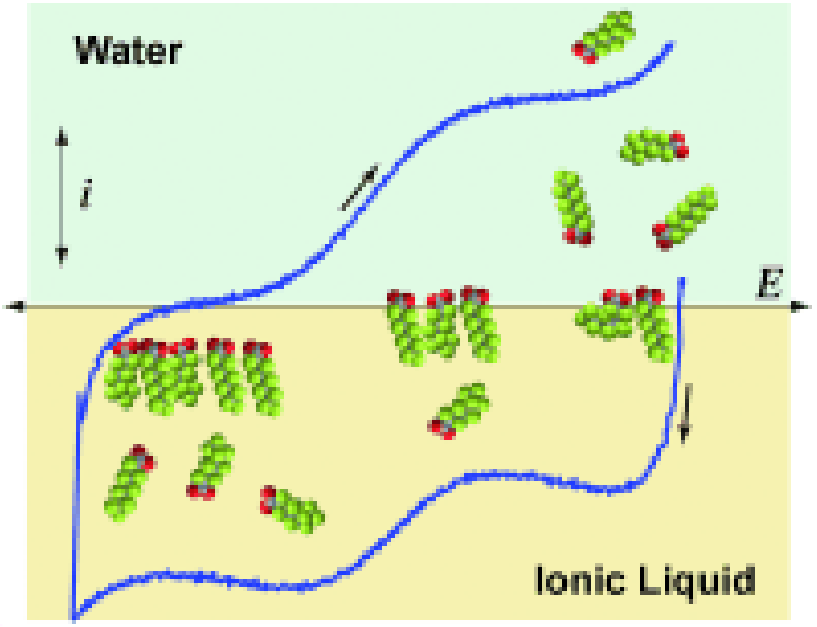




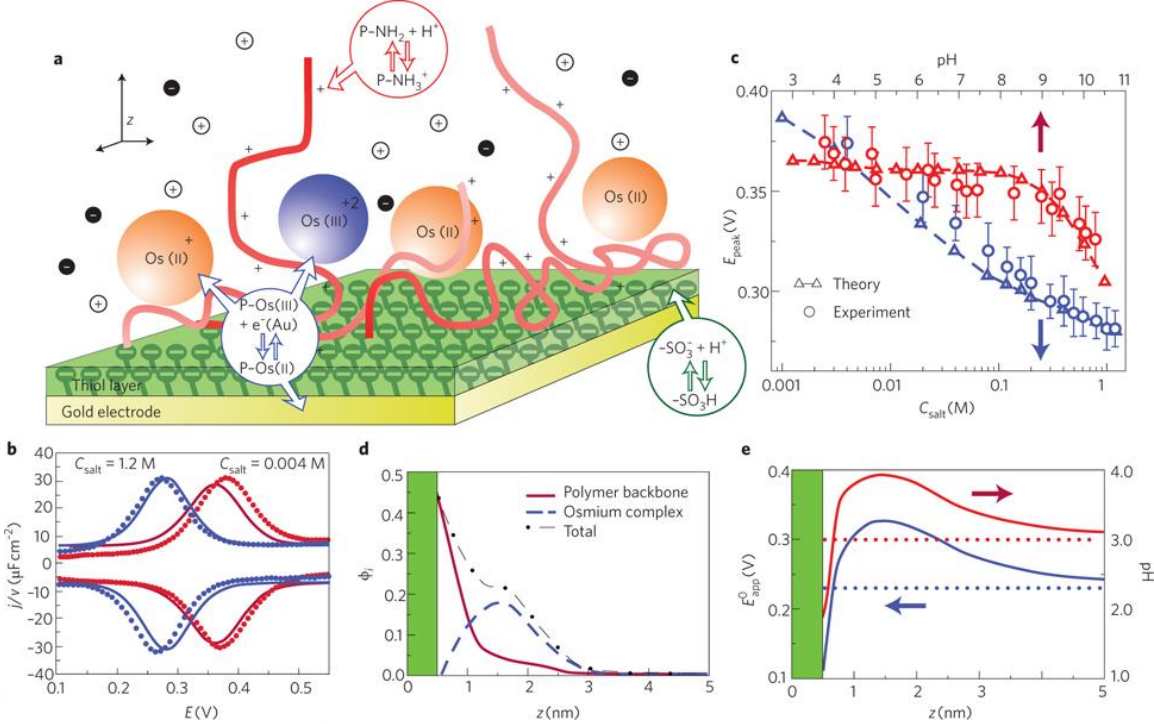


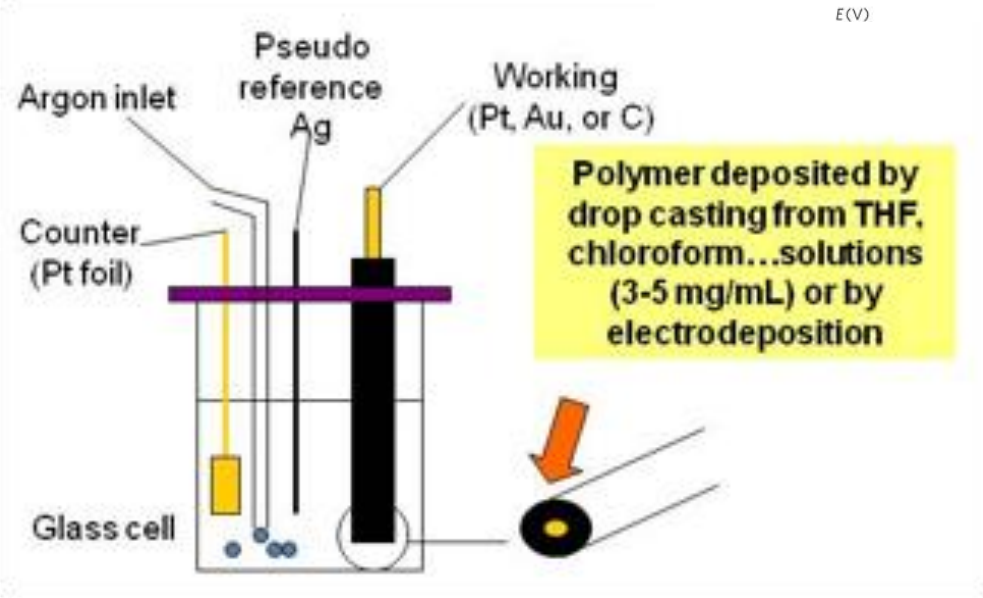
Voltammetry of ion transfer across Liquid-liquid interfaces

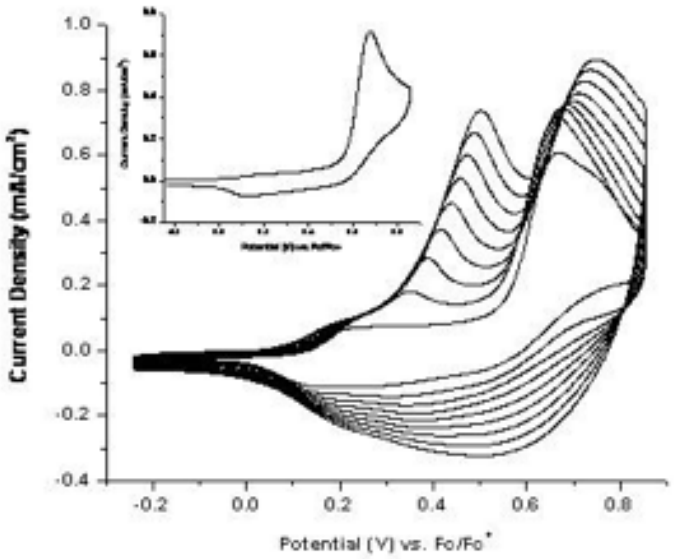




Voltammetry of Conductive Polymers

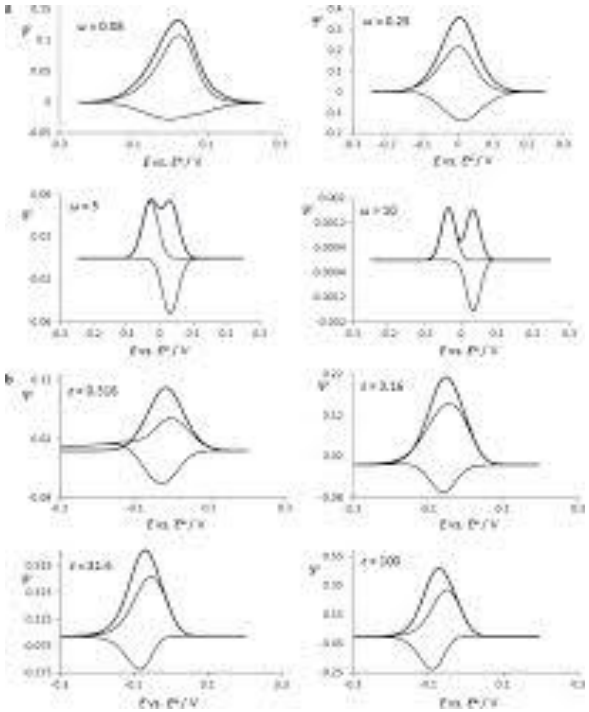


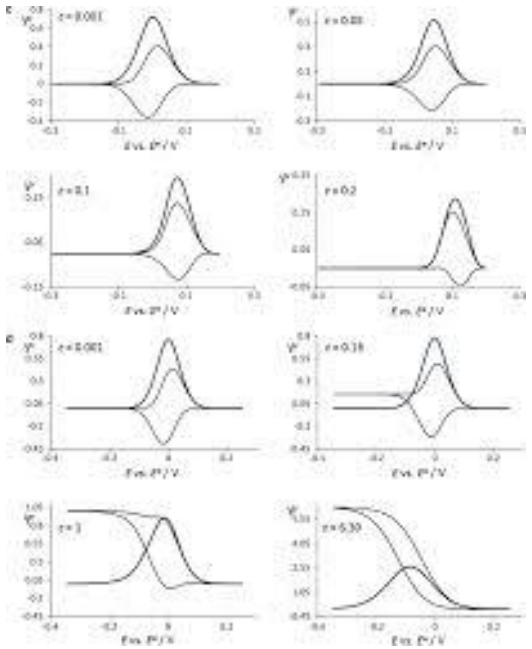




Theoretical modeling in Voltammetry

$$\frac{[\mathrm{Ox}]_{x=0}}{[\mathrm{Red}]_{x=0}} = \exp\left(\frac{nF\left(E - E^{0'}\right)}{RT}\right) \qquad i_{\mathrm{f}} = \frac{nFAD_{\mathrm{ox}}{}^{1/2}c_{\mathrm{ox}}^{*}}{\pi^{1/2}t^{1/2}}\frac{1}{1+P}$$





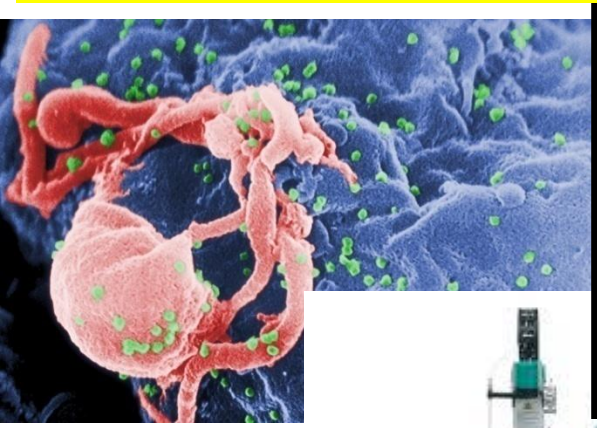
...

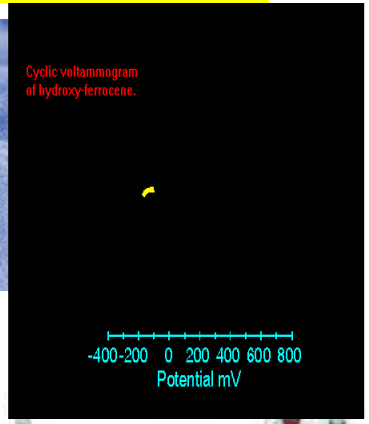
What we did not yet show about the potential applications of voltammetry?

Only few things....

...

...by Voltammetry!!!





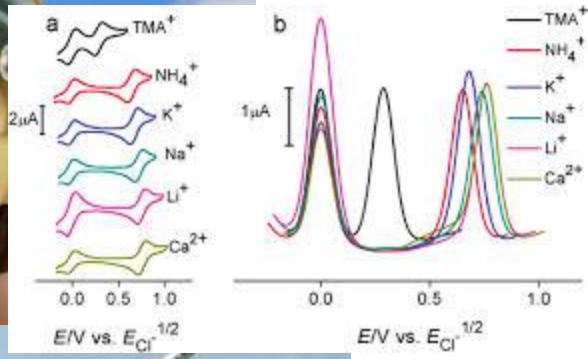
Two Macedonian Scientists

Together with

D-r Kim Jong Un have

Explored Voltammetry to

Tackle AIDS and Ebola at once



That was to be expected...

Gulaboski, Mirceski and

Kim Jong Un have

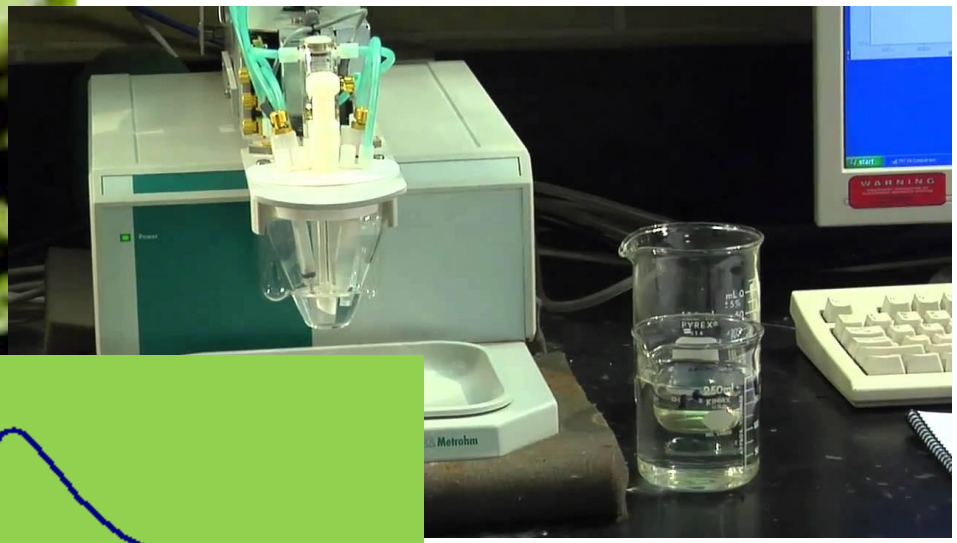
Explored Voltammetry to

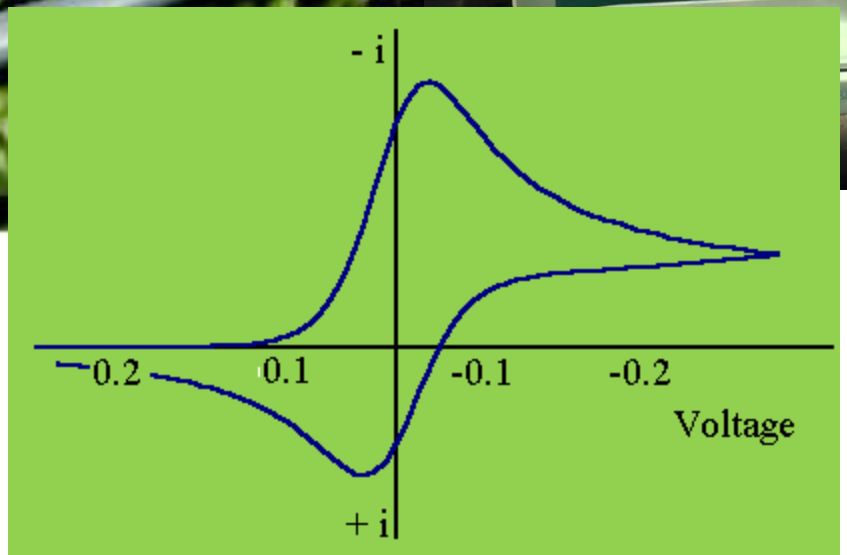
Build an Atomic Bomb

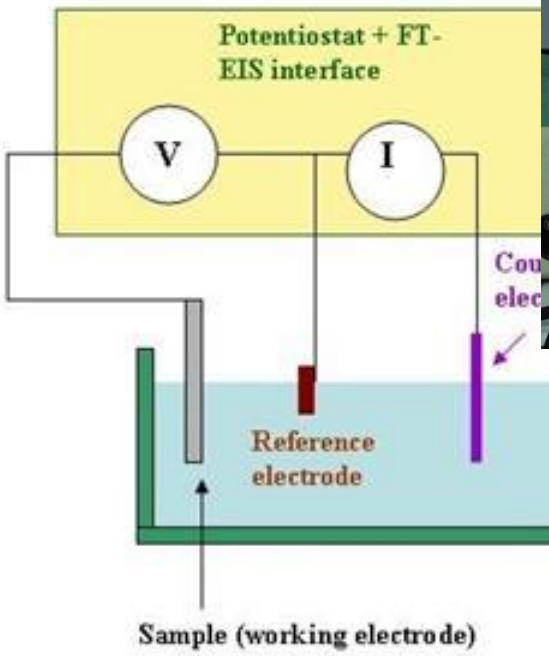
- First Atomic Bomb Used – Uranium
- Detonated over Hiroshima Aug. 6, 1945
- Weighs 9,000 pounds
- 20,000 tons of TNT explosive capacity (2,000 B-29s w/ standard bombs)

...todays Lecture will be focused on

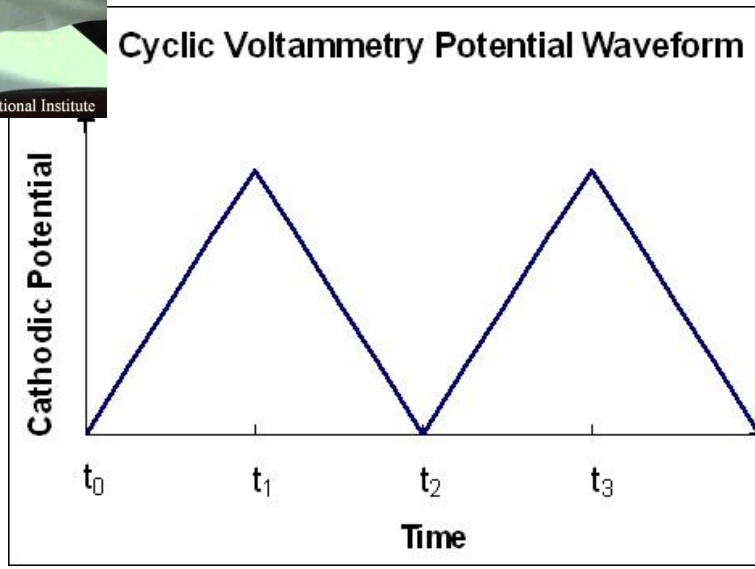
Application of voltammetry for characterization of Biomaterials...

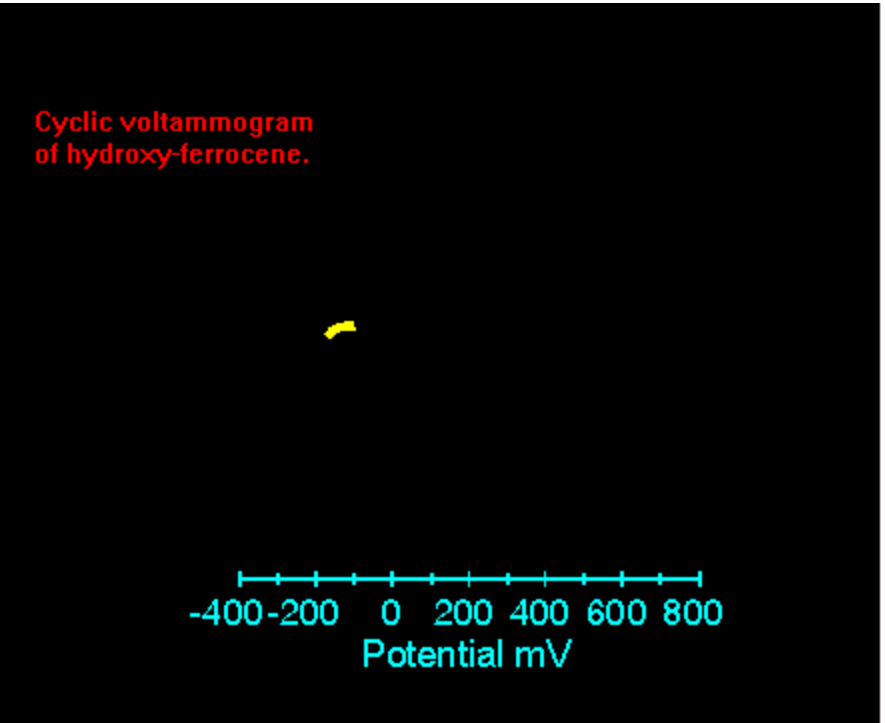


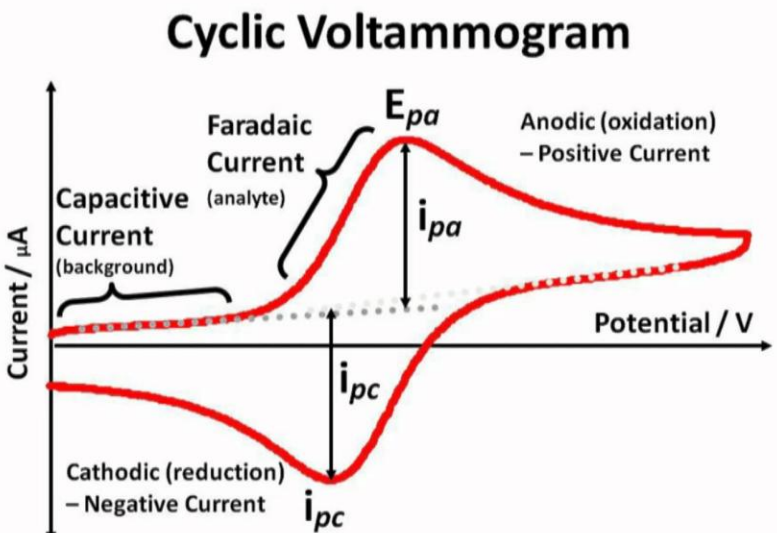



Potentiostat + FT-
EIS interface
V
I
Reference
electrode
Sample (working electrode)

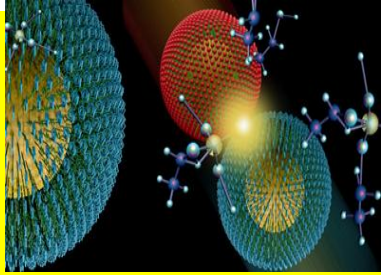

USIC, Dayalbagh Educational Institute


Cyclic Voltammetry Potential Waveform
Cathodic Potential
t0
t1
t2
t3
Time

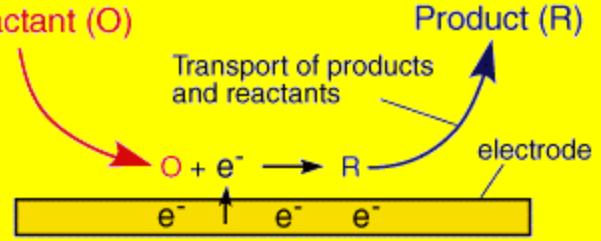

Cyclic voltammogram
of hydroxy-ferrocene.
-400 -200 0 200 400 600 800
Potential mV


Cyclic Voltammogram
Epa
Faradaic
Current
(analyte)
Anodic (oxidation)
– Positive Current
Capacitive
Current
(background)
ipa
Current / μA
Potential / V
ipc
Cathodic (reduction)
– Negative Current
ipc

What are potential applications of voltammetry for studying the biomaterials?



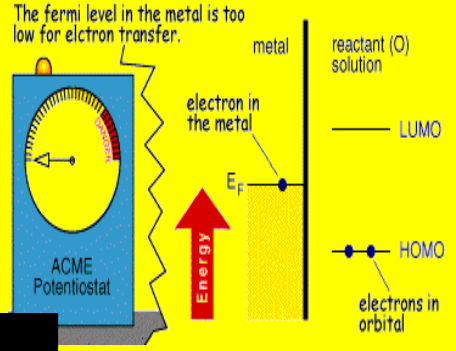
-**kinetics studies** (decomposition of the biomaterials, stability of biomaterials, Influence of various factors to the stability of biomaterials...)



-**thermodynamics studies** (for example, complexes formation between elements present in Biomaterials and various inorganic and organic ligands)

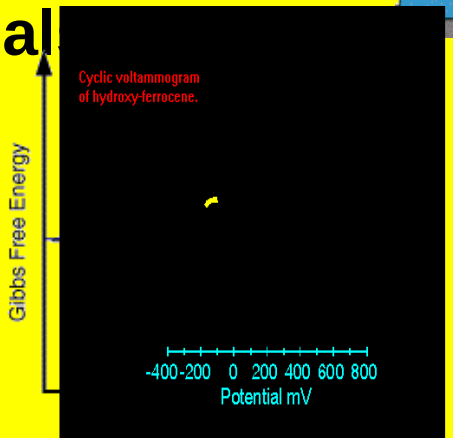
-**composition of the biomaterials**

-**Interactions of biomaterials with various substances**...

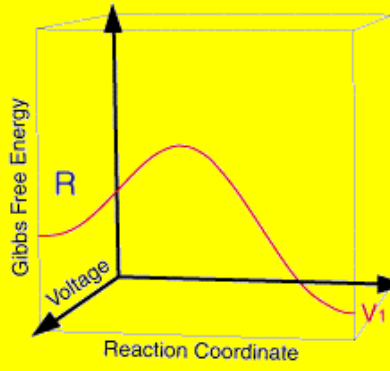


-**surface modifications of biomaterial**

-**insights into the mechanisms**...#



-**influence of the temperature**



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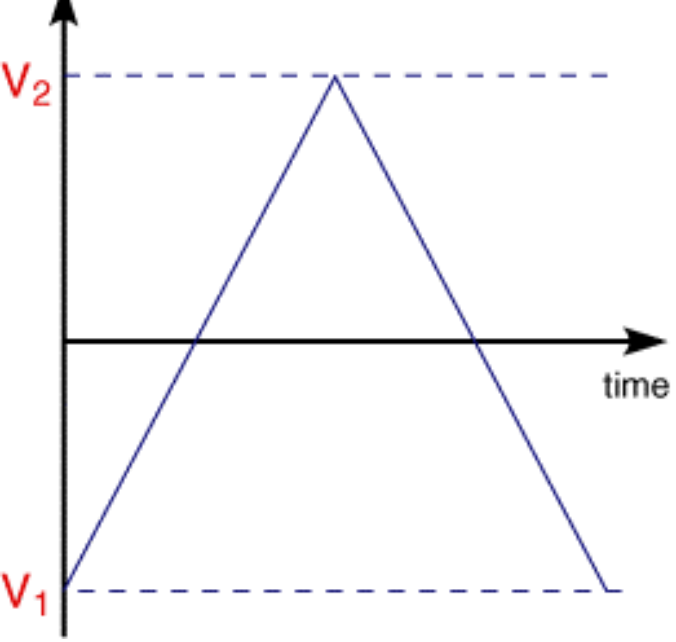
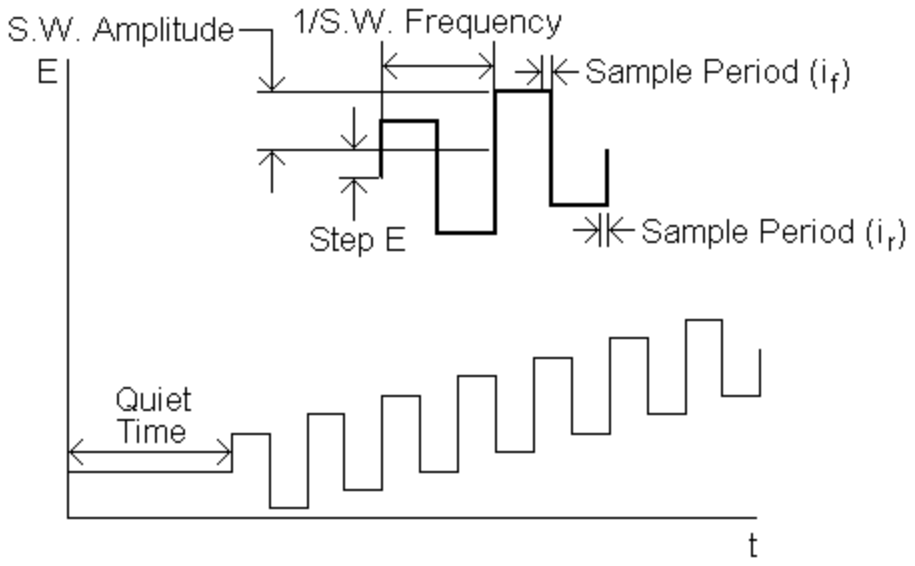
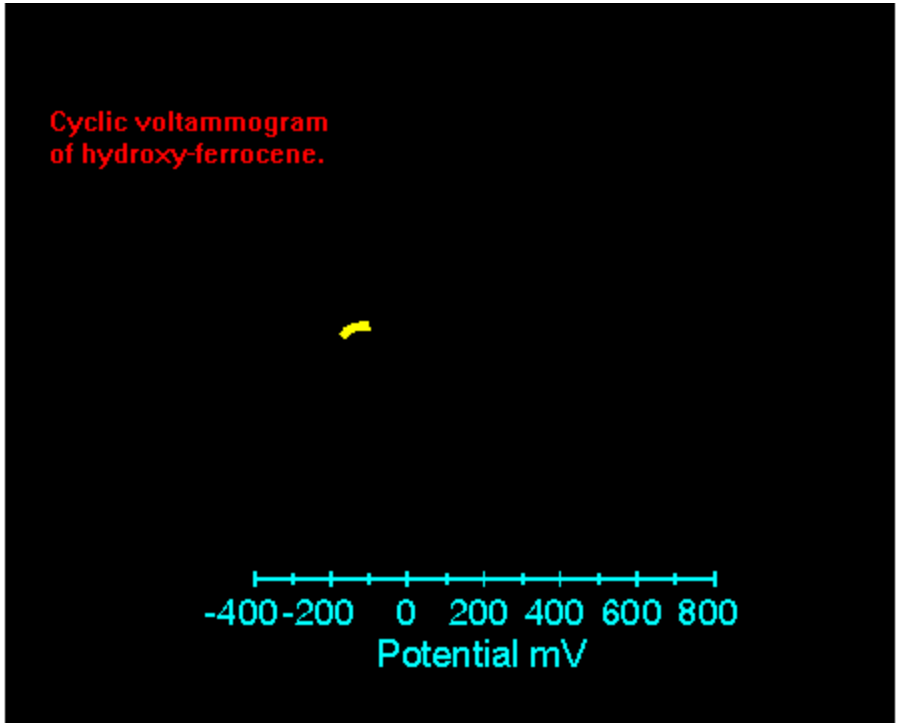
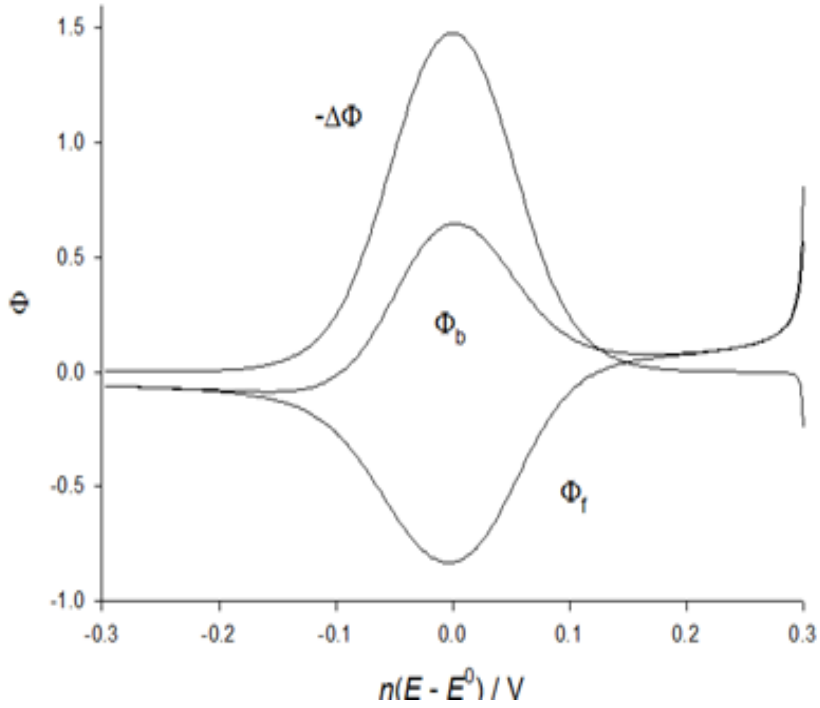
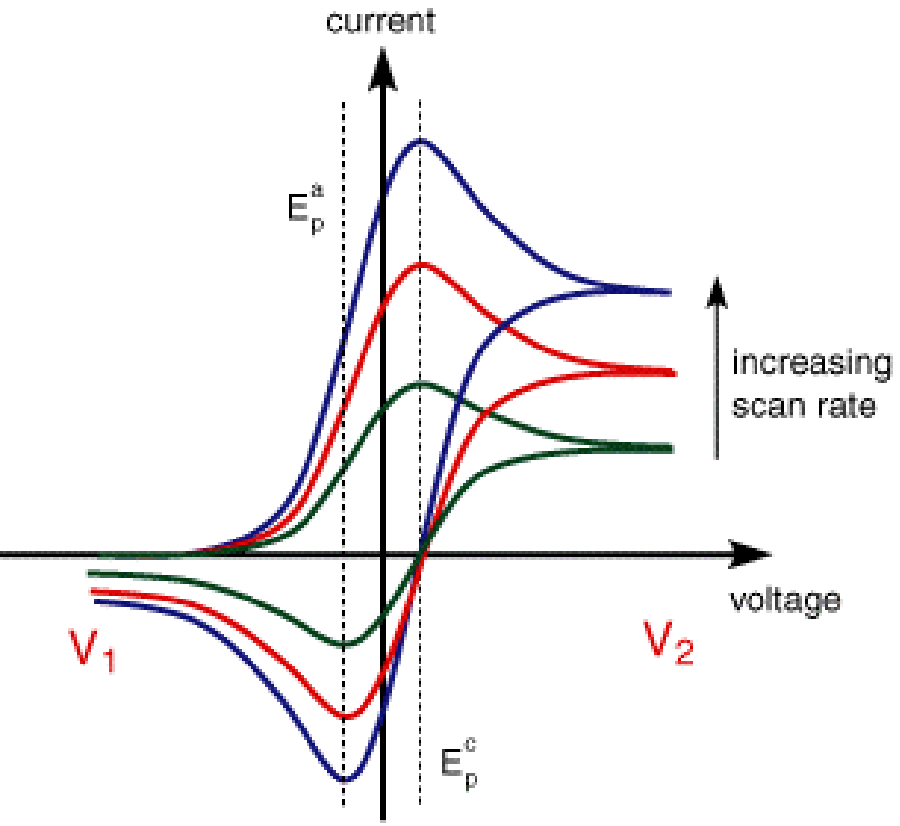

V2
time
V1

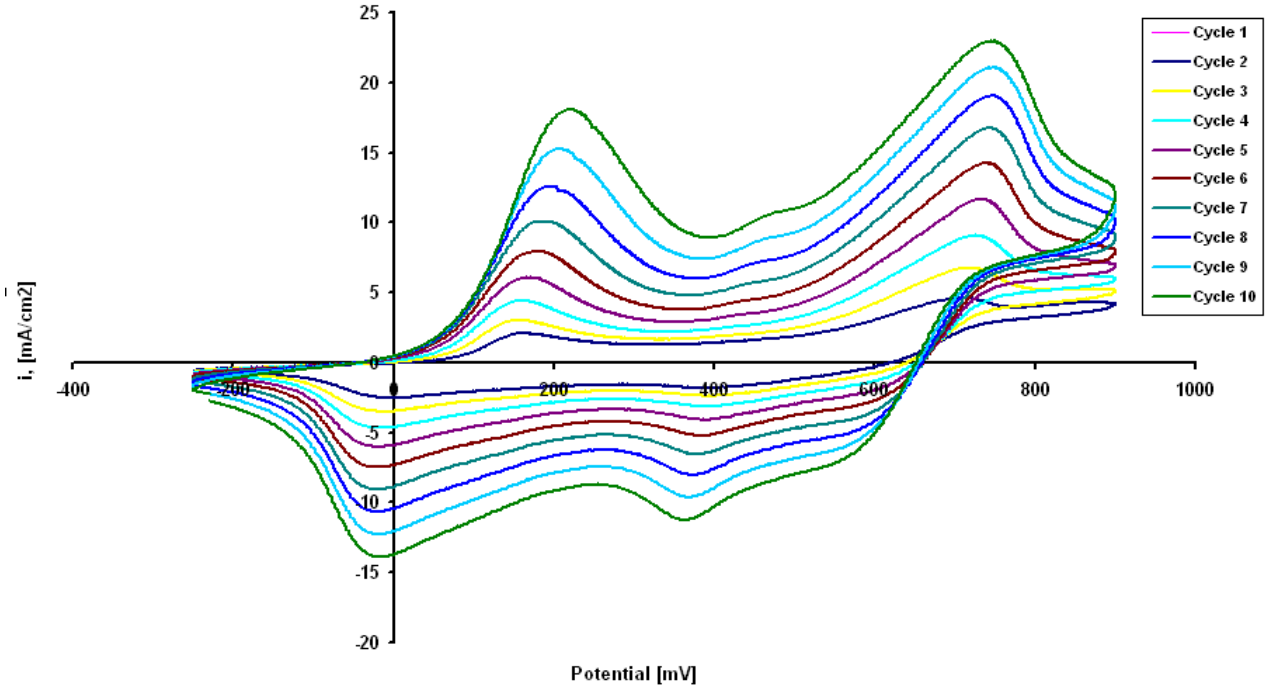

S.W. Amplitude
E
1/S.W. Frequency
Sample Period (i_f)
Step E
Sample Period (i_r)
Quiet
Time
t


Cyclic voltammogram
of hydroxy-ferrocene.
-400 -200 0 200 400 600 800
Potential mV

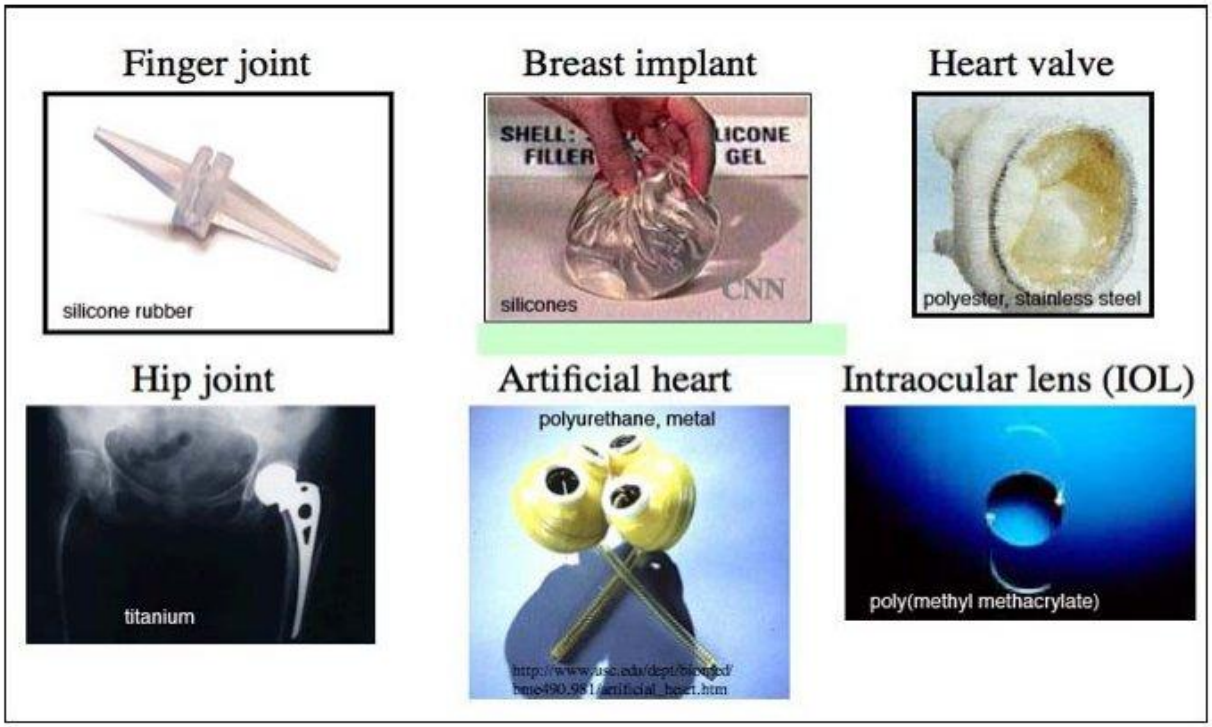

1.5
1.0
0.5
0.0
-0.5
-1.0
Φ
-ΔΦ
Φb
Φf
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
n(E - E0) / V



Time-analysis of
Tooth-implant (decay)
Recorded by cyclic voltammetry



- **Biomaterials:**
  - Any substance, other than a drug, or a combination of substances, synthetic or natural in origin which can be used for any period of time, as a whole or part of a system which treats, augments or replaces any tissue, organ or function of the body.

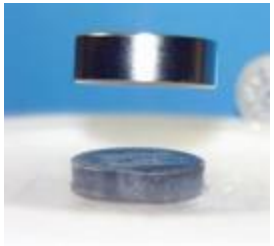


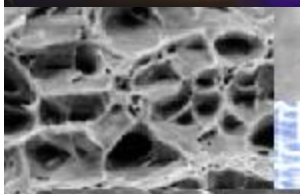
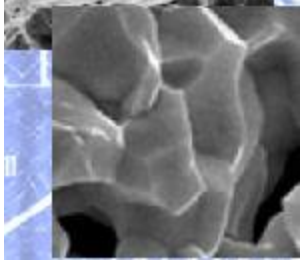
  - **A biomaterial is a nonviable material used in a medical device, intended to interact with biological systems (Williams, 1987)**

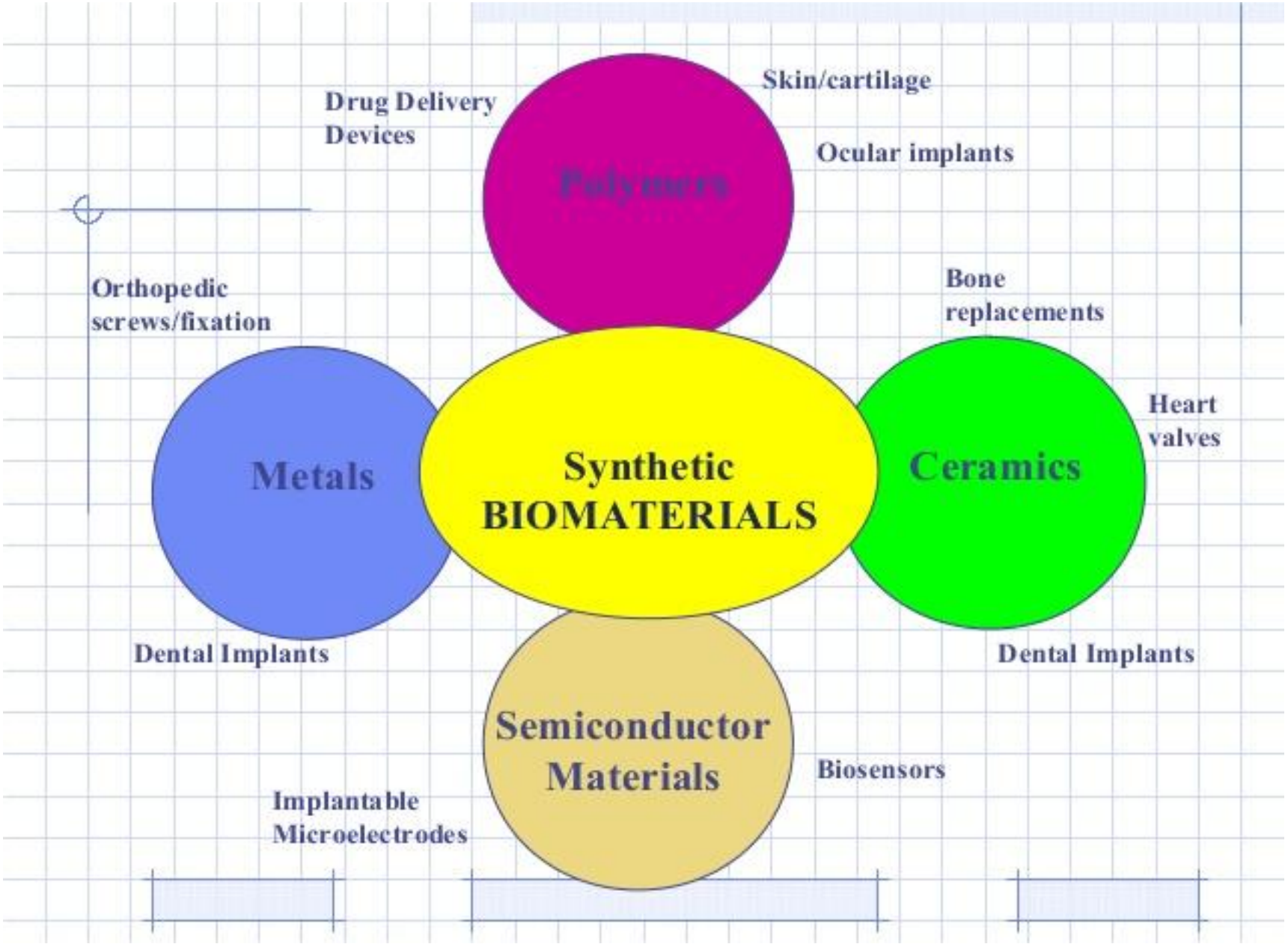
Biomaterials are Functional Materials

- Definition:
  - Material which is not primarily used for its mechanical properties but for other properties such as physical or chemical.

- Examples:
  - Superconductors
    - **An element, intermetallic, compound that will conduct electricity without any resistance below a certain temperature**
    - **Magnetic levitation**, **maglev**, or **magnetic suspension** is a method by which an object is suspended with no support other than magnetic fields
    - http://www.superconductors.org/INdex.htm
  - Dielectric Material
    - electrically insulating material
    - contains polar molecules that reorient in external electric field
    - Used as insulating material between the plates of a capacitator




Drug Delivery Devices
Skin/cartilage
Ocular implants
Polymers
Orthopedic screws/fixation
Bone replacements
Metals
Synthetic BIOMATERIALS
Ceramics
Heart valves
Dental Implants
Dental Implants
Semiconductor Materials
Biosensors
Implantable Microelectrodes

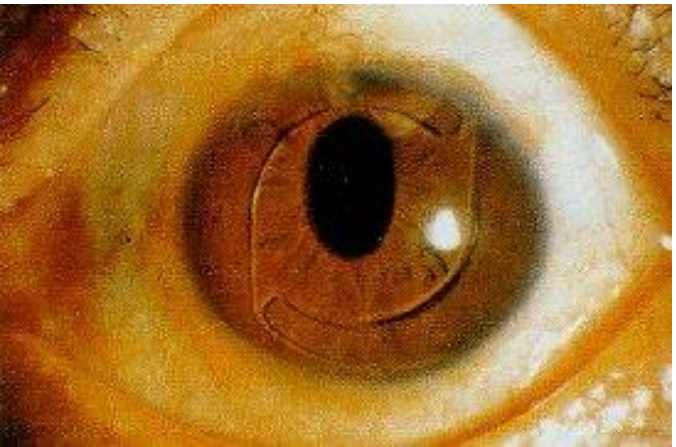
Applications of biomaterials in Dental Medicine

- Because of its bio-compatibility, malleability and resistance to corrosion, gold has been used in dental work for nearly three thousand years. The Etruscans in the seventh century BC used gold wire to hold in place substitute teeth, usually from a cow or calf, when their own were knocked out. The first printed book on dentistry published in 1530 recommends gold leaf for filling cavities.

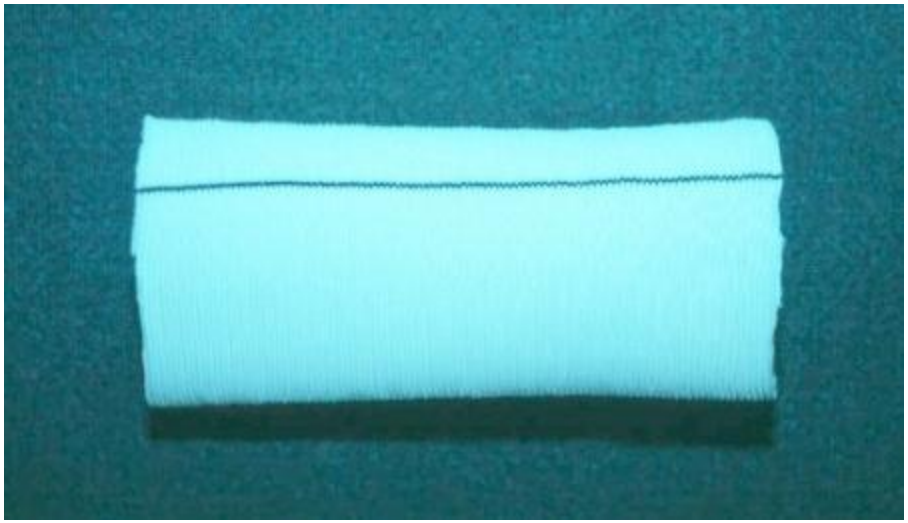
Intraocular Lens

3 basic materials - PMMA, acrylic, silicone

•An **intraocular lens** (IOL) is an implanted lens in the eye, usually replacing the existing **crystalline lens** because it has been clouded over by a cataract, or as a form of refractive surgery to change the eye's optical power.
•Advances in technology have brought about the use of silicone and acrylic, both of which are soft foldable inert materials. This allows the lens to be folded and inserted into the eye through a smaller incision
•Acrylic is not always an ideal choice due to its added expense
•For a gruesome yet painless eye procedure: http://www.youtube.com/watch?v=kN-KqYcjEqk



Vascular Implants



Parachute cloth and Dacron

Second generation implants

- engineered implants using common and borrowed materials developed through collaborations of physicians and engineers
- built on first generation experiences
- used advances in materials science

Examples — Second generation implants

- **titanium alloy dental and orthopaedic implants**
- **cobalt-chromium-molybdinum o**rthopaedic implants
- UHMW polyethylene bearing surfaces for total joint replacements
- heart valves and pacemakers

Artificial Hip Joints

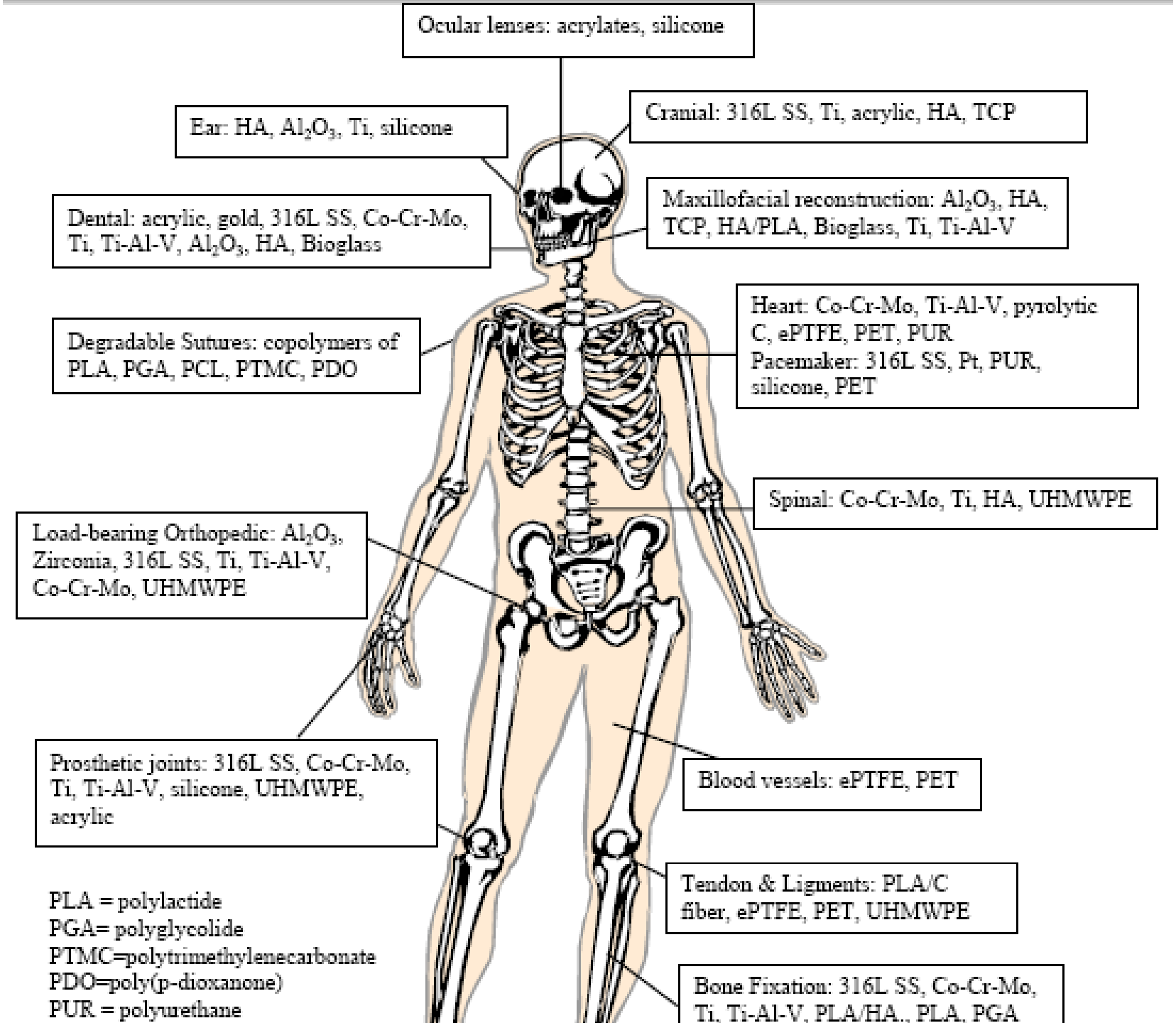
http://www.totaljoints.info/Hip.jpg

Third generation implants

- bioengineered implants using bioengineered materials
- few examples on the market
- some modified and new polymeric devices
- many under development

Example - Third generation implants

- **tissue engineered implants designed to re grow rather than replace**
- **artificial skin**
- cartilage cell procedure
- some resorbable bone repair cements
- **calcium-phosphate bone cement**s
- ***genetically engineered "biological" components***


Ocular lenses: acrylates, silicone
Ear: HA, Al_2O_3, Ti, silicone
Cranial: 316L SS, Ti, acrylic, HA, TCP
Dental: acrylic, gold, 316L SS, Co-Cr-Mo, Ti, Ti-Al-V, Al_2O_3, HA, Bioglass
Maxillofacial reconstruction: Al_2O_3, HA, TCP, HA/PLA, Bioglass, Ti, Ti-Al-V
Degradable Sutures: copolymers of PLA, PGA, PCL, PTMC, PDO
Heart: Co-Cr-Mo, Ti-Al-V, pyrolytic C, ePTFE, PET, PUR
Pacemaker: 316L SS, Pt, PUR, silicone, PET
Spinal: Co-Cr-Mo, Ti, HA, UHMWPE
Load-bearing Orthopedic: Al_2O_3, Zirconia, 316L SS, Ti, Ti-Al-V, Co-Cr-Mo, UHMWPE
Prosthetic joints: 316L SS, Co-Cr-Mo, Ti, Ti-Al-V, silicone, UHMWPE, acrylic
Blood vessels: ePTFE, PET
Tendon & Ligments: PLA/C fiber, ePTFE, PET, UHMWPE
Bone Fixation: 316L SS, Co-Cr-Mo, Ti, Ti-Al-V, PLA/HA., PLA, PGA
PLA = polylactide
PGA= polyglycolide
PTMC=polytrimethylenecarbonate
PDO=poly(p-dioxanone)
PUR = polyurethane

METALLIC BIOMATERIALS

- **Metals make attractive biomaterials because of they possess the following properties**:
  - **excellent electrical**
  - **mechanical properties**
  - **closely packed atomic arrangement resulting in high specific gravity and good strength**
  - **high melting points**

- Applications in the human body:
  - as total hip and knee joints, for fracture healing aids as bone plates and screws, spinal fixation devices, and dental implants
  - in devices such as vascular stents, catheter guide wires, orthodontic archwires, and cochlear implants

Metallic Implants

Two primary purposes

- As prosthesis – to replace a portion of the body such as:
  - joints, long bones & skull plates
- Fixation Devices – to stabilize broken bones while the normal healing proceeds
  - Bone plates, intramedullary nails, screws and sutures

Problems:

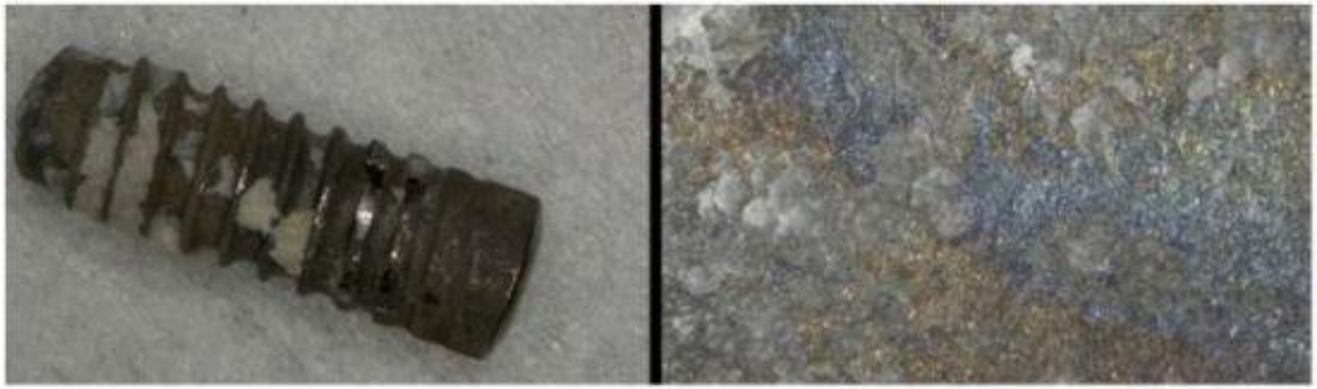
1. Biocompatibility: The ability of a material to perform with an appropriate host response in a specific situation
2. **Corrosion**
3. Design of metallic implants
4. Design limitations the of anatomy
5. **Physics properties of the tissue and reactions of the tissue to the implant and of the implant to the tissues** (Host Response)

Different Metallic Biomaterials

- Stainless Steel
  - SS 316
  - SS 316L
- **CoCr Alloys**
  - the castable CoCrMo alloy
  - The CoNiCrMo alloy which is usually *wrought* by (hot) *forging*
- **Ti alloys**
  - **Pure Ti**
  - **Ti6Al4V**
- **TiNi Alloys**
  - **Nitinol**
  - **Shape Memory effect**
- Platinum group metals (PGM)
  - Pt, Pd, Rh, Ir, Ru, and Os
  - extremely corrosion resistant
  - poor mechanical properties
  - pacemaker tips
- conductivity.

DANGEROUS CONSEQUENCES by the degradation of Biomaterials under physiological conditions :
FOR EXAMPLE:
Dental fillings decomposition by Various conditions in the mouth ...pH....presence of various harmfull substances

Corrosion of Dental implants...




Medscape®
www.medscape.com
Source: Neurosurg Focus © 2004 American Association of Neurological Surgeons


6280-3

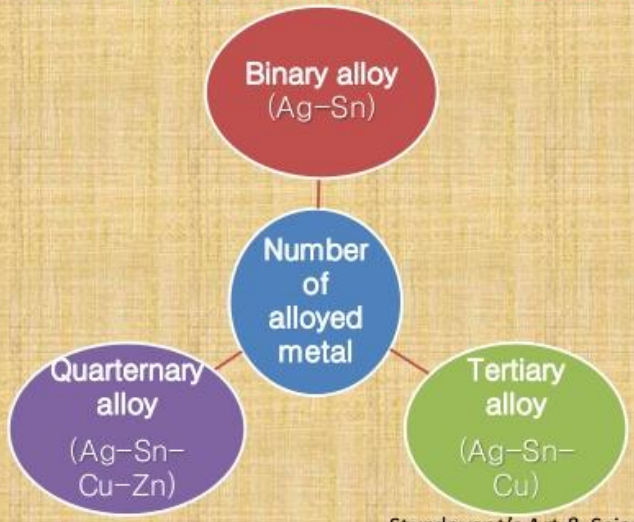
Application of Voltammetry in Dental Medicine

-dental fillings (amalgams)

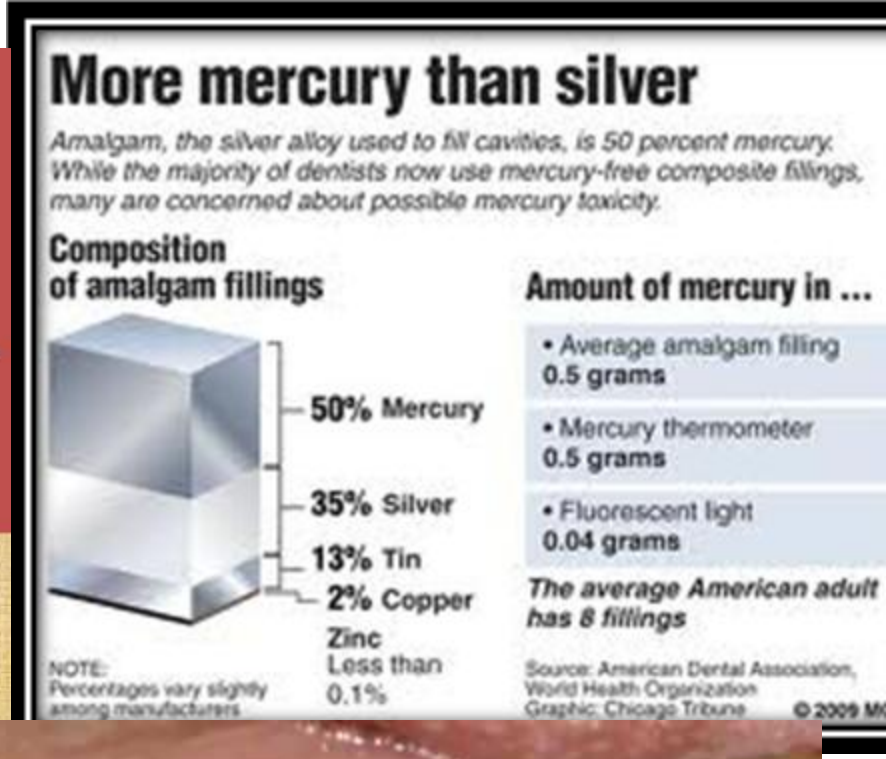
Denal implants

Classification of Amalgam

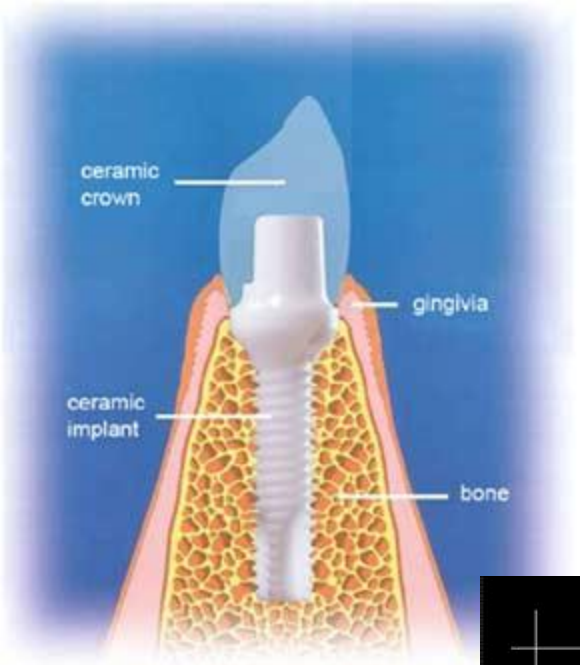
A) According to Alloyed Metals

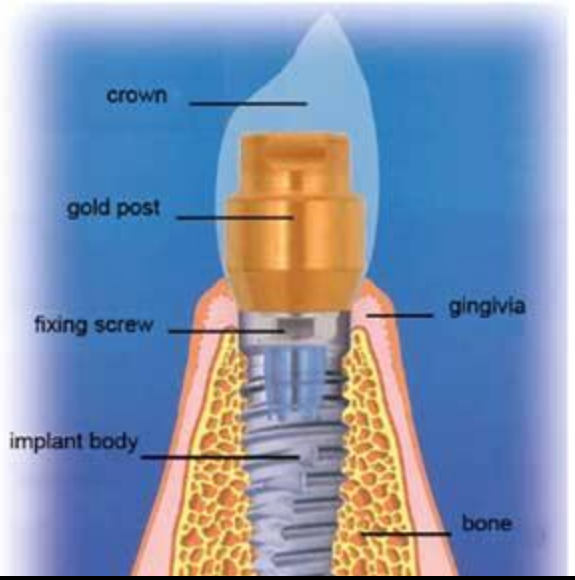


Sturdevant's Art & Science of Operati
5th ed



Dental implants





Corrosion by the dental amalgam fillings- major problem!!!

Types of Corrosion:

1) **Galvanic corrosion:**

Dental amalgam is in direct contact with an adjacent metallic restoration such as gold crown

2) **Crevice Corrosion:**

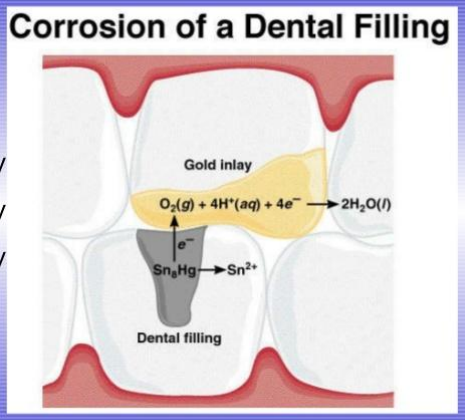
- Local electrochemical cells may arise whenever a portion of amalgam is covered by plaque on soft tissue.
- The covered area has a lower oxygen and higher hydrogen ion concentration making it behave anodically and corrode.

Chemistry In Action: Dental Filling Discomfort

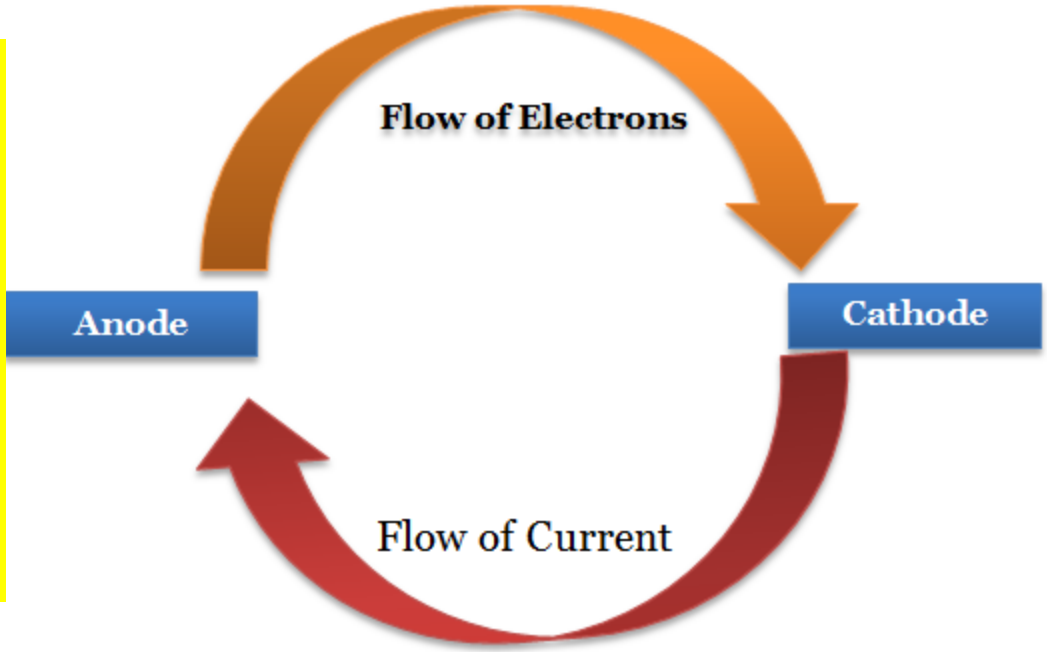
Hg_2^{2+}/Ag_2Hg_3 0.85 V

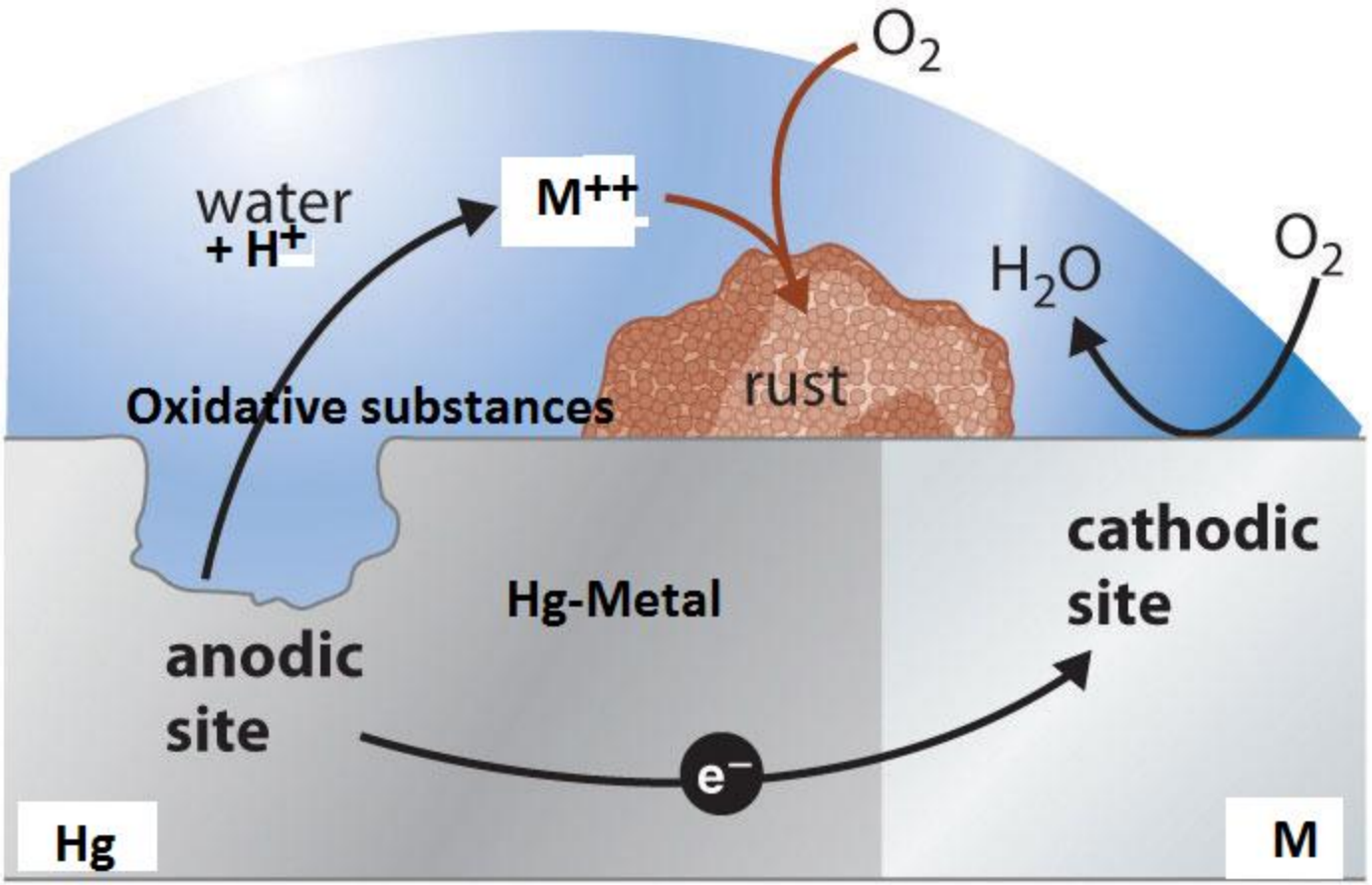
Sn^{2+}/Ag_3Sn -0.05 V

Sn^{2+}/Ag_3Sn -0.05 V



Galvanic microelement is formed if Amalgam and a Gold filling are in close Contact, for example, which causes Amalgam dissolution




O_2
water
+ H^+
M^{++}
H_2O
O_2
rust
Oxidative substances
cathodic
site
Hg-Metal
anodic
site
e^-
Hg
M

The processes of amalgam degradation are more significant in presence of:

-Oxidative substances
(**hypochlorates** present in the water, **Quinones** from the food...)

-in acidic pH

-in presence of some organic ligands

-...peroxides and free radicals

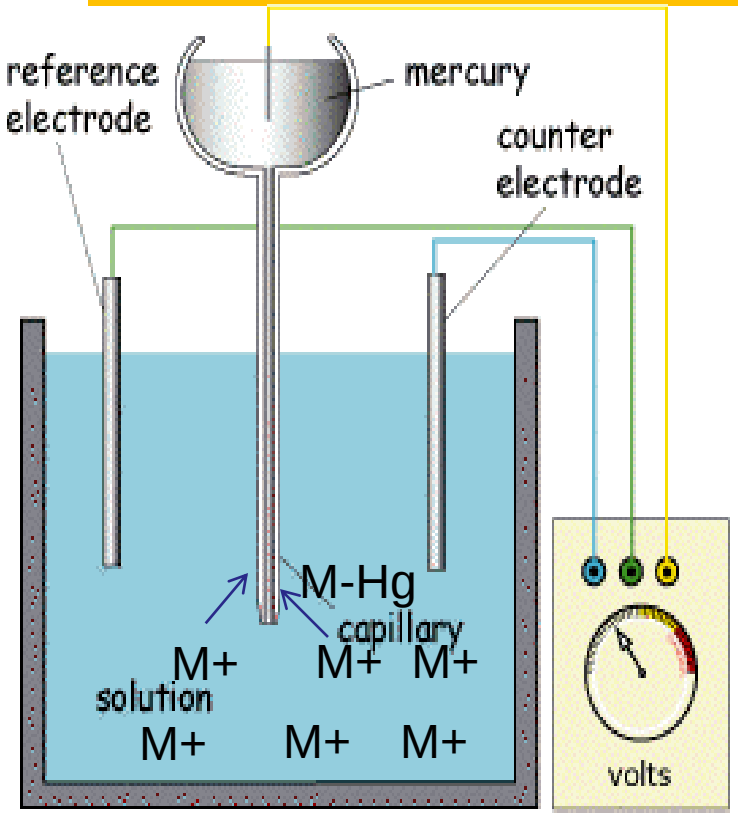
...

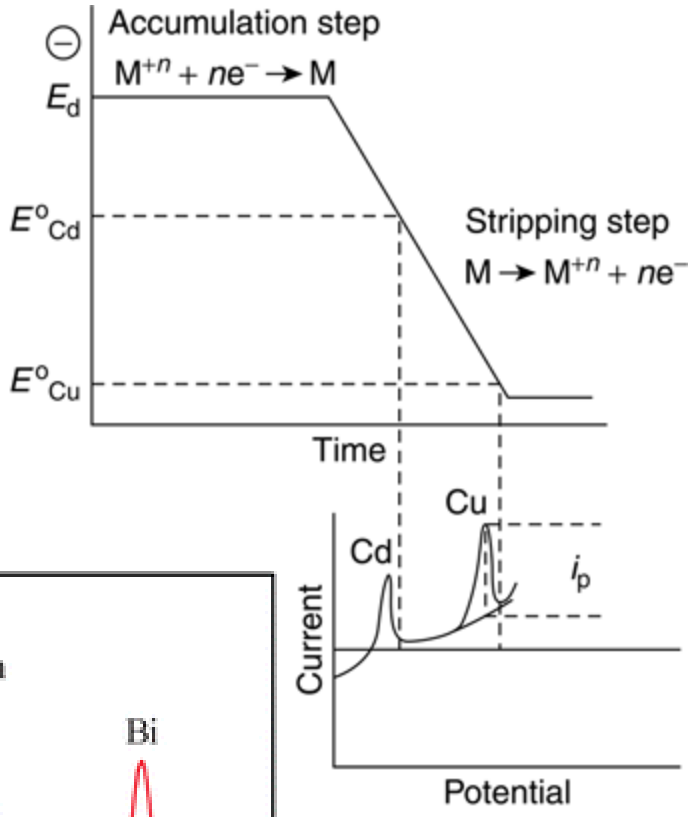
Low copper amalgam system:-

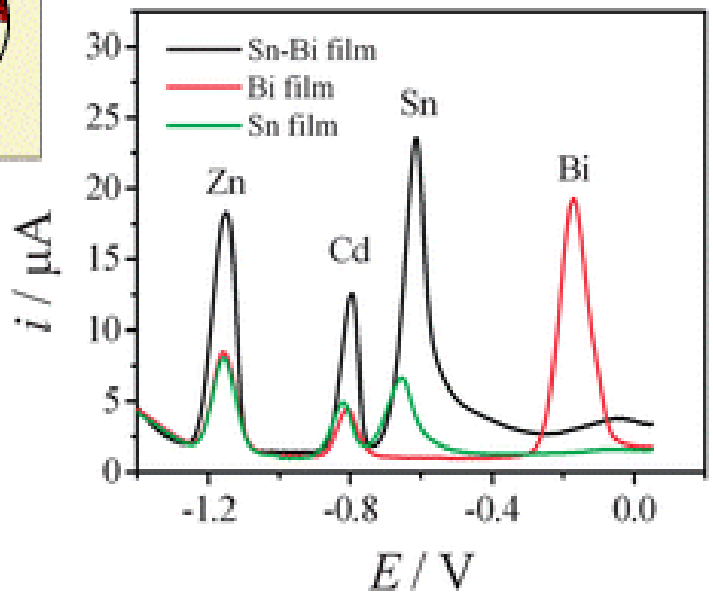
- Most corrodible phase is tin-mercury or γ_2 phase.
- Neither the γ nor the γ_1 phase is corroded as easily.
- The corrosion results in the formation of tin oxychloride, from the tin in γ_2 and also liberates Hg.

$$Sn_7\text{-}_8Hg + 1/2O_2 + H_2O + Cl^- \rightarrow \underset{\text{Tin oxychloride}}{Sn_4(OH)_6Cl_2} + Hg$$

Anodic Stripping Voltammetry-a Technique
Suitable to study the Features of the Amalgams







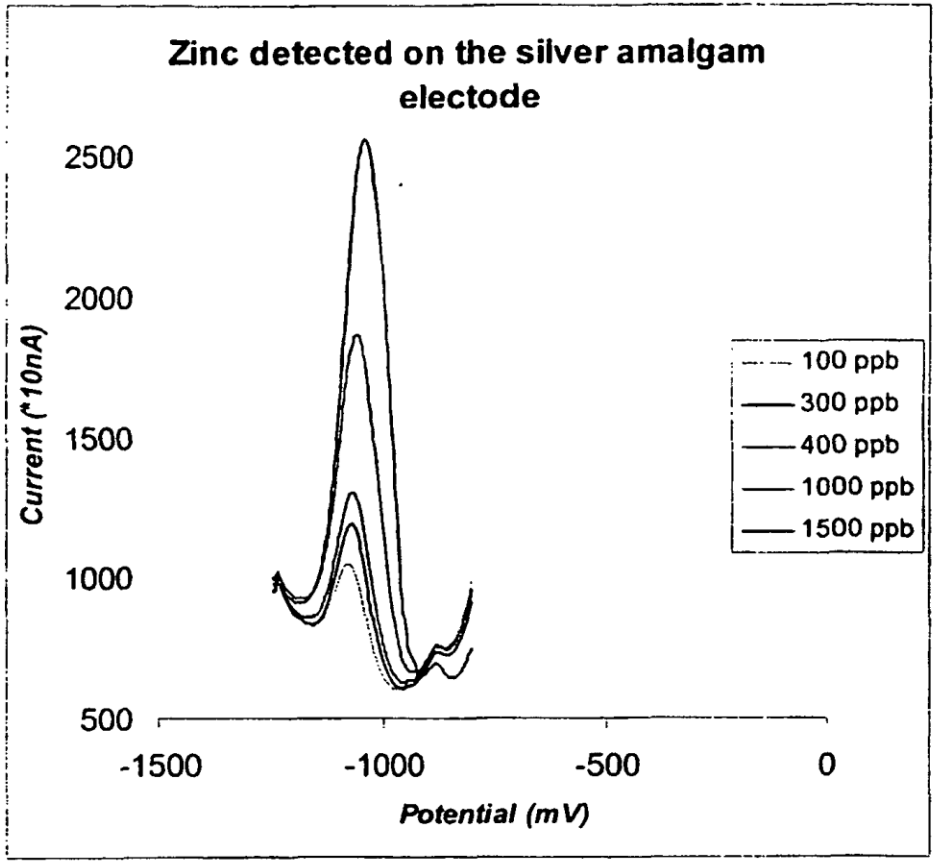

Zinc detected on the silver amalgam electode
2500
2000
1500
1000
500
Current (*10nA)
-1500
-1000
-500
0
Potential (mV)
100 ppb
300 ppb
400 ppb
1000 ppb
1500 ppb

Figure 4

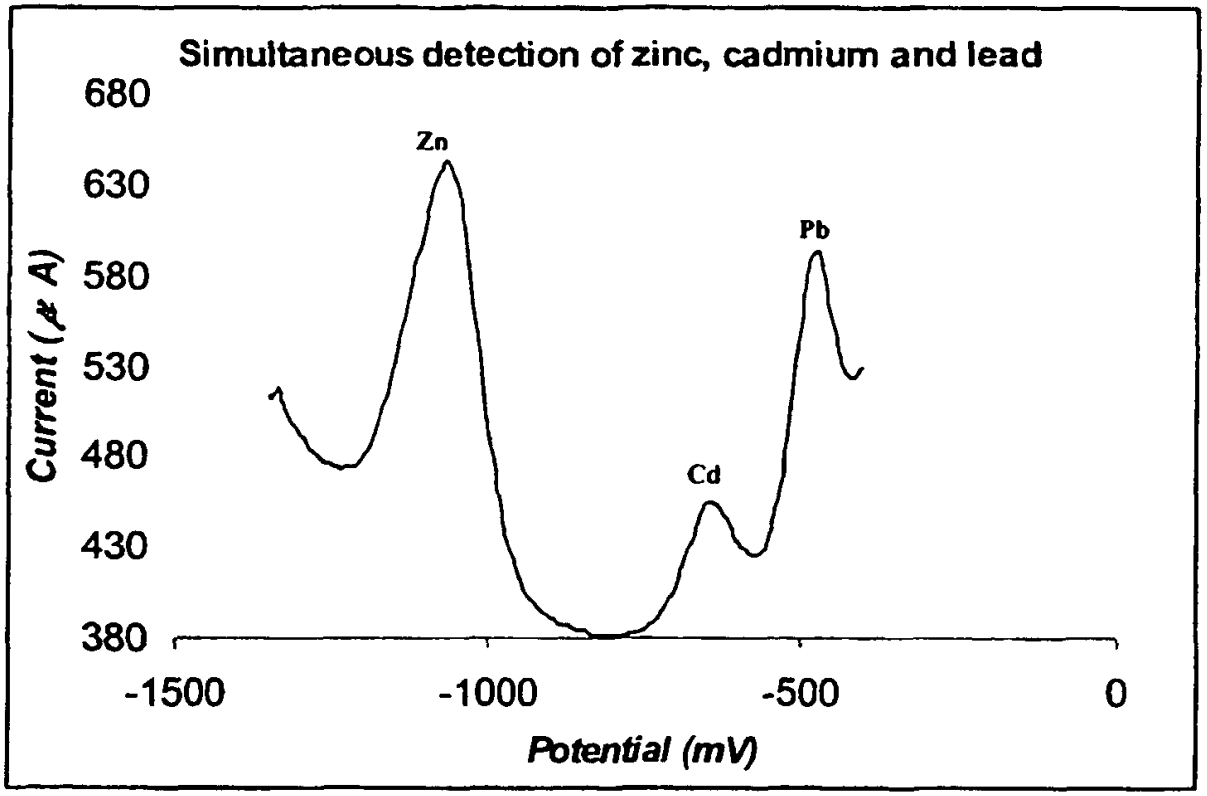
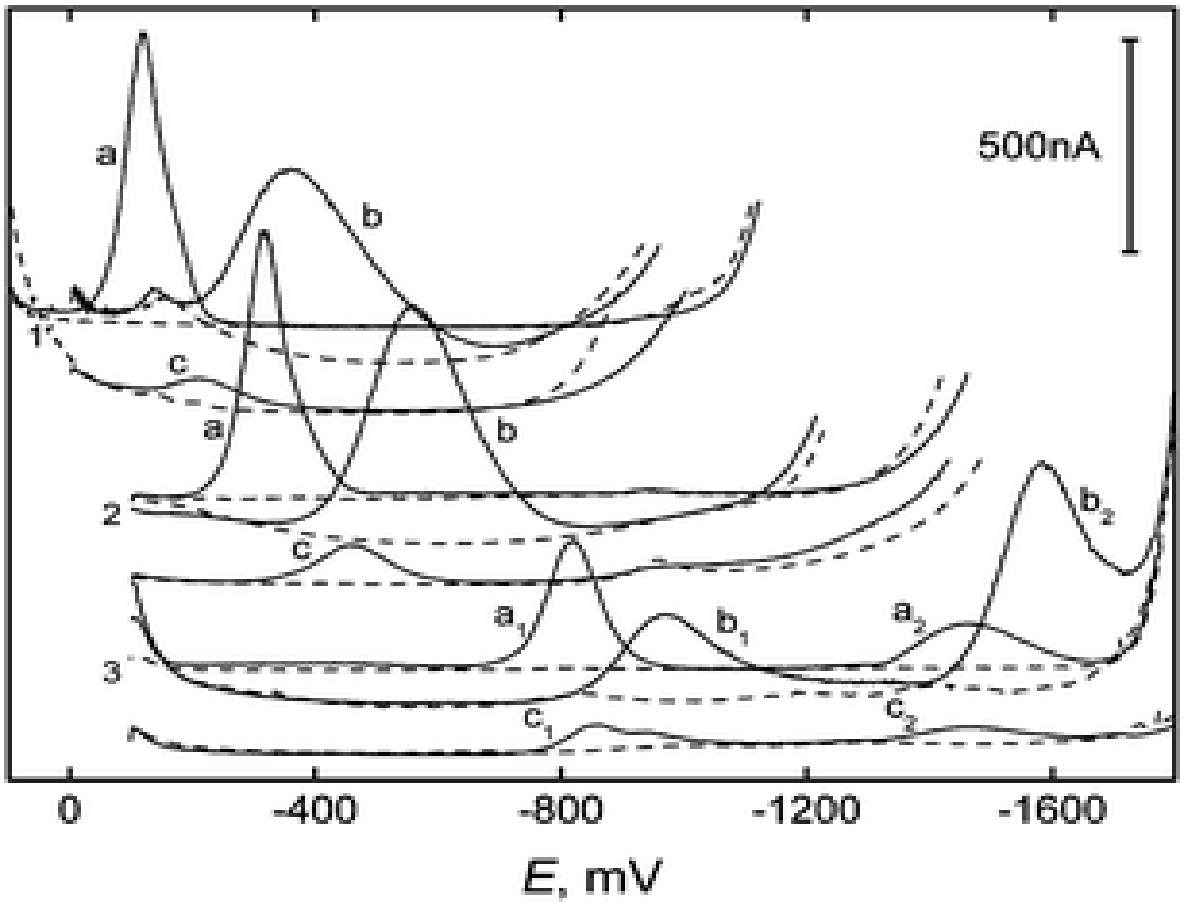
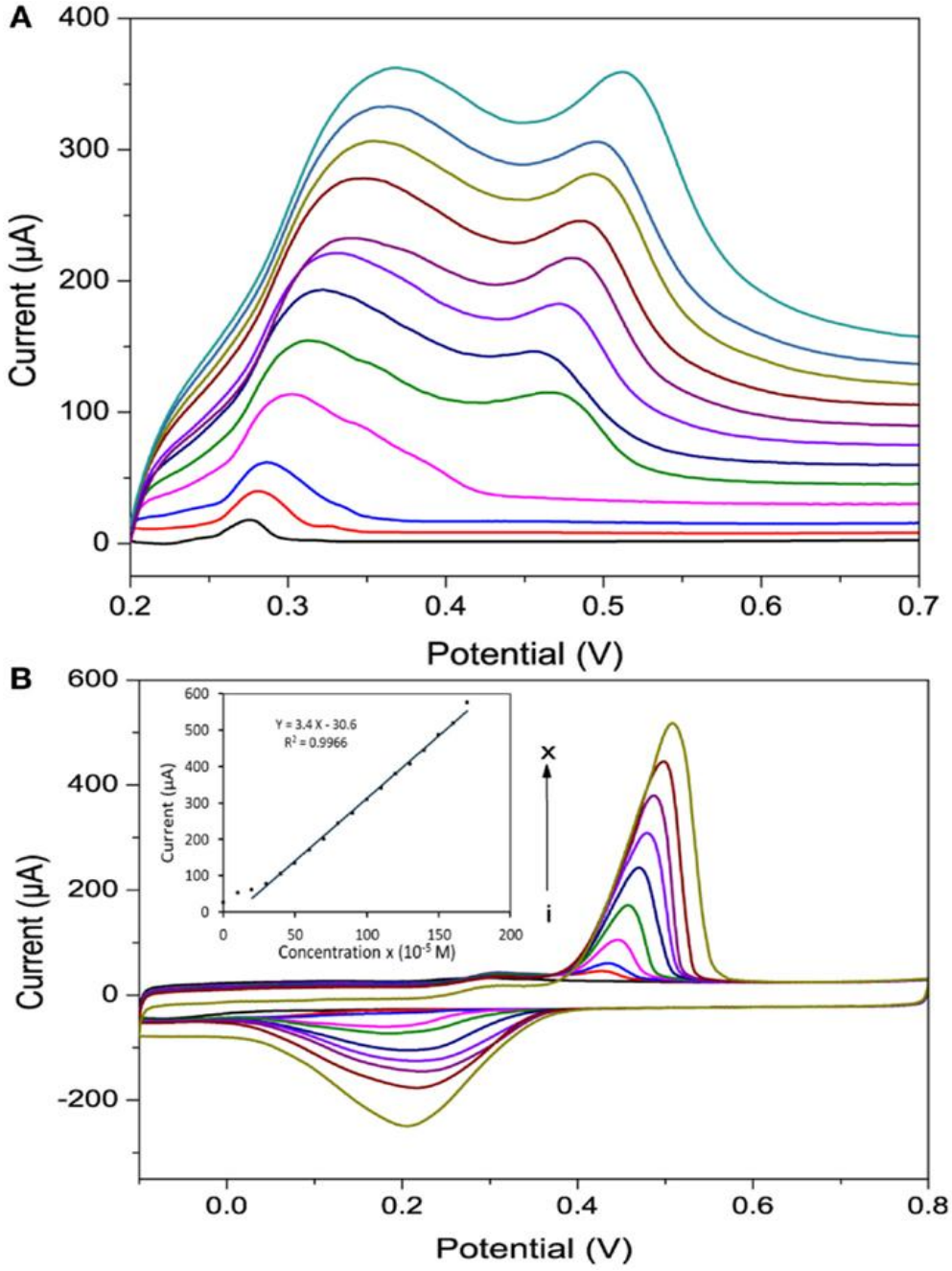

Simultaneous detection of zinc, cadmium and lead
680
630
580
530
480
430
380
Current (μ A)
Zn
Pb
Cd
-1500
-1000
-500
0
Potential (mV)

Figure 6



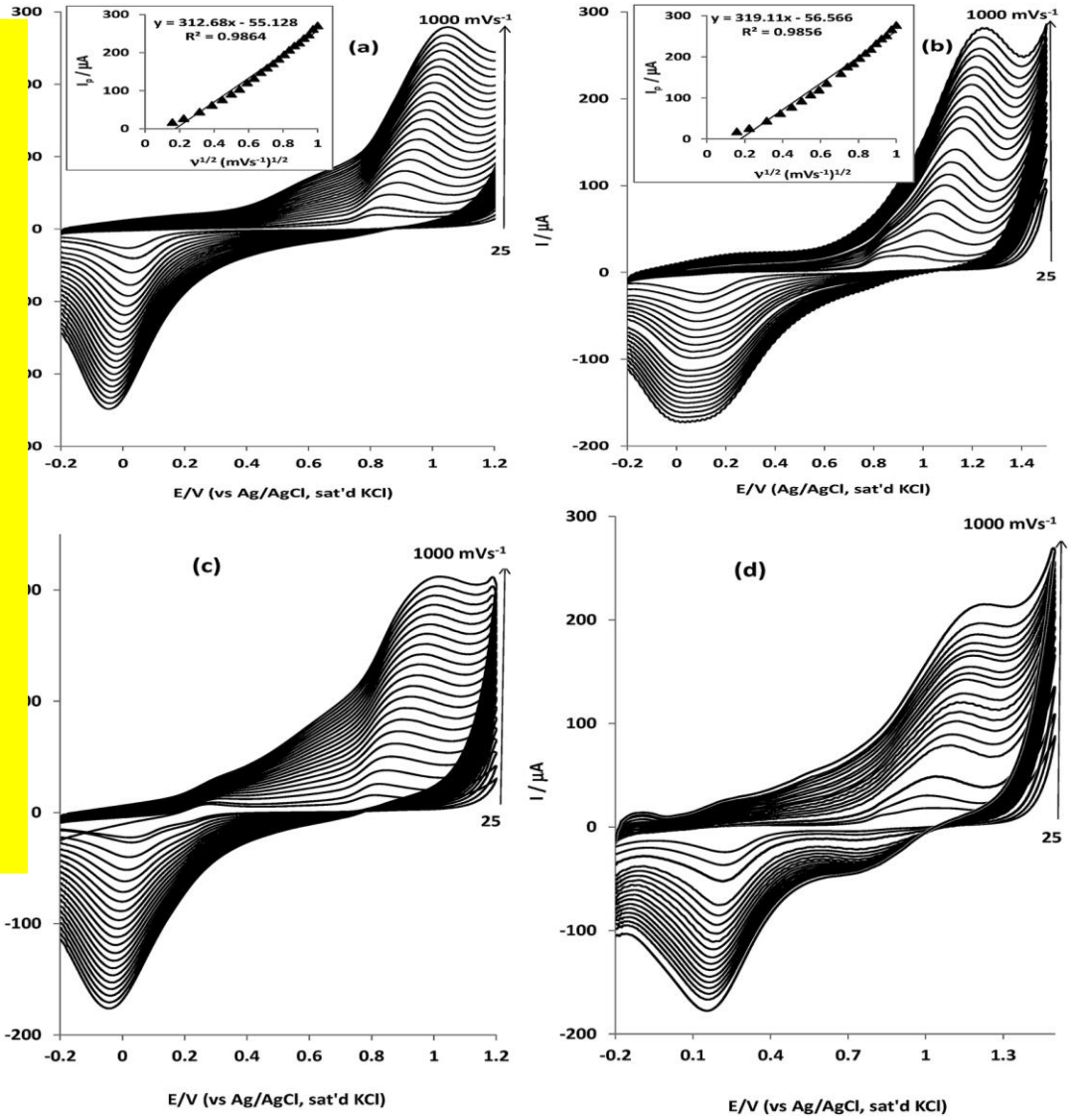
Voltammograms of **silver amalgam** in presence of ***nitrophenols*** in various pH
pH ranging from acidic to basic



Voltammetry of dental amalgams in presence of different concentrations of hypochlorites and chlorides...
Mercury dissolution!!!

Voltammetry
-Surface
modification
of dental fillings

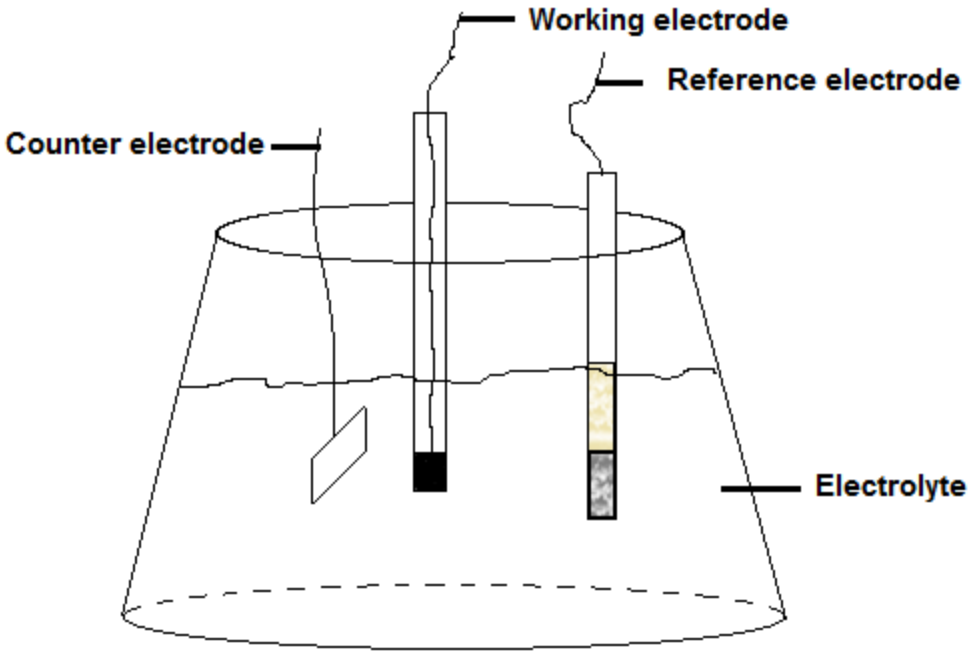
...This operation is performed to protect Amalgam dental Fillings of corrosion

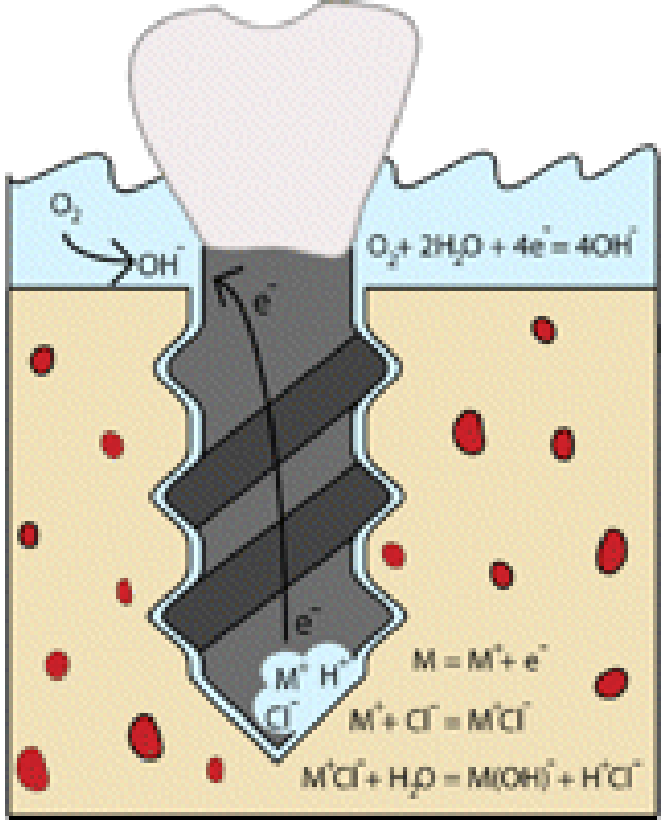


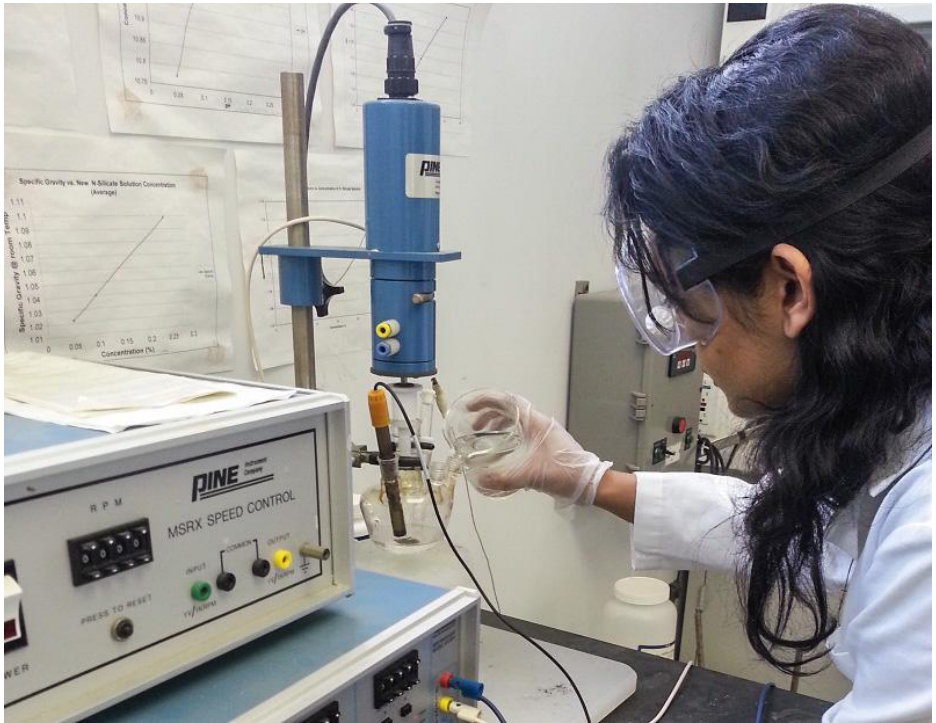
Dental implants corrosion

Co –Cr or Ti-Cr Alloys

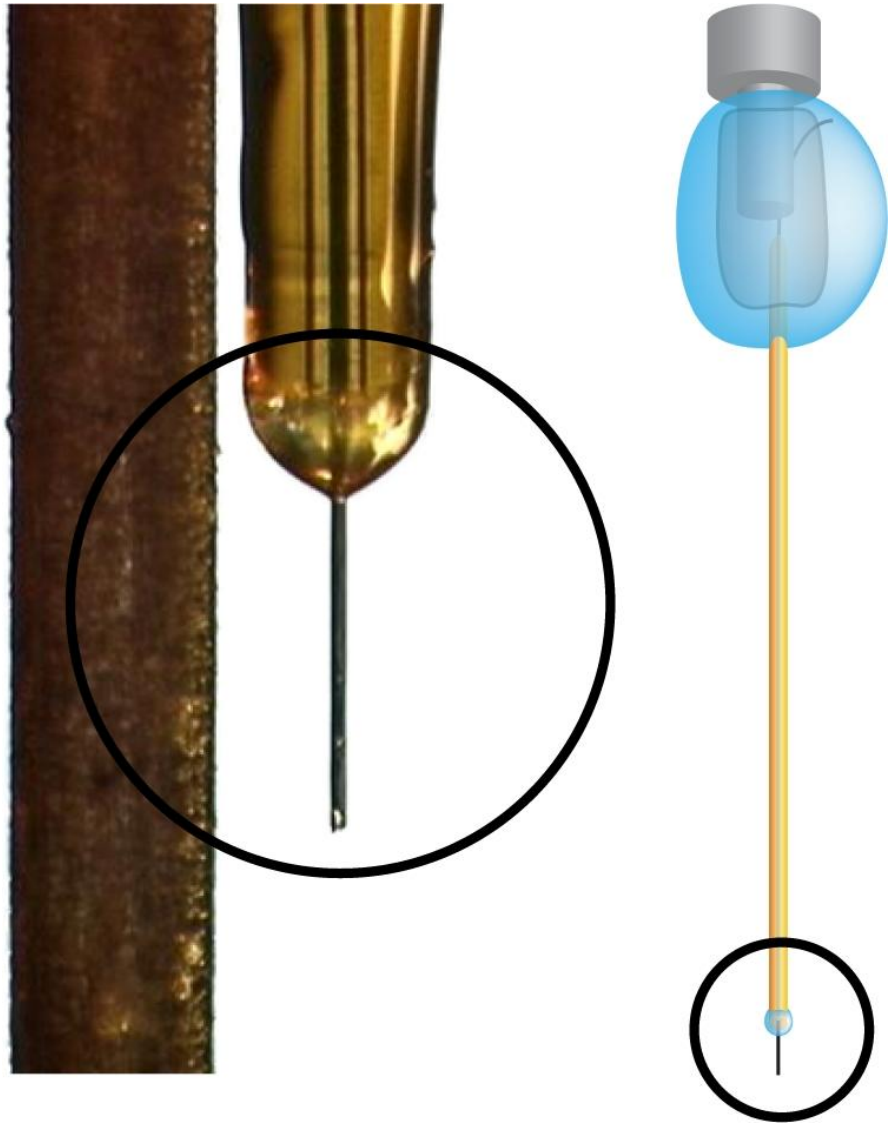
- Co between Fe and Ni
- Forms solid solution with Cr
- **Molybedum added to produce fine grains which results in higher strength**
- **The chromium enhances corrosion resistance as well as solid solution strengthening of the alloy.**
- Metallic Co –used in beginning of the century but was not very ductile or corrosion resistant
- 1930s – vitallium – 30% Cr, 7% W 0.5% C in Co
  - Mostly for metallic dental castings
  - To replace the more expensive gold alloys
  - Larger partial denture castings
- Cast vitallium: dentistry and now recently in artificial joints
- Wrought vitallium: stems of heavily loaded joints such as femoral hip stems


Working electrode
Reference electrode
Counter electrode
Electrolyte

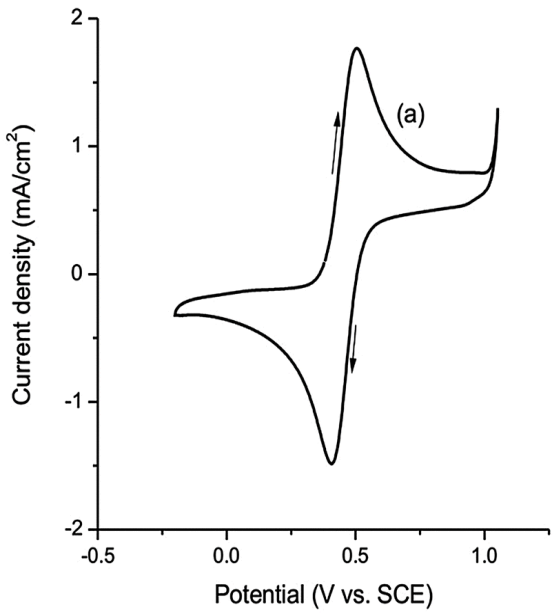

O2
OH-
O2 + 2H2O + 4e- = 4OH-
e-
e-
M+ H+
Cl-
M = M+ + e-
M+ + Cl- = M+Cl-
M+Cl- + H2O = M(OH) + H+Cl-

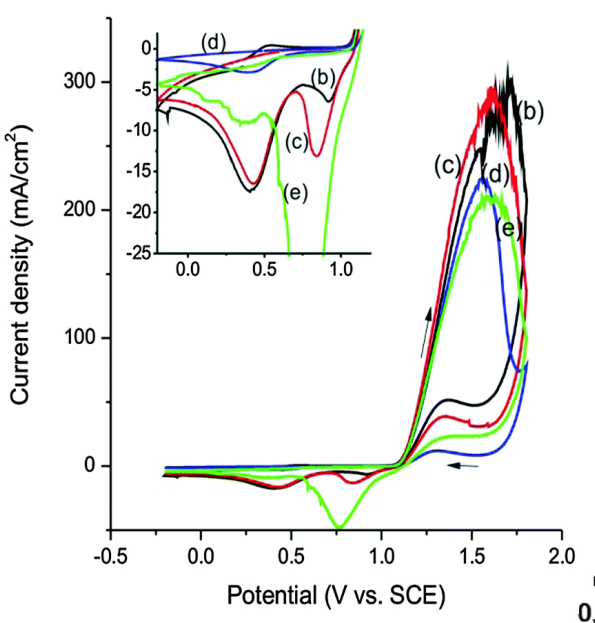

PINE
MSRX SPEED CONTROL
RPM
PRESS TO RESET

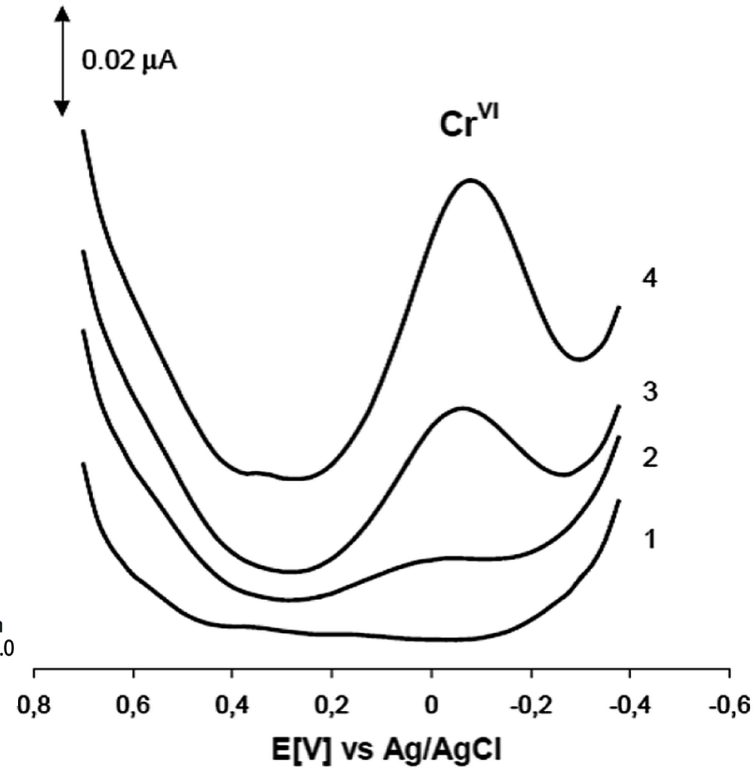
Strategy of designing Electrochemical Experiment with Dental Implants and other alloys used as biomaterials...



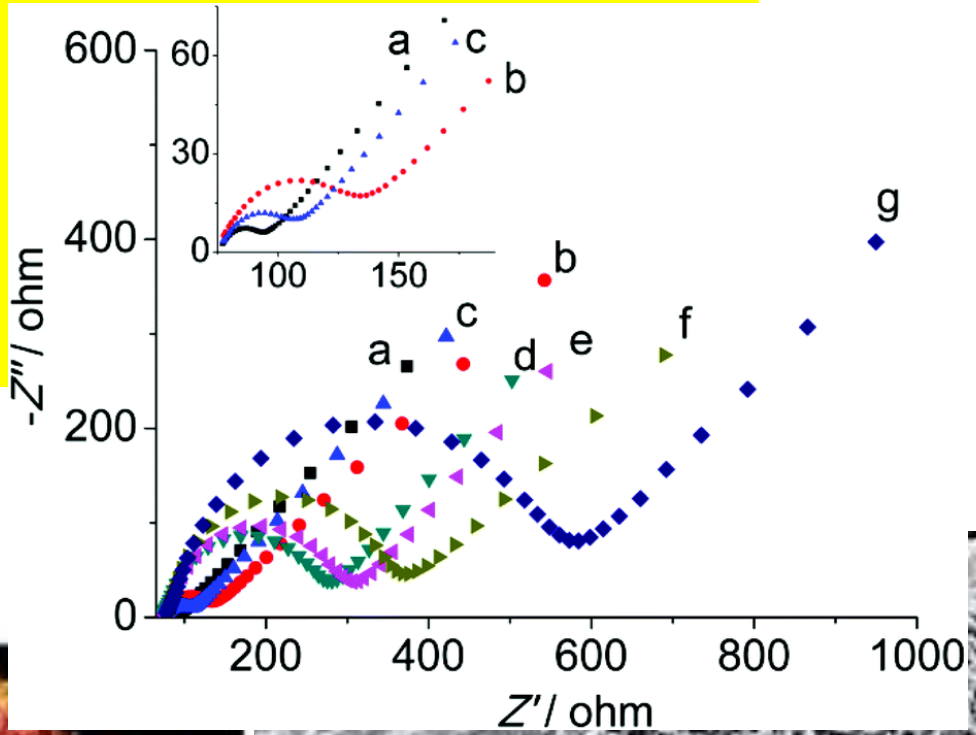

20-25 GPa
115 GPa

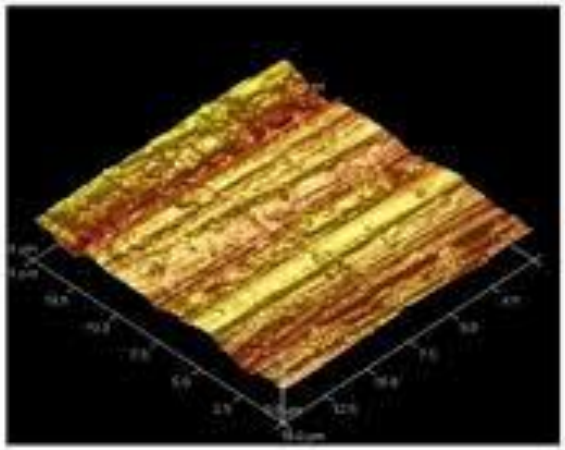

Current density (mA/cm^2)
Potential (V vs. SCE)
(a)

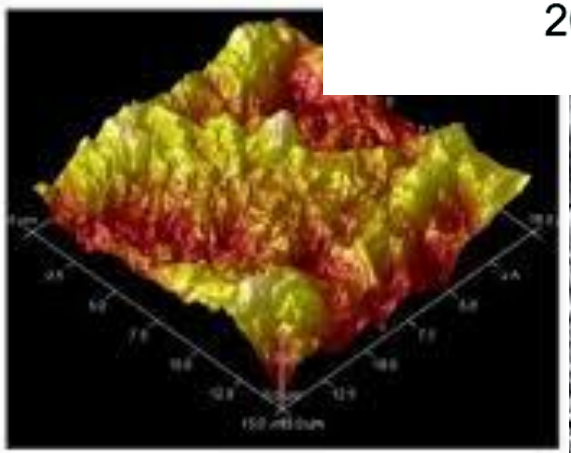

Current density (mA/cm^2)
Potential (V vs. SCE)
(a)
(b)
(c)
(d)
(e)

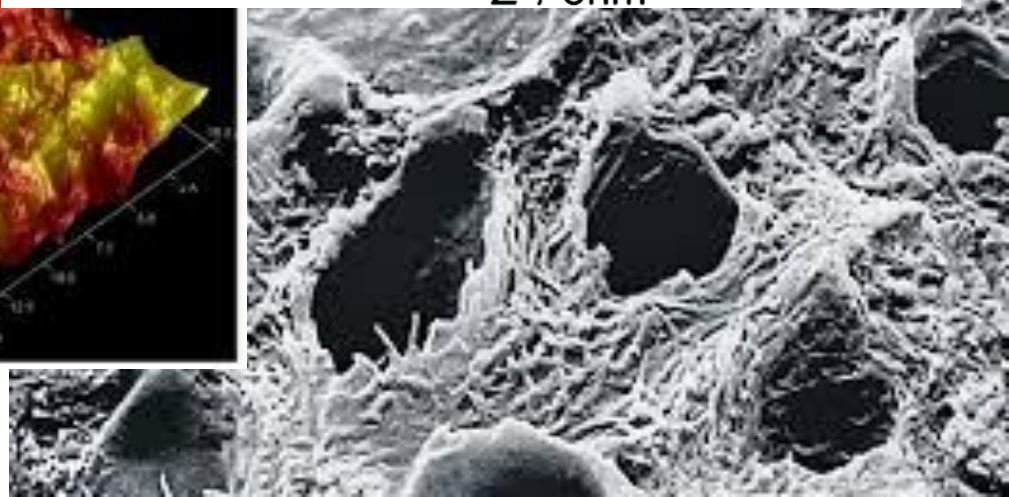

0.02 µA
Cr^{VI}
4
3
2
1
E[V] vs Ag/AgCl

...voltammetry is not a self-sufficient technique...
Other techniques are required for complete characterization of the Biomaterials, i.e.
Impedance Spectroscopy
AFM
SEM....

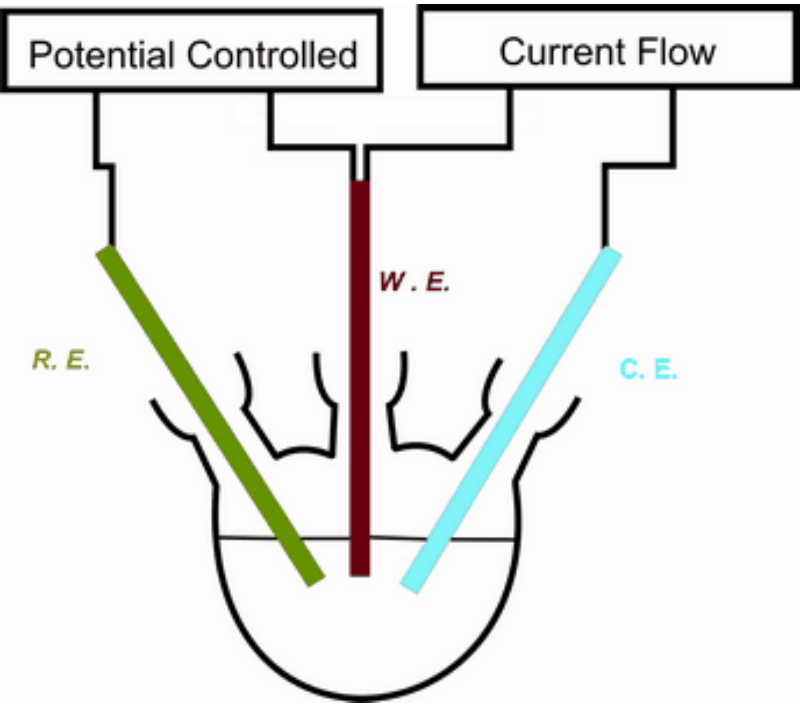


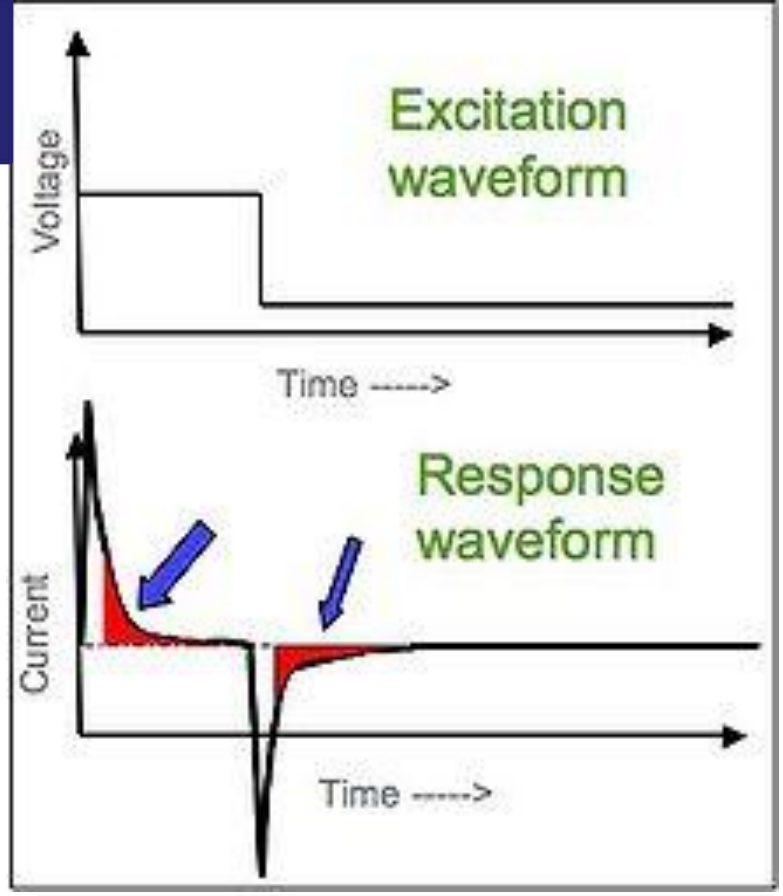


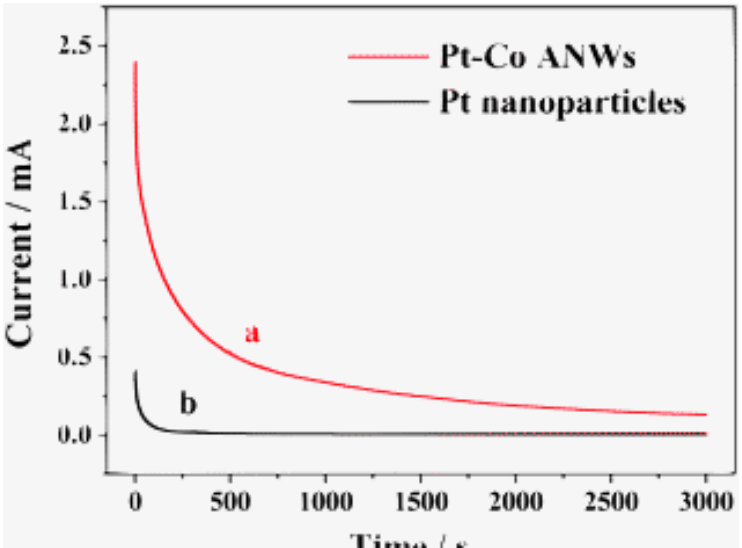




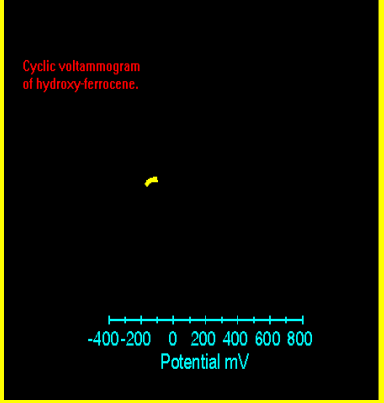
Chrono-amperometry







Concluding remarks



...ADVANTAGES of using Voltammetry for characterization of biomaterilas:

-fast înstrumental technique

-extremely cheap instrumentation

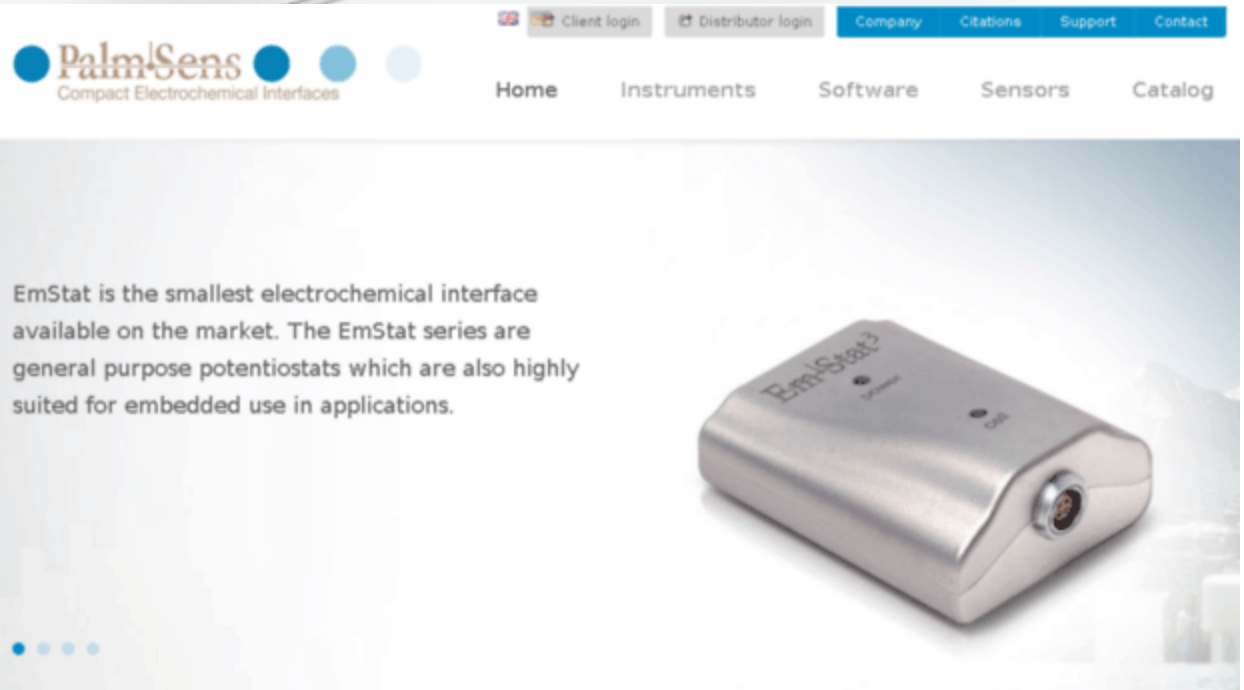
-common chemicals are used available in every Lab

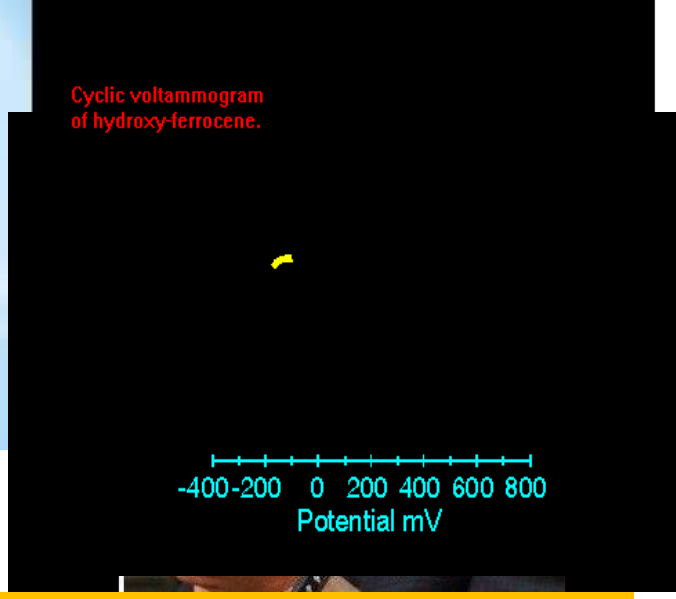
-...suitable for qualitative, quantitative studies, Mechanistic studies, kinetic and thermodynamic measurements

Total costs for the voltammetric instrumentation

3-4000 Euros!!!!

Amazing!!!





Thanks ...K. J. UN...more voltammetric results .....NEXT YEAR