

Research in the Department of Chemistry

Graduate Degrees Offered:

Master of Science

MS 30 hrs with thesis

MS 36 hrs non-thesis

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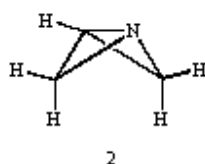
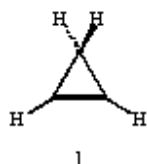
See:

www.shsu.edu/academics/chemistry/ and SHSU's graduate catalog www.shsu.edu/graduate-catalog for more info.

Dr. Benny E. Arney, Jr.

Organic Chemistry: My research interests in organic chemistry focus on the synthesis and chemistry of highly reactive and strained small-ring systems such as cyclopropenes (1) and 1-azabicyclo[1,1,0]butane (2). Small highly distorted molecules, though

difficult to prepare, are excellent models for the examining the relationship between molecular



structure and bonding. It is through the reactions of these energetic species that we can elucidate the nature of the effects that structural distortion has on the bonding and orbital overlaps in the molecules. For example, our studies on the extremely reactive bicyclo[4.1.0]hept-1,6-ene using experimental techniques revealed the double bond to be vastly more reactive than expected. Computational studies revealed high fluxionality in the double bond with very little barrier to folding along the double bond itself.

Additionally, my research interests include the chemistry of selenium; specifically, selenoxides and selenones. Methyl selenones are reported to undergo a rearrangement to form methyl alkylseleninates on heating in methanol or setting in aqueous solution.

We have been exploring methods for the handling of the odoriferous precursors to these compounds as we prepare a number of derivatives to examine substituent effects and perform kinetic studies.

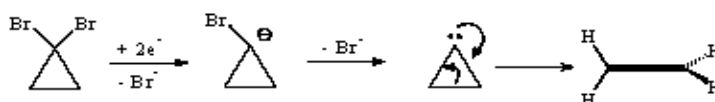


Organic Electrochemistry: Electrochemical techniques are being explored in our research to investigate reactions involving

electron transfer, such as direct metallation of an alkyl halide, and to develop environmentally clean, economically efficient synthetic procedures. We are currently optimizing a biphasic flow system capable of direct electrolytic reactions or electrocatalytic reactions. Preparation of geminal dinitro groups and nitro-olefins on a preparative scale using these procedures has been quite facile with virtually no waste.

Along more classic lines of research, we have also been exploring the use of electrochemical reductions and zero-valent metals to effect a Skattebøl reaction. This involves the reduction of a geminal dihalocyclopropane to the α -haloanion or α -halometallated species (carbenoid) which rearranges to the allene after forming the intermediate cyclopropyl carbene. Use of electrochemical methods will remove the necessity for alkyl-lithiums.

Physical Organic Chemistry: Integral to the experimental



work pursued in my work is the use of computational methods to model and illustrate potential interpretations and results as well the use of kinetic studies to gain insight into the pathways and energetics of reactions under investigation. In particular, the reaction to form 1-azabicyclo[1.1.0]butane by transannular cyclization has been under investigation in my lab and found to be a single-step concerted process. Kinetic measurements of thermodynamic properties are being conducted for comparison with theoretical values.

Arney's Recent Funding

Petroleum Research Fund \$18,000

SHSU Faculty Enhancement Grants \$20,000

Robert A. Welch Foundation \$226,000

SERDP Center for Energetic Research \$780,000

Gibbs-Farrington Chair in Chemistry \$24,500

Dr. Thomas G. Chasteen

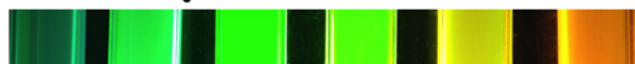
I. Nanoparticle Synthesis

Cadmium telluride (CdTe) nanoparticles can be synthesized abiotically by the reaction of Cd- and Te-containing salts using glutathione and heat. CdTe nanoparticles fluoresce when exposed to UV light as the adjacent image shows. These are crude nanoparticles that had been heated (incubated) for 2 hours after the reagents were mixed. The circular dish is being exposed to 302 nm light (that is, invisible UV light) and the particles glow in visible wavelengths.

Changing the length of time the nanoparticles are heated changes the sizes of the particles, and interestingly, changes the wavelength at which they fluoresce. The approxi-



↓ Exposure to 302 nm light

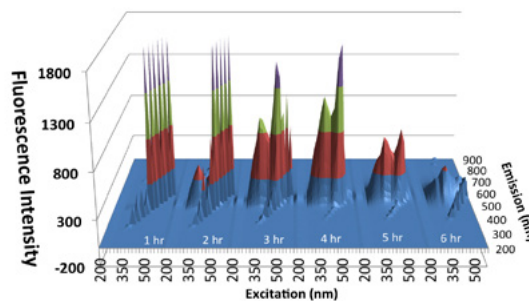


CdTe nanoparticles fluoresce when exposed to 302 nm UV light.

Recent work in my analytical research group, in collaboration with biochemists and microbiologist at the Universities of Santiago and Chile and Andrés Bello University in Santiago has focused on characterizing these so-called quantum dots. For instance, we are studying the thermal- and photo-stability of CdTe nanoparticles by watching the changes in their fluorescent emission spectra of stored particles over time.

The adjacent image shows multiple absorption vs emission spectra of CdTe in UV and visible wavelength regions, showing the importance of time in the steps to produce these particles. Some of this nanoparticle work has been published in the journal *PLoS ONE* and *Analytical Biochemistry*.

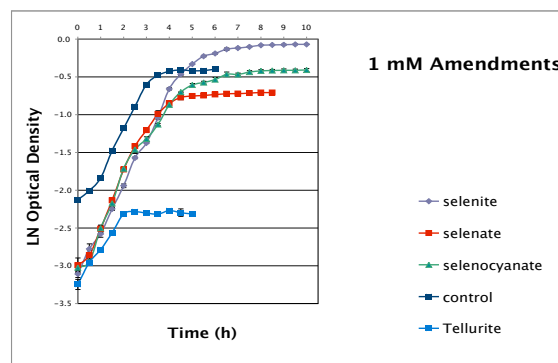
Excitation vs. Emission Scans of CdTe Nanoparticles



CdTe nanoparticles fluorescence/emission spectra for different synthesis times heated at 90°C. Two hours is optimum.

II. Toxicity of selenocyanate anion, an environmental important by-product of petroleum refining

Understanding the relative toxicity of biospherically important forms of selenium and tellurium is important to help focus resources on the most important environmentally-damaging aspects of these metalloids as they are released into the biosphere from natural weathering (like in the San Joaquin Valley) mining (think Telluride, Colorado) and oil refining. Selenocyanate is particularly difficult to remediate because it is water soluble, and therefore hard to precipitate and sequester in settling ponds; relatively chemically unreactive, and therefore hard to convert to other more-easily-removed forms; and yet still relative toxic to organisms in the environment. We have used bacterial microorganisms to evaluate this relative toxicity without the need for mammalian test subjects. We've published this work in multiple papers in *Environmental Toxicology and Chemistry*, *Environmental Technology*, and *Environmental Biotechnology*. As you'll see below, the bacterial response to this toxic exposure for bacteria that have evolutionarily developed resistance to these elements, ranges from the creation of insoluble,

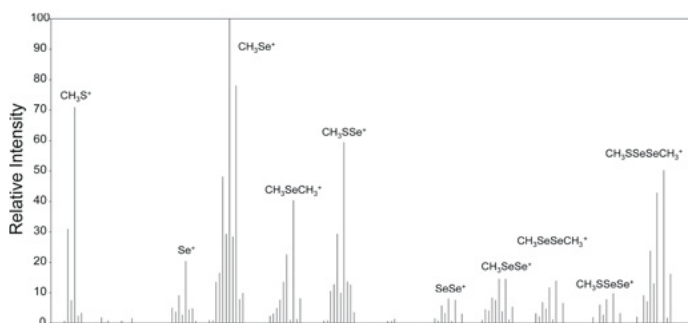


Growth rate experiments: TeO_3^{2-} is the most toxic of these anions.

elemental Te (gray solid) and elemental Se (beautiful reddish orange) to the production of volatile organo-metalloidal compounds like CH_3TeCH_3 and $\text{CH}_3\text{SeSeSCH}_3$. These gaseous compounds are much less toxic than the water soluble, highly toxic oxyanions of Te and Se found in the environment in soil and water.

III. Genetically-Modified Bacteria Gain Tellurium Resistance

In collaboration with our Chilean counterparts, we have been analyzing the microbial production of volatile tellurium compounds by an *E. coli* clone which has Te resistance conferred by a plasmid from a thermophilic bacterium with native tellurium resistance



Mass spectrum of $\text{CH}_3\text{SSeSCH}_3$.

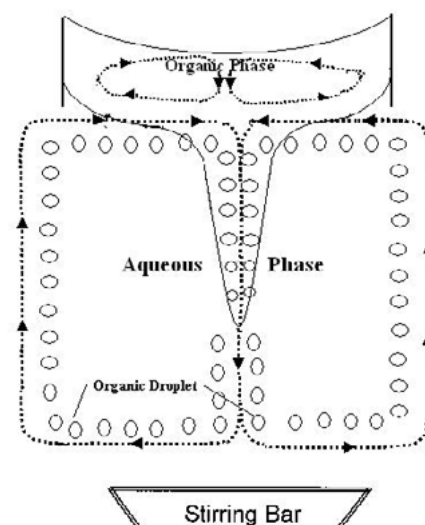
(published in *Applied and Environmental Microbiology*). Before insertion of this plasmid, *E. coli*'s tellurite resistance (measure as the minimal inhibitory concentration that prevents growth) is only about $1.25 \mu\text{g/mL}$; after plasmid insertion it is $25 \mu\text{g/mL}$, an increase of 20 times. With these organisms, one of the results of this conferred resistance is the ability to reduce and methylate the toxic metalloids we add to their cultures. We have determined the presence of dimethyl telluride, dimethyl ditelluride, and for the first time, dimethyl tellurenyl sulfide ($\text{CH}_3\text{TeSCH}_3$) in the gas

produced by live cultures of this cloned bacterium.

We carried out experiments in which that bacterial clone was exposed to the toxic tellurate anion (0.01 mM) and, after 48 hrs of growth, produced organosulfur and detectable amounts of organotellurium in the form of dimethyl telluride, CH_3TeCH_3 (published in *Journal of Biological and Inorganic Chemistry*). Work announcing the determination of the mixed organosulfur/tellurium compound dimethyl tellurenyl sulfide has been published in *Analytical Biochemistry*. Further results have shown that this and another organism also produce mixed selenium/sulfur compounds: $\text{CH}_3\text{SeSSCH}_3$ and $\text{CH}_3\text{SeSeSCH}_3$ (these results were also published in *Analytical Biochemistry*). These are only the second and third mixed Se/S compound known to be produced by metalloid-resistant bacteria.

IV. Liquid Phase Microextraction of Organochalcogens

Extremely small volumes of nonpolar solvents can be used to extract volatile organochalcogens—such as CH_3TeCH_3 —from aqueous solutions collected from the environment. In collaboration with Dr. Mahdi Hashemi—on sabbatical from Bu-Ali Sina University in Iran—students in my lab helped developed this sensitive extraction method in conjunction with gas chromatography with fluorine-induced chemiluminescence detection. The aim of this work was to develop a simple, fast and precise methodology based on the liquid phase microextraction for determination of dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, dimethyl diselenide and dimethyl telluride as most common volatile organochalcogens produced by microorganisms, in biospheric water samples and bacterial cultures—using GC with fluorine-induced chemiluminescence detection. Aqueous sample detection limits from 5 to 620 ng L^{-1} were achieved for organo-sulfurs, -selenides, and -tellurides. Real-world samples from the near-by pond at the Huntsville's Sam Houston Memorial Museum were used in this work. The extraction process moved analytes from the large volume aqueous phase into the smaller volume organic phase with enrichments from 100–250 times (published in the journal *Environmental Biotechnology*).



Schematic of liquid phase microextraction process, drawn by Mahdi Hashemi, Bu-Ali Sina University, Hamedan, Iran

V. Field work in Antarctica

Nanoparticles can also be produced by metal- and metalloid-resistant microorganisms. Extremeophiles collected in the high-UV, low-temperature environments of Antarctica have shown promise to provide genes that can help to biologically produce nanoparticles upon exposure to soluble metal/metalloidal salts. Harvesting these microbes involves sampling soil, sediments, and water in biospherically “unusual environments. Chasteen—financed by the Chilean government—travelled to Antarctica for a 15 day research trip in (austral) spring of 2013 to collect soil, water, and sediment samples from Antarctic islands and the Antarctic peninsula above 63 south latitude.

Samples taken at Hannah Point on the Antarctic Livingston Island

(62 south longitude, 60 west latitude) were harvested in amongst penguins and seals and a photo of Elephant Seals is nearby. We collected samples inside the penguin colony (as defined by white streaks and stench everywhere) and the further around the beautiful cove of Punta Hannah. The face of the glacier off in the distance is about 50 meters tall where it meets the water. The air temperature moved close to 10°C during this day. Each sample collection event had a minimum of the following: temperature of soil or water where sample was collected, coordinates of the sampling site taken from an hand-held GPS, sample transferred to the falcon tube via a spatula thoroughly clean in the medium near the sample, and a photograph of the process or site. Written sample descriptions included physical description of the sample itself, location where it was taken, and distance from prominent nearby features, for instance, number of meters from the beach, proximity to penguins, etc.

On another island (Robert Island), we discovered a surprising temperature profile in a biomass-rich pool that contained, what appeared to be, decaying marine algae blown in from the beach or from a particularly high tide. Here's the scenario: the air temperature at Robert Island at this sampling was 8° and the water (snow melt with ice nearby) in a shallow pool was measured as 1.2°,

but 1 cm down into what we called primordial ooze—sediment covered with 1 cm of the snow melt water—the temperature had heated up to 2.2°, and 3 cm down in the primordial ooze, it was 4°C. Again we posit that this is microbially-powered warming. Note that solar warming could have made the top of the sediment warmer than the associated snow melt because it was dark and poorly reflective of the afternoon sunlight, sunlight that would have heated it more than the water above, but the temperature profile in the sediment increased with depth down into the sediment. This strongly suggests something besides solar heating. These are the kinds of bacteria we collect on this trip. Work from Antarctic samples collected from this grant was published in the journal *Polar Science*.

Chasteen's Research Funding

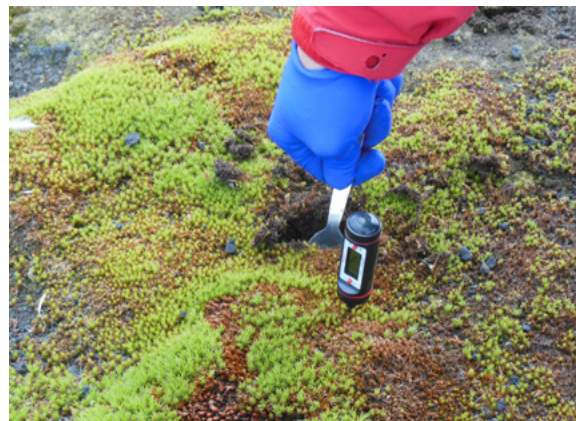
Texas Army National Guard \$137,000

Texas Research Institute for Environmental Studies \$18,800

CONICYT (Chile) \$20000 (for summer visits to Santiago)

Gibbs-Farrington Chemistry Chair \$24k + \$10k + \$10k + \$10k

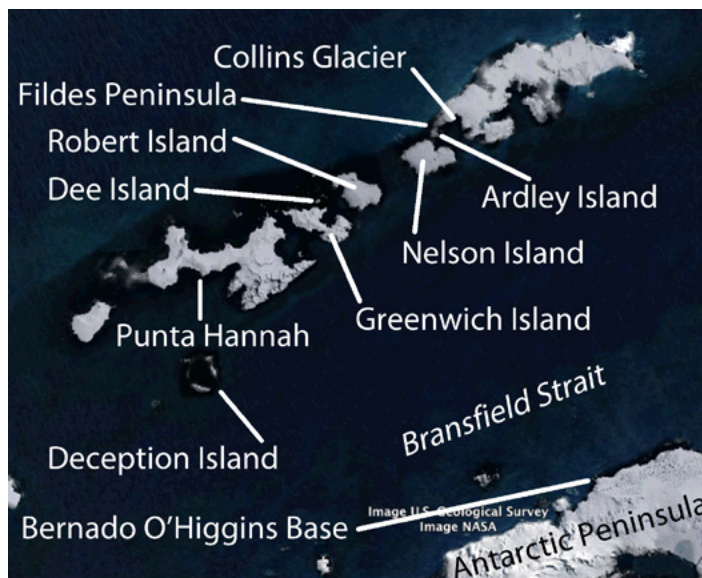
Funding for the 2013 Antarctic trip : \$40,900



Sampling microbes in the rhizome beneath an Antarctic moss
[Click to see the blog](#) of this research trip to Antarctica.



Elephant seals (Mirounga leonina)
on Punta Hannah, Antarctica



Dr. Donovan C. Haines

Overview. Our research lies at the interface of chemistry and biology, with application in medicine and biotechnology. We study enzymes, lipids, and microbes.

Cytochrome P450 in the metabolism of lipids, hormones, and drugs. Cytochrome P450 is a superfamily of enzymes involved in the metabolism of drugs, toxins, steroid hormones, cholesterol, vitamin D, prostaglandins, leukotrienes, and many other medically important small molecules. These enzymes use a heme cofactor to reduce molecular oxygen, while oxidizing their substrates (Figure 1). They are the major component of Phase I drug metabolism, which controls among other things how often most medications have to be taken.

One major thrust of our lab is to study how these enzymes work. To do this we use protein modeling to design novel substrates and inhibitors (Figures 2 & 3), use organic chemistry to synthesize the substrates and inhibitors, and kinetics and spectroscopy to use the compounds to probe how the enzymes work. We also characterize products of the oxidation reactions.

P450s in the fight against infection. We have discovered that cytochrome P450s involved in lipid metabolism are able to degrade bacterial signal molecules called autoinducers in a reaction that should help fight certain kinds of infection. The autoinducers are basically bacterial versions of hormones, and turn genes on and off as a function of cell population density. Destroying the molecules can interfere with the bacterial pathogens and help fight infection. We characterize human and microbial P450 metabolism of these signals, and believe this reaction is an important reason why Cystic Fibrosis patients get the infections that often prove fatal to them.

The role of P450 in disease. We also study human P450 cytochromes important in the brain in memory formation and in normal skin development. For example, we study the role of an enzyme called CYP4F22 that when defective prevents the proper formation of skin, resulting in lamellar ichthyosis type 3. To test this, we make advanced probes (Figure 3).

Enzyme engineering for biodiesel generation. We have a project where we are trying to alter a natural enzyme to allow formation of biodiesel (methyl esters of fatty acids) in cells without the need for a transesterification plant. If successful, we hope to greatly reduce the cost of production of biodiesel.

Mitochondrial electron transport. We collaborate with Ilona Petrikovics in our department to measure the electron transport chain activity of mitochondria as a way of assessing the effectiveness of potential cyanide poisoning antidotes.

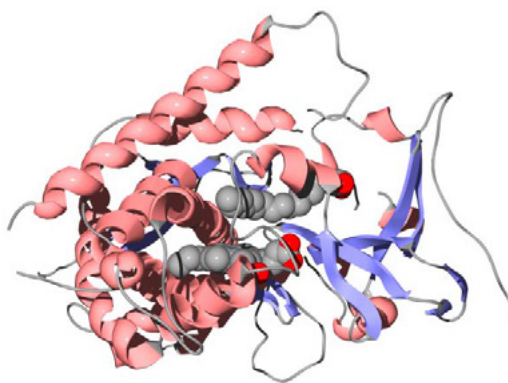


Figure 1. A ribbon structure for the cytochrome P450 called P450BM-3 from *Bacillus megaterium* complexed to an acylamino acid substrate.

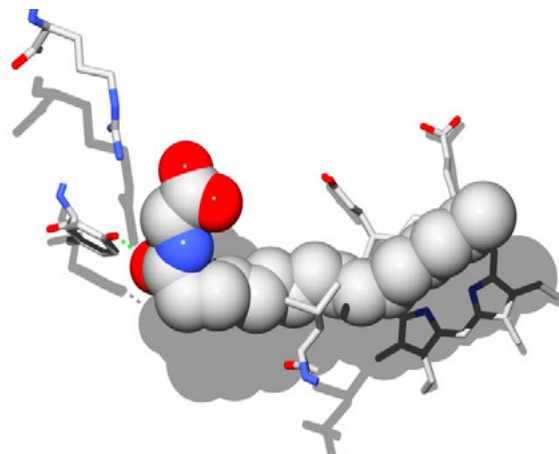


Figure 2. Amino acid side chains of a bacterial P450 which allow it to interact with an acylamino acid substrate (larger spheres).

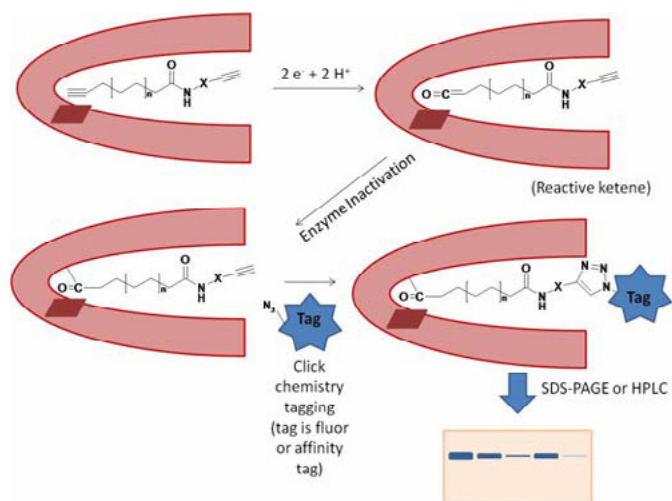


Figure 3. Some of our substrates and inhibitors are probes that can be used for advanced proteomics experiments like Activity Based Protein Profiling.

Haines' Recent Funding

American Cancer Society (\$15K, former university)

Welch Foundation (\$150K, former university)

SHSU Faculty Research Grant (\$5K)

Dr. Dustin E. Gross

The overarching goal of our research is to develop new molecular architectures for organic materials. Due to their high availability and ease of processibility, organic materials are being incorporated into flexible electronic devices on large scale and at low cost. These devices include but are not limited to sensors, OLEDs, OFETs, and OPVs. There are common problems related to each of these, such as performance and lifetime. Our research aims to address these shortcomings by improving molecular and supramolecular design. Material interface and carrier mobility are two specific examples. These involve phase separation and charge conductance, respectively, which suffer when a material is randomly ordered and there is a lack of structural control on the nanoscale level. To address this lack of organization we will create shape persistent two or three-dimensional frameworks. The properties of these networks are highly dependent on molecular order, which in organic materials can be tuned on the molecular level to achieve macroscopic efficiency. To accomplish this we will design and synthesize large precisely nanostructured materials from the bottom up. Discrete shape persistent building blocks are of interest because they possess several advantages compared to their polymeric counterparts. Despite many advances in synthetic methods and preparations of novel organic materials, we have yet to reach the limits of this so called bottom up approach, and a greater understanding and development of larger building materials will extend the limitations of current methods.

To approach this goal we are focused on developing and understanding methods for the synthesis of novel organic based shape-persistent architectures. This objective will be realized on multiple fronts: *I) investigation of dynamic covalent reactions that allow for self-correction and applying them to the synthesis of shape persistent structures, II) exploring the size limits of these discrete organic structures and III) incorporation of heteroatoms in polycyclic aromatic frameworks to afford non-planar 3D structures.* Specific projects pertaining to these objectives are outlined below.

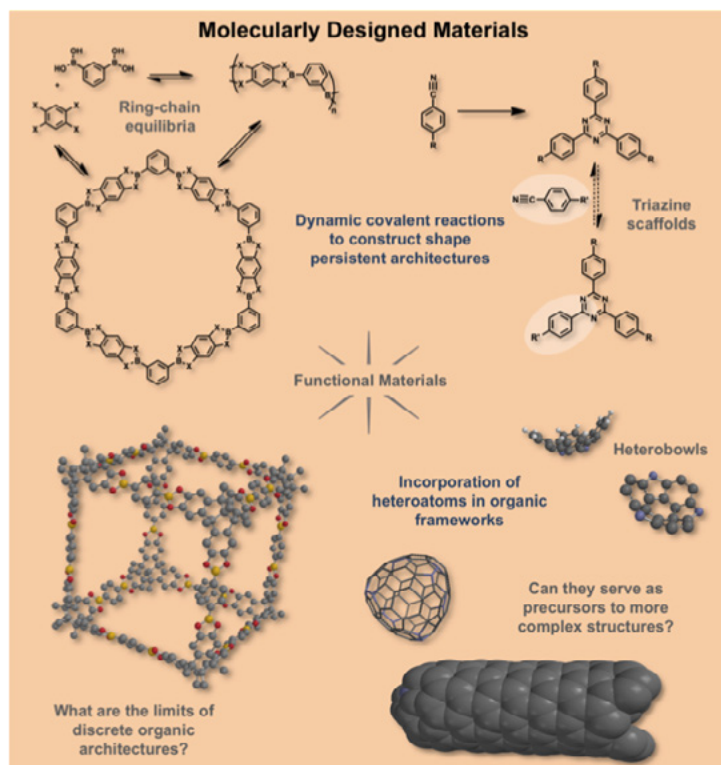
I. Dynamic covalent macrocycles

Using dynamic covalent reactions it is possible to prepare large and structurally complex molecules from relatively simple small-molecule precursors in a single synthetic transformation. We are exploiting the potential of this method to allow for systematic development of diverse molecular systems in relatively few steps. Studying the effect of systematic variations will permit for a funda-

mental understanding of the molecular control of structure and how it relates to the materials' physiochemical properties. These structure property relationships, which lie at the heart of chemistry, can then be optimized by further modifications of the molecular subunits.

II. Triazine frameworks

Triazines have gained attention recently as scaffolds for materials and various applications. An attractive feature of triazines is that they can be synthesized at room temperature via Lewis acid catalyzed cyclotrimerization in high yield. We are exploring the potential of appropriate difunctional nitriles to cyclize into novel macrocycles and cage compounds. These systems have the potential to be dynamic in nature and we are also exploring that capability.



III. Hetero-graphene derivatives

The third approach we plan take is to introduce heteroatoms into carbon frameworks. By switching out carbons with nitrogen the frameworks may be more curved due to the ability of nitrogen to maintain sp^2 or sp^3 hybridization. It is also proposed that this will allow for the introduction of fused pentagons, thereby increasing curvature. These materials are potential precursors for the rational synthesis of nonplanar heterographene derivatives such as fullerenes or nanotubes. They are expected to display unusual behavior due to there unusual structural features caused by the heteroatom substitution.

By achieving order on the nanoscale we will affect the size, diversity, stability, processibility, self-assembly, structural rigidity, and electronic behavior of new organic materials. The resulting properties will allow for new sensory and optoelectronic materials.

Dr. Rick Norman

Bioinorganic and Transition Metal Chemistry

Dr. Ozcan Gulacar

Chemical Education (Problem Solving, Cognition, Instructional Technology)

Dr. Ilona Petrikovics

Chemical Defense, Nanotechnology, and Enzymes in Drug Antagonism

Dr. David E. Thompson

Surface Enhanced Raman and Nonlinear Spectroscopies, Environmental Nanosensing

Dr. Adrian Villalta-Cerdas

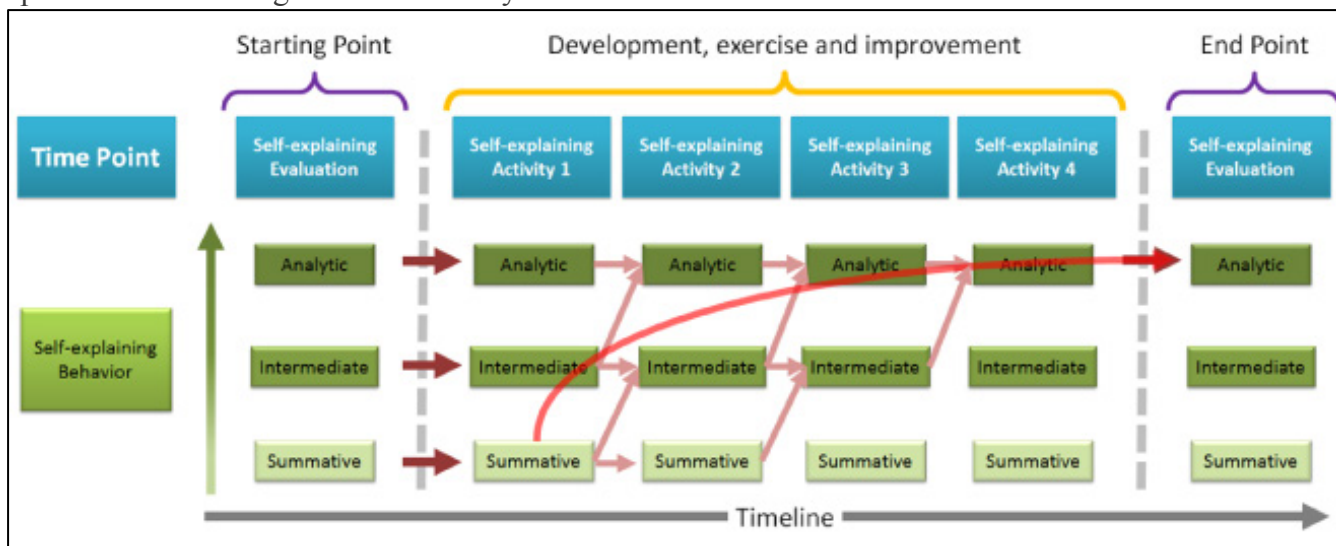
(www.avc-chemed.com/)

In my chemistry education research, I focus on learning strategies that foster scientific skill development in lecture and laboratory settings in chemistry courses at college level.

Research Projects

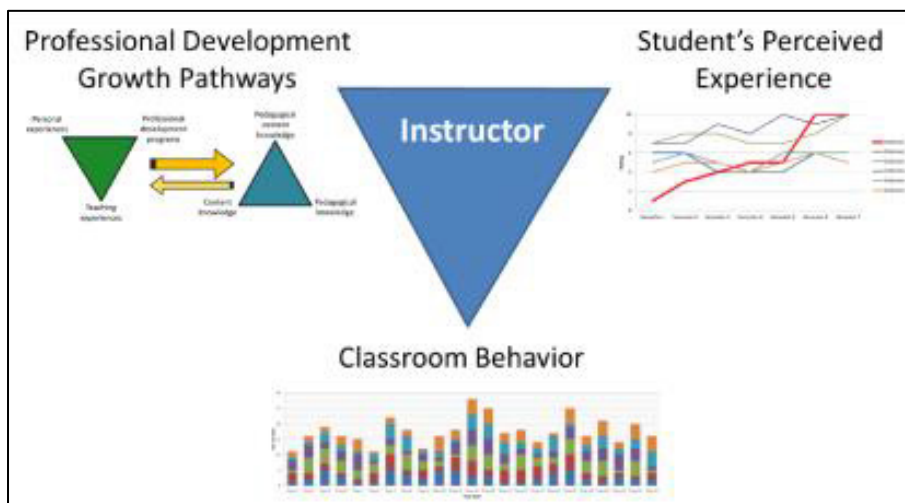
Effect of self-explaining on chemistry conceptual learning

The purpose of this project is to investigate the development of self-explaining as a skill using a multiple activities. Findings from the project will shed light into the applicability of self-explaining as an active component of chemistry learning. Research on the self-explaining effect has shown that careful design of activities can lead to authentic learning in the sciences. However, little direct evidence exists that self-explaining (as a learning strategy) provides a useful function in the way(s) students learn chemistry at college level. In a recent review of literature on research on self-explaining at college level only two papers (out of 57 papers) investigated chemistry content knowledge, and in the last year only two papers (out of 20 papers) did. This indicates that the study of the self-explaining effect on chemistry education at college level is an under-researched field. Also, more than 70% of the published papers were done in laboratory settings, that is, non-naturalistic learning environments. This study comes to fill that void in knowledge by investigating the self-explaining effect in the natural environment of chemistry courses. For this purpose, I will study the effect of self-explaining on students' conceptual understanding and skill development, via multiple in-class activities along the duration of the chemistry course. The in-class activities consist of chemistry problems that present students with experimental data for them to develop their self-explaining skill. This approach will maintain the outcomes of the project truthful to the undergraduates' experience in chemistry courses. The outcomes of this project will provide a deeper understanding of effectiveness of self-explaining in chemistry thus contributing to the improvement of undergraduate chemistry education.



Student evaluation of effective teaching practices in General Chemistry: What makes effective instruction effective?

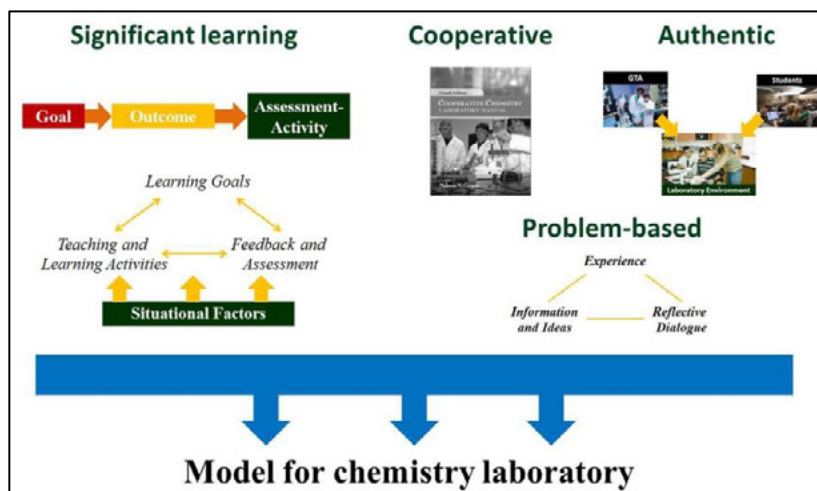
This project proposes a study of effective teaching practices that uses a naturalistic approach and encompasses all three components of the learning environment (i.e., the instructor, the students, and the classroom). This approach intends to distill the instructional strategies—active components—that characterize effective teaching practices in general chemistry courses. For this purpose, this project studies the learning environment of



instructors who are effective based on students' perception. The factors that influence student success in their learning experience relate to the instructors' behaviors, the instructional strategies, the learning settings, and the learning processes. These factors influence and affect the students within the context of the learning environment. Therefore, making the quality of teaching and students' experiences in general chemistry courses a top priority will contribute to attracting and retaining students in chemistry and chemistry-related fields.

Integration of Cooperative, Project-based, Experiments for Chemistry Laboratory Programs

I am also interested in the integration of cooperative, project-based, experiments for chemistry laboratory programs. Research evidence shows that traditional, verification laboratory activities are not effective in attaining the desired goals of laboratory education, such as those put forth by the National Research Council in 2005: “development of scientific reasoning, understanding of the nature of science, developing practical skills, cultivating interest in science and in learning science, developing team working skills and supporting mastery of subject matter”. However, this instructional model prevails in college science education. Three obstacles that may hamper successful lab reform are: (a) not using a systematic instructional design approach, (b) lack of collaboration between chemistry educational researchers and practitioners, and (c) insufficient support for instructors to face the period of design and implementation. I am interested in design and implementation of the academic environments that introduce students to authentic experimental learning opportunities in chemistry courses. In such environments, learners will be able to *experiment* and not simply go through the motions of reproducing procedures in verification lab activities. The curricular reform I am interested will be in alignment with current principles of instructional theory and instruction design, and uses an Integrated Course Design approach.

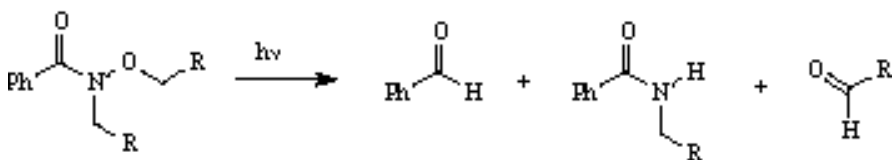


Dr. Rick C. White

Photochemistry of Amides and Hydroxylamine Derivatives

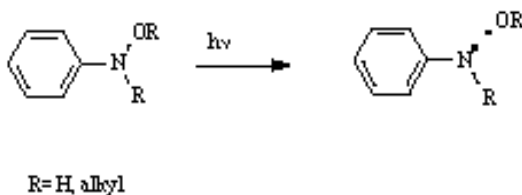
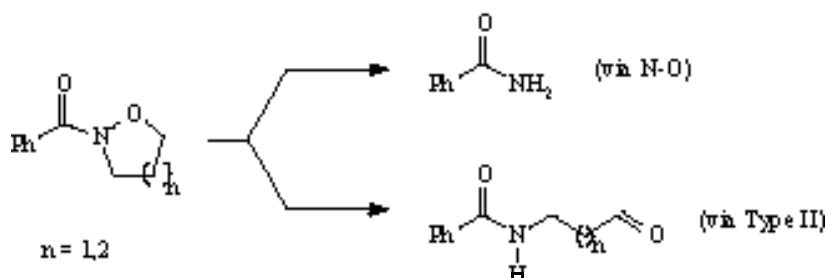
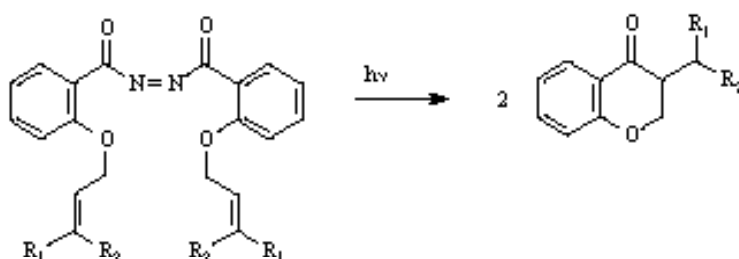
We are currently involved in the photochemistry of organonitrogen compounds. This research looks at the cleavage of the N-O bond as a route to photoactivated DNA cleavage reagents. First, we are examining the factors that influence the N-O bond cleavage in hydroxamic acid derivatives. We have found that acyclic benzohydroxamate derivatives undergo N-O bond cleavage primarily by way of the Type II photoreaction.

In the cyclic series of compounds, it appears that the size of the ring influences the relative amounts of Type II reactions versus N-O bond cleavage.



We also are looking at the photochemistry of hydroxylamines such as phenylhydroxylamine derivatives that serve as potential sources of alkoxy or hydroxyl radicals that can photoinactivate plasmid DNA.

Finally we are looking at the long wavelength induced photolysis of dibenzoyldiazene derivatives as a route to chromanone derivatives via a double radical cyclization process. The dibenzoyldiazene chromophore should allow one to use a long wavelength such that the products do not compete for light absorption.



White's Recent Funding:

Petroleum Research Fund, \$20,000

Concurrent Technologies (with Paul A. Loeffler) \$2,900,000

Deutscher Akademischer Austauschdienst, DM 11,100

Gibbs Foundation, \$16,000

Dr. Darren L. Williams

The determination of the degradation products that result from long-term material incompatibilities remains a difficult problem in the material science community.

Topics in this area include the following.

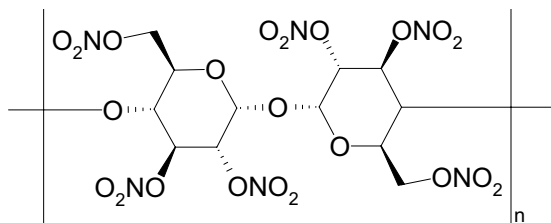


Materials Compatibility

The integrity and safety of military munitions in long-term storage depends upon the compatibility of the explosive formulation materials, the packing material, and in some cases the storage containers. Artificial aging and accelerated aging studies are used to reveal physical and chemical changes associated with material incompatibilities.

An artificial aging study evaluates material mixtures containing artificially large amounts of degradation products. An accelerated aging study uses high temperature to accelerate the aging process. The reactivity of the system may be further tested by the addition of humid air, oxygen, or other gases.

Nitrocellulose – a nitrated natural material – has a complicated degradation chemistry. Discovered in 1832 by Henri Braconnot, the

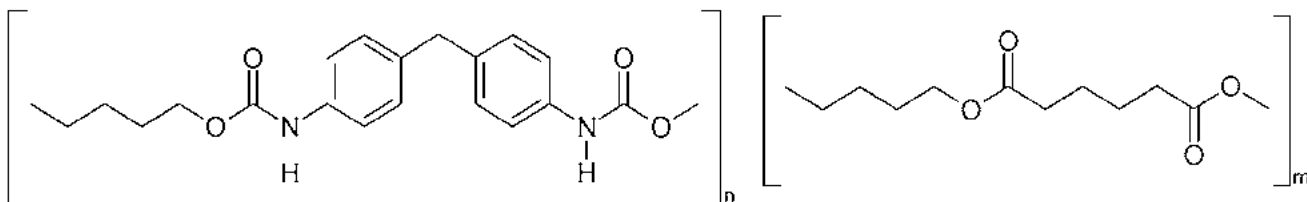


process for nitrating cotton fibers to make gun cotton was optimized by F. J. Otto in 1946. Since then, nitrocellulose (NC) has been used in a variety of applications from military munitions to magic tricks. The complex degradation chemistry of NC disfavors its use in long-shelf-life munitions

Spectroscopic Signatures of Degradation and Environmental Damage

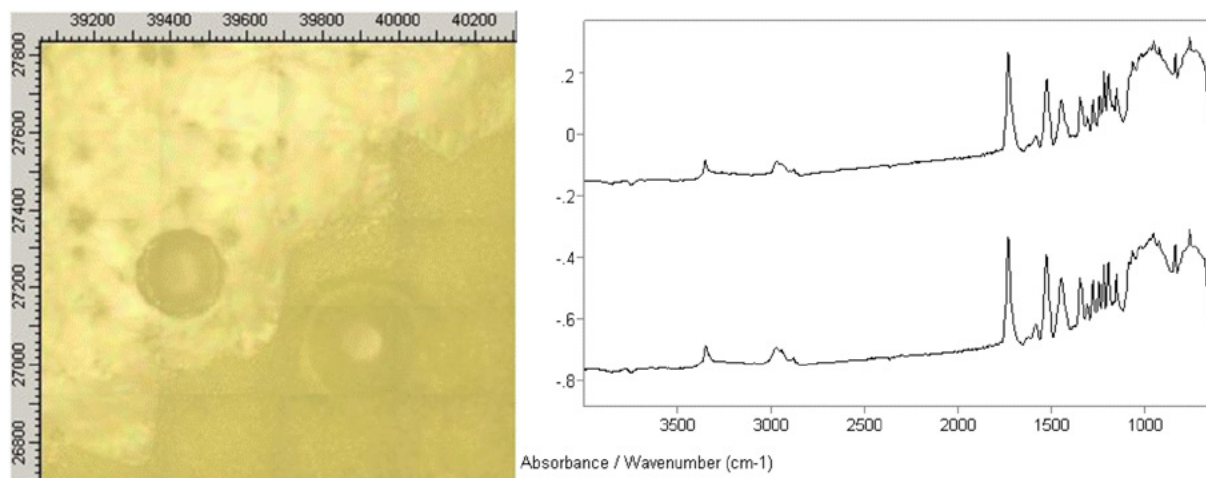
The stability of high explosives depends upon the molecular properties of the explosive, binder, stabilizer, and plasticizer. Micro-infrared (IR) spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, ion mobility spectrometry (IMS), and gas / liquid chromatography – mass spectrometry (LC-MS-MS, GC-MS) are all available to investigate changes to the molecular species present in an explosive formulation.

These various techniques are combined to determine the spectroscopic signatures that indicate compatibility issues and aging mechanisms.



The structure of a poly(ester urethane) block co-polymer that is used in some explosive formulations

The spectral signatures of the nitrated polyurethane segment have been determined by synthesizing nitrated model compound fragments of the aromatic region of the polymer. The model compound spectra ([IR](#) and [Raman](#)) were fully assigned using *ab initio* calculations ([Gaussian Inc](#)). The quantitative method for analyzing the extent of nitration was determined with solvent-cast films and micro and macro-ATR-FTIR. The micro-ATR-FTIR was able to see segregation and crystallization of the solvent-cast films, and the macro-ATR-FTIR was insensitive to segregation and crystallization in the quantitation. The image below shows the depressions made by the germanium micro-ATR crystal. The image ruler is in microns. The crystalline nitrated material is seen on the top-left half of the image, and the poly(ester urethane) matrix is seen on the lower-right half of the image. Likewise, the FTIR spectrum of the crystalline region is shown on top and the spectrum of the polymer matrix is shown on bottom.

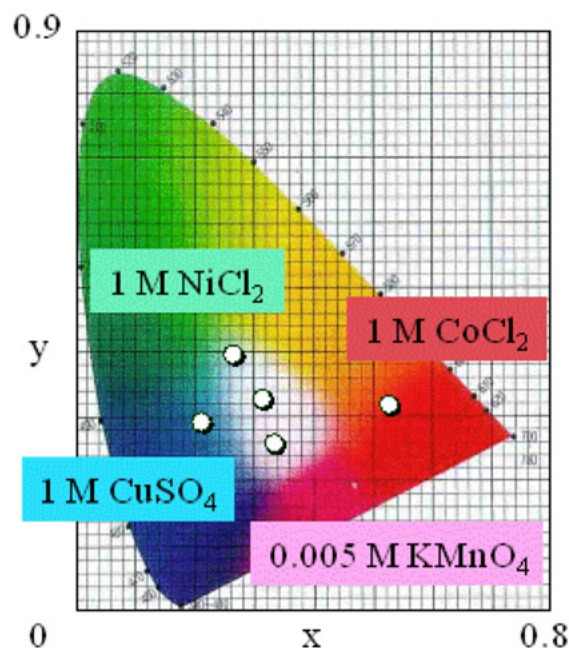


Color Changes

Another signal of chemical change is the color of the material. Many colorless polymers become yellow over time as they are oxidized. The chemical changes are concentrated at the surface of the material, so surface-sensitive reflectance and scattering techniques are favored for studying these phenomena. IR, Raman, and reflectance visible spectroscopy techniques can be used to link the color change to specific chemical changes in the surface of the material.

The study of color changes requires a specific definition of color, such as the CIE tristimulus values, the chromaticity coordinates, and the standard red-green-blue (sRGB) values. For example, the chromaticity coordinates of potassium permanganate, nickel (II) chloride, cobalt (II) chloride, and copper sulfate are shown in the figure to the left. Color changes in a material will create a measureable shift of the chromaticity coordinates.

The precise method has been published for transforming visible spectra to the CIE tristimuli, chromaticity coordinates and sRGB values. A standard technique for simulating the specific color values for a molecule using semi-empirical modeling methods has also been submitted for publication.



Some publications related to these topics include:

- Flaherty T. J., Timmons J.C., Wroblewski D. A., Orler E. B., Langlois D. A., Wurden, K. J., Williams, D. L. *, Infrared and Raman Spectral Signatures of Aromatic Nitration in Thermoplastic Urethanes, *Applied Spectroscopy*, 61(6), (2007) DOI: 10.1366/000370207781269792
- Williams, D. L. *, Flaherty, T. J., Al-Naslah, B. Beyond Lambda-Max Part 2: Predicting Molecular Color, *Journal of Chemical Education*, MS#2007-0645, to be published in 2008.
- Williams, D. L. *, Flaherty, T. J., Jupe, C. L., Coleman, S. A., Marquez K. A., Stanton J. J., Beyond Lambda-Max: Transforming Visible Spectra into 24-bit Color Values, *Journal of Chemical Education*, 84, 1873-1877, (2007)
- Lopez, E. P. *, Moddeman, W. E., Birkbeck, J. Williams, D.L., Benkovich M.G., Solvent Substitution – PART 2: The Elimination of Flammable, RCRA and ODC Solvents for Wipe Application, *CleanTech Magazine*, 4(10); 14-16 (2004)
- Lopez, E. P. *, Moddeman, W. E., Birkbeck, J. Williams, D.L., Benkovich M.G., Solvent Substitution – PART 1: The Elimination of Flammable, RCRA and ODC Solvents for Wipe Application, *CleanTech Magazine*, 4(9); 16-19 (2004)
- Williams, D. L., A Gage Repeatability and Reliability Study on the Use of Two Identical Gas Chromatography Systems to Perform Chemical Reactivity Testing, *Pantex Technical Report*, July, 2004.
- Williams D. L., A Measurement System Evaluation of the Calibration of the Differential Scanning Calorimeter, *Pantex Technical Report*, April, 2004.
- Williams D. L., Timmons J. C., Woodyard J. D., Rainwater K. A., Richardson B. R., Lightfoot J. M., Burgess C. E., and Heh J. L., UV-Induced Degradation Rates of 1,3,5-Triamino-2,4,6-Trinitrobenzene, *Journal of Physical Chemistry A*. 107(44); 9491-9494 (2003)
- Williams D. L., Ashcraft R. W., A Technical Review of the Radiological Characterization of Nuclear Weapons at Pantex, *Pantex Technical Report*, April, 2003.