Nate Bowling (Organic Chemistry)

Organic Solar Cells

In photosynthesis, nature provides an excellent model for converting light to electrical energy using primarily organic molecules. With this model in mind, students will design highly conjugated, carbon-rich organic molecules explicitly for the purpose of mimicking photosynthetic processes. We anticipate that this research will lead to better understanding of highly conjugated organic molecules, in particular, how these molecules interact with light.

Molecular Memory Devices

As computer chips get smaller, the limitations of current chip-making techniques are presenting more and more challenges. Some of these limitations arise from the bulk properties of the materials used. One way to avoid these limiting factors would be to design memory devices out of individual organic molecules. Students working on this project will make conjugated organic molecules that can exist in two different, stable states. These two states can be used as a source of molecular memory, much like the "1" and "0" states in a computer chip. Additionally, these molecules can serve as molecular switches for an array of processes, ranging from metal recognition to molecular self-assembly.

Design and Synthesis of Carbon-rich Compounds

Novel, highly conjugated, carbon-rich compounds can be synthesized from readily available precursors. The delocalized nature of the electrons in these molecules has generated excitement in the fields of organic light emitting diodes, thin film organic transistors and optical storage devices. With careful synthetic design, one can tune the electronic properties of these molecules through appropriate placement of chemical functionalities in order to achieve a specific function. Students working on this project will be involved in the synthesis of new organic molecules in order to learn more about their behavior and the "tunability" of their electronic properties. During the course of their work, students will become familiar with an array of synthetic techniques, as well as spectroscopic methods, such as IR, UV-vis and NMR spectroscopy.

James Brummer (Physical/Inorganic Chemistry)

Luminescence and Photochemistry of Transition Metal Complexes

We are currently investigating the properties of complexes possessing tungsten and rhenium centers that bind molecular nitrogen and/or aromatic isonitrile ligands. When these complexes absorb visible and/or ultraviolet light, an excited state is created which exists for nanoseconds up to seconds. These energized complexes display modes of chemical reactivity not usually seen in unexcited molecules, and may emit light (phosphorescence or fluorescence) upon returning to the unexcited ground state. Students become involved with the synthesis of compounds under an inert atmosphere, photochemical measurements, and measurements of absorption and emission properties. Many measurements must be made on samples cooled to cryogenic temperatures (4-77K). Students acquire experience with the use of mercury lamps, lasers, monochromators, photometers, oscilloscopes, infrared spectrometers, nuclear magnetic resonance spectrometers, absorption spectrophotometers, and spectrofluorimeters. The ultimate goal of my research is to understand the electronic properties of the lowest energy excited states of metal complexes in order to guide the design new complexes that will display desirable photophysical properties.

Laura Cole (Analytical Chemistry)

Bioanalytical investigations using separation methods

Separation methods are a powerful tool for purifying, identifying and quantifying components in complex mixtures. High performance liquid chromatography (HPLC) and capillary electrophoresis (CE) are techniques that my group uses to answer questions about biological samples. HPLC separates materials based on their interaction with a stationary phase, while CE separates materials based on their charge and other characteristics. One recent research project was the determination of St. John's Wort's amounts in herbal supplements using HPLC. Other materials that are of interest are metabolites from biological processes and pesticides in environmental or biological samples.

Kevin Czerwinski (Organic Chemistry)

My research group specializes in directed organic synthesis for the purpose of preparing compounds for pharmacological study. The specific aim of our research is to investigate the inhibitory activity of substituted canthin-6-one and canthin-5,6-dione indole alkaloids against human cAMP phosphodiesterase (PDE4) isoenzymes. In the past, canthin-6-one indole alkaloids have been shown to elicit inhibitory activity against bovine PDE4 but the particular molecular features necessary for optimum inhibitory activity against human isoforms are unknown. My research entails three distinct activities: 1) the synthesis of a series of canthin-6-one and canthin-5,6-dione indole alkaloid derivatives, 2) the screening these compounds for inhibitory activity against human PDE4 isoforms, and 3) the development of a three-dimensional quantitative structure activity relationship (3D-QSAR) by computational quantum mechanical methods so as to provide a direction for further study.

Students that work in my laboratories gain expertise in the methodology of synthetic organic chemistry and modern instrumental characterization of natural products by such means as nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy. Students also gain an appreciation of experimental design, monitoring, analysis, and the time it takes to conduct a proper experiment.

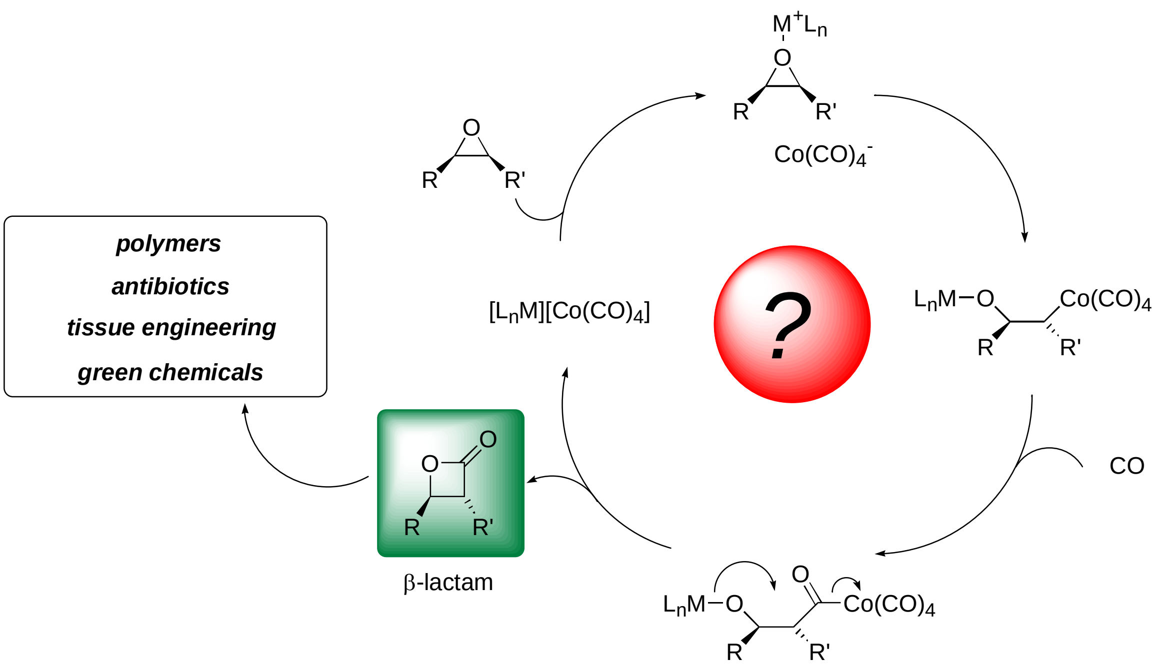
Jason D’Acchioli (Inorganic Chemistry)

Computational chemistry, inorganic chemistry, spectroscopy, reaction mechanisms

Broadly defined, my research interests are in computational chemistry. That essentially means that if an interesting chemical problem presents itself—whether it is inorganic, organic, or physical in nature—I am interested in trying to understand it. My specific interests are in two main areas.

1. Electronic effects and site-selectivity: Designing new catalysts.

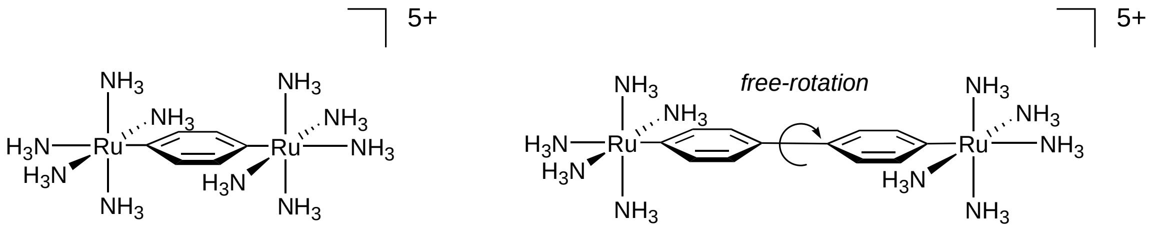
The synthetic work involved in designing new transition metal catalysts is daunting. We propose utilizing a computational "screening" methodology to probe both steric and electronic effects on a variety of catalytic systems *prior* to synthetic work. The investigation will be facilitated through collaboration with Professor Geoffrey Coates at Cornell University. The system of interest (Scheme 1) is under investigation by Coates and coworkers; it illustrates both the elegance and sheer complexity of this area of chemistry. The products of interest are β-lactams, which have a number of uses in polymer chemistry, tissue engineering, and green chemistry. The route involved in trying to obtain the product, however, involves modifying the catalyst by changing the metal center, ligands, or functional groups. Through the use of computational methods we hope to guide the synthetic abilities of the Coates group.



Scheme 1

2. Electronic coupling between metal centers.

How do metal centers talk to each other? The answer to this question has important implications in materials chemistry and nanotechnology. We have found that electronic coupling can, in part, be elucidated through the use of density functional theory methods. However, does DFT do the "best" job at gauging electron delocalization? We know from a variety of spectroscopic techniques (electron-spin resonance—10^{-7} sec; UV-Visible spectroscopy—10^{-15} sec; electrochemical methods—$1 – 10^{-7}$ sec) that electron delocalization can be probed experimentally. A consensus on describing delocalization utilizing computational methods, however, is not readily available. I propose a thorough investigation of electronically delocalized systems, starting with the Creutz-Taube ion as the classic paradigm (Scheme 2). This complex, which contains Ru atoms that are known to "talk" to each other, has been probed with many spectroscopic and computational methods, e.g. DFT and CASSCF. However, there are other ways to utilize the theory we have available to us, and here we need to be creative. How does a point charge perturb the delocalized system (if, in fact, it is delocalized)? What role, if any, does solvent play in electron transfer? The answers to these questions should lead to a more satisfying picture of electron delocalization.



Creutz-Taube ion
Delocalized

biphenyl bridged analogue
less delocalized

Scheme 2

3. Metal-metal multiple bonds in materials.

In collaboration with Dr. Matthew Byrnes at Monash University in Australia, we will be investigating the use of metal-metal (M_2) multiply bonded complexes in materials applications. We will be using density functional theory techniques to both probe and guide the synthesis of novel complexes. This is a new project, and more details will be forthcoming.

John Droske (Organic/Polymer Chemistry, Polymer Education)

Biomedical Polymers

We are preparing a series of copolymers that show promise for use as bone adhesives and tissue scaffolds. A focus of this research is to prepare porous materials that will provide strength to damaged bones as they heal, but will allow bone to grow through the materials. When the bone is healed, the copolymers will bioresorb, leaving new bone in its place. This work currently is funded by a special UW System grant. Students interested in this work ideally should have completed Chem 325/6 (Organic), but there are parts of the project that are suitable for very interested students who are currently enrolled in these courses.

Polymers in Museums

Synthetic polymers are relatively new materials and little is known about the stability of these materials in long term storage. For example, some of the materials in the Apollo spacesuits are undergoing degradation more rapidly than expected and this is a major concern to conservators. This has lead to the establishment of a special “Save America’s Treasures” project at the Smithsonian Institution National Air and Space Museum. We are assisting with this project by analyzing the spacesuit materials and trying to develop improved ways for storing this collection. This project uses our thermal analysis system and other tools and students interested in this project should have completed at least one year of chemistry.

Thermally Stable Polymers

Much of our research has focused on the development of composite matrix resins for use at elevated temperatures. A major purpose for our work is the synthesis of monomers with electron withdrawing and donating groups to see how these influence the thermal stability of the matrix resins. This project utilizes organic laboratory techniques to prepare the monomers needed for the synthesis of the matrix resins. A major part of our effort is developing synthetic methodology for the preparation of novel monomers. Much of this work has been done in collaboration with NASA-Glenn Research Center. Students interested in this project should have completed Chem 325/6 (Organic).

POLYED National Information Center for Polymer Education

POLYED is the joint education committee of the Polymer Divisions of the American Chemical Society. In 1989, POLYED established the National Information Center for Polymer Education at UWSP, the first center of its kind for materials education in the United States. The Center serves as a clearinghouse for information on polymer education and distributes resources to teachers throughout the U.S. The American Chemical Society Committee on Professional Training recently has revised its guidelines for accreditation of undergraduate chemistry programs (UWSP's Chemistry Department is ACS-accredited). In the new guidelines, ACS said that principles of macromolecular science should be integrated throughout the foundation courses in chemistry. Although many other countries have already adopted this, this is the first time that ACS has called for macromolecular chemistry in the undergraduate chemistry curriculum. ACS has asked the POLYED Center to work with CPT to assist them in developing materials to help other undergraduate chemistry programs incorporate macromolecular concepts in their courses. Students, especially those considering teaching as a career, are encouraged to become involved in the various activities of the Center.

Paul Hladky (Polymer Chemistry, Surface Chemistry)

Random Walk Polymers

The shape or configuration of a polymer molecule can often be pictured as the path of a random walk. Starting with this simple picture leads to models of rubber elasticity, size exclusion chromatography (SEC), and colloid stabilization. A project in this area will give a student the chance to start with a simple theoretical model of a polymer and predict experimentally observable properties such as the force vs. extension of elastic materials and the equilibrium of a polymer between a bulk liquid phase and a porous phase.

Mathematica™ in Physical Chemistry

Mathematica™ is a software package that is revolutionizing how mathematics is done on a computer. For example, with *Mathematica™* it is now routine to solve the differential equations describing the kinetics of fairly complex chemical reactions and plot the concentrations of the reactants and products as functions of time. By changing the starting concentrations and varying the rate constants the behavior of any reaction mechanism (from small molecules in the gas phase to large enzyme catalyzed reactions in solution) can be studied. As a second example, real gases deviate from ideal gas behavior at high pressures or low temperatures. The Van de Waals equation is one attempt to account for the attractive and repulsive forces present in real gases and can be used to predict a variety of properties of gases such as their liquid-vapor phase diagrams and Joule-Thomson coefficients. Using *Mathematica™* it is possible to calculate and plot these predictions for a series of compounds. With these plots one can look for trends among related compounds and ultimately understand how intermolecular interactions affect physical properties.

Jim Lawrence (Biophysical Chemistry)

IGFBP-4 Protease Specificity and Mechanistic Research
Protein Biochemistry Lab

IGFs are polypeptides with potent mitogenic effects. IGF activity is closely regulated in humans. IGF bioavailability is largely restricted by six distinct IGF Binding Proteins (IGFBP 1-6) (Shimisaki and Ling (1991) Prog. Growth Factor Res. 3, 243-266). These IGFBPs bind IGF and restrict their availability to IGF receptors, hence inhibiting IGF activity. IGFBPs are in turn regulated by a group of proteases which cleave IGFBPs thus releasing the IGFs. IGFBP-4 is an especially interesting protein and has been implicated in several biological roles such as wound healing, bone remodeling and atherosclerotic plaque development. In 1999, while working in Dr. Cheryl Conover's lab I identified the IGFBP-4 protease activity as belonging to Pregnancy-Associated Plasma Protein-A (PAPP-A) (Lawrence *et al*. (1999) Proc. Natl. Acad. Sci. 96, 3149-3153). This discovery was the first to link IGFBP-4 protease activity with fetal development. Despite active research into the mechanism of PAPP-A mediated IGF signaling, intriguing questions remain to be solved. It is unknown how or why PAPP-A specifically recognizes IGFBP-4. PAPP-A may have inherent sequence specific recognition machinery or it may rely on other co-factors for this specificity. In our lab at UWSP, we use an array of protein biochemical tools to try to understand the mechanism of PAPP-A's specificity. We are also working to identify additional substrates which will more clearly reveal PAPP-A's role in fetal development, bone remodeling, ovarian cancer and atherosclerosis.

Shuhua Ma (Physical Chemistry, Computational Biochemistry)

My research interests lie in the areas of the molecular simulation of enzyme catalytic mechanism and the development of viral enzyme inhibitors using computer‒aided drug design techniques.

Molecular simulations and computer‒aided drug design methods have provided powerful tools for the drug discoveries. Molecular simulation is a computational technique that uses computer models to describe chemical or biochemical systems at the atomic level. In a molecular simulation, a system is described using the individual positions and orientations of every atom or molecule. Both thermodynamic and kinetic properties of the system can be obtained through different molecular simulation methods. Computer-aided drug design is closely related to the molecular simulation and involves using the three-dimensional structures information of target biological molecules (receptors) to design small molecules (ligands) with high binding affinity to the active site or allosteric sites of the corresponding receptors.

Current projects include applying computational techniques to investigate the catalytic mechanism of human T cell leukemia virus type I (HTLV-I) protease and designing inhibitors against this enzyme using the information obtained from mechanistic studies. Being involved in these projects, students will gain experience of using a wide range of molecular simulation software, employing molecular simulation techniques to answer questions related to chemical or biochemical systems.

Human T cell leukemia virus type I (HTLV-I) is a retrovirus, it is associated with adult T cell leukemia (ATL), tropical spastic paraparesis/HTLV-I associated myelopathy (TSP/HAM), and a number of chronic diseases, including uveitis, arthritis and infective dermatitis. HTLV-I protease cleaves the Gag precursor into the matrix, capsid and nucleocapsid proteins in the life cycle of human T cell leukemia virus. Because of its essential role in viral replication, HTLV-I protease is an attractive target for the development of inhibitors to treat HTLV-I infection.

Robin S. Tanke (Organic/ Synthesis of New Materials)

Semiconductor Nanoparticles

In collaboration with professors Susan M. Kauzlarich and Timothy E. Patten at University of California-Davis, we have begun preparing by solution synthesis germanium nanoparticles with various termination groups.

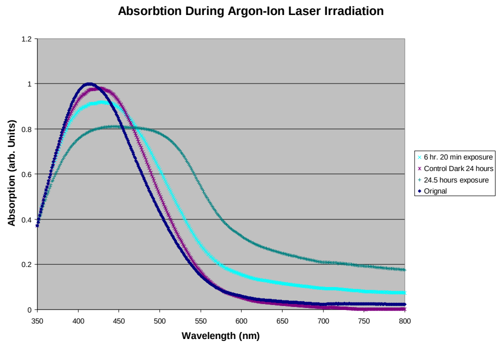
In 1959, Richard Feynman speculated that when the size of a particle was smaller than the critical length associated with any property, the property would change and could be engineered by controlling the size. Nanometer sized particles are smaller than the critical length of a number of properties. Consequently, the properties of nanometer sized particles are different from the atom that makes up the particle and different from a large particle of the material. In fact, 3 nm sized particles have different properties than from 5 nm sized particles of the same element!

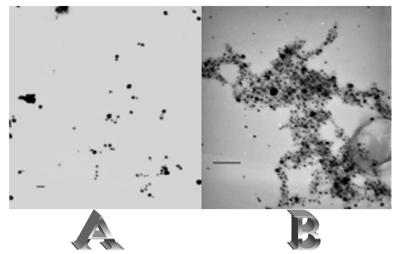
Our research focuses on semiconductor nanoparticles that are useful for a number of applications including chemical and biosensors, single electron microelectronics, and light emitting devices. Several features of semiconductor nanoparticles are noteworthy. As previously mentioned, the fundamental optical and electronic properties are strongly dependent on the size of the nanoparticle. Another important feature of nanoparticles is the termination group. The termination group attaches to the surface atoms of the nanocluster and is important because it keeps the nanoparticles separated from one another; otherwise they would form larger particles. Additionally, the termination group is key to connecting nanoparticles to one another or to biomolecules.

We are interested in changing the termination group and noting its impact on the nanoparticle properties. The kinds of termination group to be explored include aliphatic and aromatic hydrocarbons, metals, and organometallic fragments. Techniques used to characterize the particles include ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, UV-VIS spectroscopy, photoluminescence spectroscopy, and ICP analysis.

Silver and Gold Fractal Aggregates

In collaboration with James Brummer, chemistry; Greg Taft and Sasha Popov, Physics, and Robert Schmitz, biology, we are interested in exploring the optical properties of metal aggregates. In our current study, silver nanoparticles where prepared from silver nitrate by reduction with ethanol and aggregates were formed by irradiation with an Argon-Ion laser. The formation of the aggregates was determined by absorption spectroscopy and transmission electron microscopy as shown in the figure below.





These aggregates are expected to enhance the fluorescent and Raman spectra of materials.

<u>Development of Undergraduate Laboratory Exercises Based on Current Chemical Research</u>

In order to provide our undergraduates with a variety of experimental techniques and inform students about current research topics in chemistry, I am interested in taking preparations from the current literature and testing their feasibility as a laboratory activity. Students involved in this project may undertake projects in organometallic chemistry, organic synthesis, coordination chemistry, or solid state chemistry.

Tony Timerman (Biochemistry)

My research interests include the biochemistry and biophysics of integral membrane proteins. Specifically, my experience relates to the isolation and characterization of the ryanodine receptor, which is the intracellular calcium release channel of rabbit skeletal muscle sarcoplasmic reticulum. The ryanodine receptor plays an important role in muscle excitation-contraction coupling. Excitation-contraction coupling refers to the series of events beginning with stimulation (excitation) of a muscle fiber which concludes with shortening of the fiber length (contraction). Muscle contraction is triggered by a rapid increase in the concentration of calcium ions bathing the contractile proteins. In skeletal muscle, the calcium ions used to trigger contraction are stored in a specific intracellular compartment called the sarcoplasmic reticulum and the ryanodine receptor serves as the calcium release machinery of sarcoplasmic reticulum which triggers muscle contraction! Projects in this area may introduce students to strategies and techniques of tissue fractionation, protein purification, methods of monitoring ion channel activity, and immunomethods utilizing antibodies as probes in biochemical investigations.

Steve Wright (Chemical Education, Inorganic Chemistry, Environmental Health and Safety)

<u>Chemical Education</u>

Upon thoughtful reflection, one can always find classroom problems that interfere with student learning. Projects in this area will identify and seek solutions to these classroom problems, and collect data to determine the effectiveness of those solutions. A current project focuses on a classroom strategy that is designed to enhance students' ability to think critically – specifically, to analyze observations and reach appropriate conclusions. Another project seeks a curriculum that will help students recognize, understand, and apply the central, unifying themes of chemistry. We ask the question; what must a student know to become an effective, competent chemist, and we build a curriculum with that end in mind. This, perhaps, reduces to several central themes that can be universally applied. A third project will attempt to develop teaching practices that help will students improve their problem solving skills.

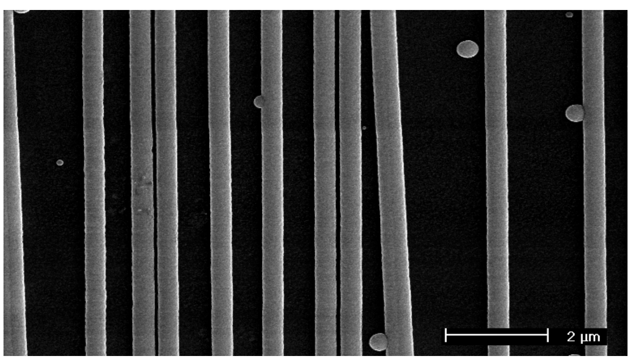
Environmental Health and Safety

These projects focus on the development and dissemination of comprehensive safety programs for high school and university chemistry laboratories. This may include hazard communication and safe storage and disposal of laboratory chemicals.

Michael Zach (Nanotechnology, Materials Chemistry, Sensor Development)

Electrodeposition

A wide variety of materials including conductive metals, semiconductors, superconductors and even insulators are able to be deposited on the surface of an electrode by controlling the solution composition and electrode potential. Nanowires of many materials can be deposited by controlling the defects initially present on the electrode surface. Because materials deposited come from individual ions in solution, synthesis of materials at the nanoscale are possible with simple instrumentation. The tools are relatively simple so a student with little chemistry is quite capable of making good scientific contributions. The variety of materials and the possible methods of analysis are unlimited so more advanced experiments could involve learning manipulation of air sensitive materials, operation of instruments like scanning electron microscopes or collaborating with leading scientists at Argonne National Laboratory with superconductivity experiments.



MoO_2 nanowires formed by electrodeposition on graphite electrodes.
These wires utilize simple techniques on a bench top and can be transformed into sensors. These can be used for the starting material for other devices and may someday be controlled to make active circuitry at the nanoscale.

Instrument Design – Combinatorial electrodeposition

Once the basic techniques of electrodeposition are mastered, the more advanced student can learn to interface a computer with instruments for robotically mixing of solutions, filling multiple electrochemical cells with precision timing and programming automated electrodeposition techniques. Rapid performance of electrochemical experiments by incrementally changing important parameters allows for discoveries that might be missed using slower, less reproducible, manual experimentation methods. Proper control using instruments is a very valuable skill to have for future work or academic studies.

Development of Nanostructured Chemical Sensors

Exploiting the fundamentals of intermolecular forces and self-assembly processes allow control of materials for making the World's fastest hydrogen sensor with miniscule amounts of materials. We are working on making and testing these sensors in our laboratory. These sensors are capable of measuring 2% concentration of hydrogen in as little as 70ms and have lower limits of detection of just 25ppm. Additional systems will be explored to find new applications and other chemical systems that can be sensed with this new sensor design. This is a surprising new discovery with great commercial applications and many new discoveries are yet to be made.

Tom Zamis (Biochemistry, Environmental Chemistry)

Enzyme Characterization and Reaction Kinetics

These projects will include the study of various aspects of enzyme isolation, purification, and catalytic activity. Students will be involved with the techniques of extracting and purifying enzymes from plant material (leaves, roots, fruit). These enzymes will then be characterized by things such as molecular weight, number of subunits, absorption spectra and specific activity. Students should expect to gain experience in general biochemistry laboratory preparations (buffer solutions, precipitation of proteins, protein assays, use of centrifuges), gel filtration chromatography, electrophoresis, spectrophotometry and analysis of enzyme kinetics. The objective of these investigations is to determine the factors that inhibit enzyme activity or alter the protein structure, things such as metal ions and organic free radical molecules.

Removal of Trace Organic Contaminants from Water

There is increasing concern about the state of the environment, particularly in the areas of air pollution and groundwater pollution. One of the most immediate threats to groundwater supplies, the major source of drinking water in the United States, is contamination with toxic organic chemicals from sources such as gasoline storage tank leaks, herbicides, and chemical industry effluent. Many of these substances are biologically degraded, but many are resistant to bacterial degradation. The objective of this study is to see if free radical molecules generated from hydrogen peroxide in the presence of iron ions can be used to chemically degrade these substances into non-toxic products. Students should expect to use gas chromatography, liquid chromatography and thin layer chromatography along with UV-visible and infrared spectroscopy to analyze the contaminants in water and the substances produced after the chemical treatment.