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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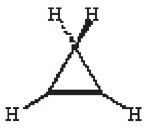
Dr. Benny E. Arney, Jr.

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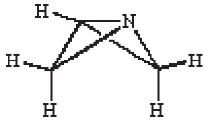
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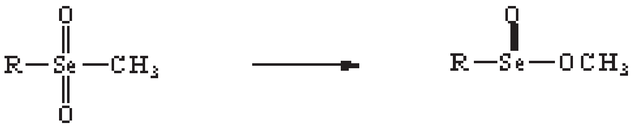
Additionally, my research interests include the chemistry of selenium; specifically, selenoxides and selenones. Methyl selenones are reported to undergo a rearrangement to form methyl alkylseleninates on heating in methanol or setting in aqueous solution.

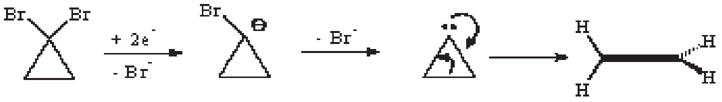
We have been exploring methods for the handling of the odoriferous precursors to these compounds as we prepare a number of derivatives to examine substituent effects and perform kinetic studies.


$$R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Se}}}}-CH_3 \longrightarrow R-\overset{O}{\overset{\|}{Se}}-OCH_3$$

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 has also been exploring the use electrochemical reductions and zero-valent metals to effect a Skattebøl reaction. This involves the reduction of a geminal dihalocyclopropane to the a-haloanion or a-halometallated species (carbenoid) which rearranges to the allene after forming the intermediate cyclopropyl carbene. Use of electrochemical methods will remove the necessity for alkyllithiums.

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.



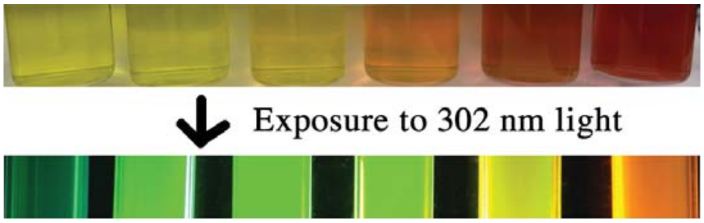
Arney's Recent Funding

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

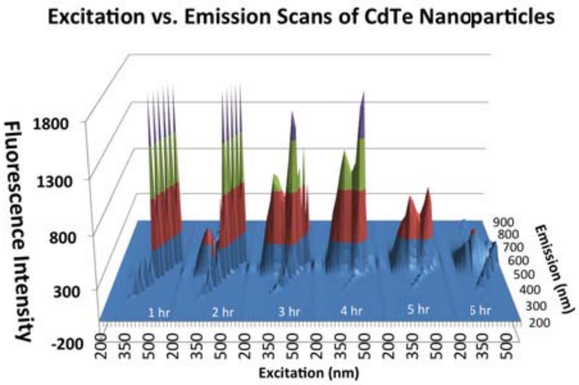
Cadmium telluride (CdTe) nanoparticles can be synthesized abiologically by the reaction of Cd- and Te-containing salts using glutathione and heat. CdTe nanoparticles fluoresce when exposed to UV light as the image below shows.



CdTe nanoparticles fluoresce when exposed to 302 nm UV light.

The small 4 to 5 nm size particles produced have applications in medicine—as tumor targeting agents and in bioimaging, in solar cells—as photoreactive surfaces, in instrument design—as photodetectors, and in analytical toxicology—as analytical probes to detect poisonous ions in solution.

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-, chemical-, and photostability of CdTe nanoparticles by watching the changes in their fluorescent emission spectra of stored particles over time.

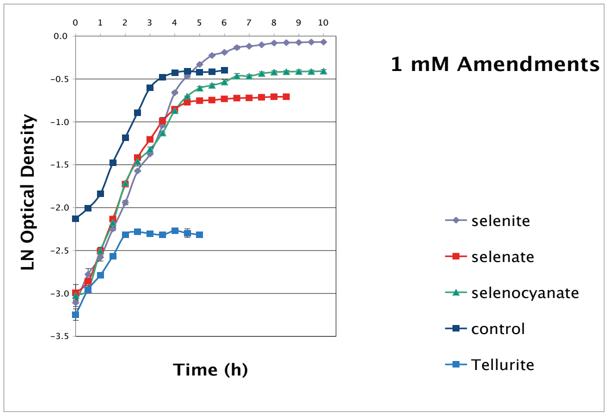


CdTe nanoparticles fluorescence/emission spectra for different synthesis times heated at 90°C. Two hours is optimum.

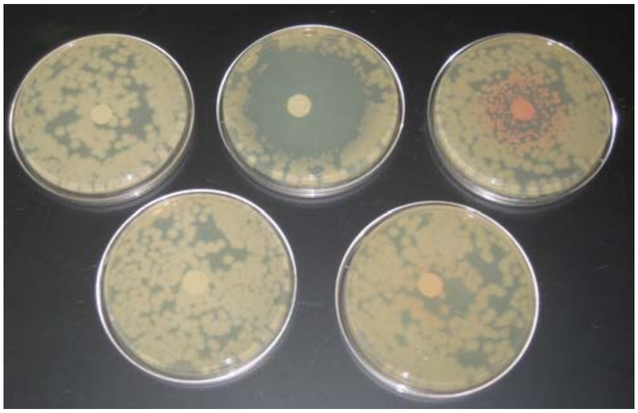
The adjacent image shows multiple absorption vs emission spectra of CdTe in UV and visible wavelength regions, showing the importance of time in the steps to produce these particles. This nanoparticle work has been published in the journal *PLoS ONE*.

II. Toxicity of selenocyanate anion, an environmental important byproduct 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 mining 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*.



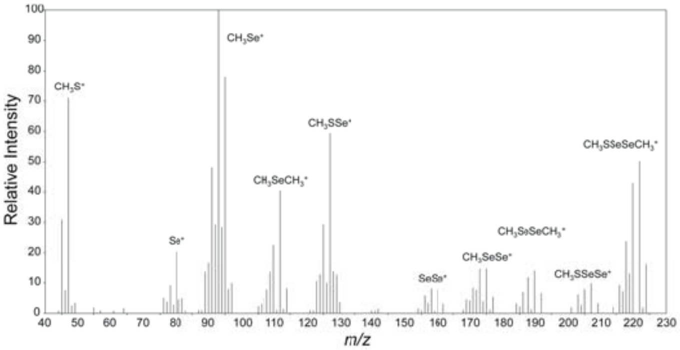
Growth rate experiments: TeO_3^{2-} is the most toxic of these anions.



Zone of inhibition toxicity experiments: TeO_3^{2-} is in center-top plate and elemental Se is biologically produced in the top right plate.

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 (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 μg/mL; after plasmid insertion it is 25 μg/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 (**CH_3TeSCH_3**) in the gas produced by live cultures of this cloned bacterium.

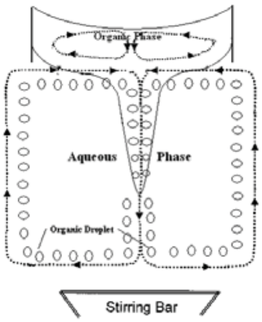


Mass spectrum of dimethyl diselenenyl sulfide, $CH_3SSeSeCH_3$.

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: **$CH_3SeSSCH_3$** and **$CH_3SeSeSCH_3$** (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

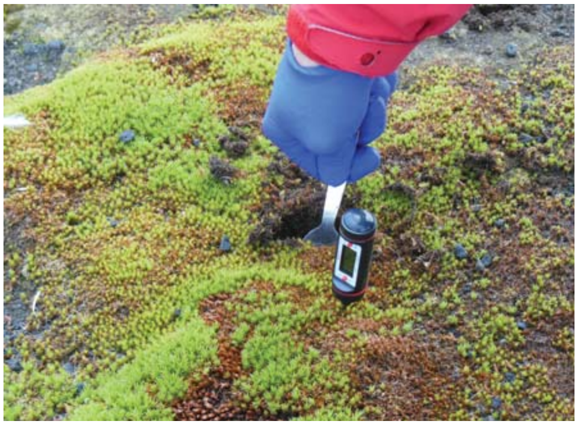
Extremely small volumes of nonpolar solvents can be used to extract volatile organochalcogens—such as **CH_3TeCH_3**—from aqueous solutions collected from the environment. In collaboration with Dr. Mahdi Hashemi—on sabbatical from Bu-Ali Sina University in Iran—students in my lab helped developed this sensitive extraction method in conjunction with gas chromatography with fluorine-induced chemiluminescence detection. Aqueous sample detection limits from 5 to 620 ng L^{-1} were achieved for organo-sulfurs, -selenides, and -tellurides. 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

IV. 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. Recently Chasteen—financed by the Chilean government—travelled to Antarctica for a 15 day research trip to collect soil, water, and sediment samples from Antarctic islands and the Antarctic peninsula above 63 south latitude.



Sampling microbes in the rhizome beneath an Antarctic moss
Click to see the blog of this research trip to Antarctica.

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 Antarctic trip :	\$40,900

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.

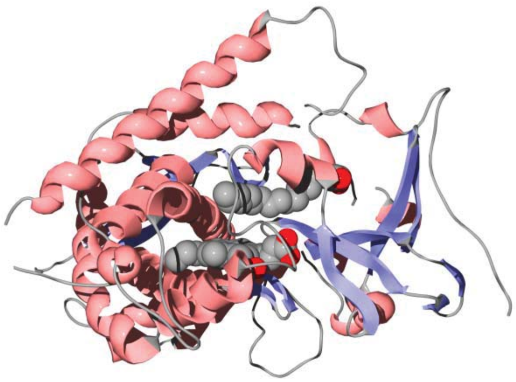


Figure 1. A ribbon structure for the cytochrome P450 called P450BM-3 from *Bacillus megaterium* complexed to an acylamino acid substrate.

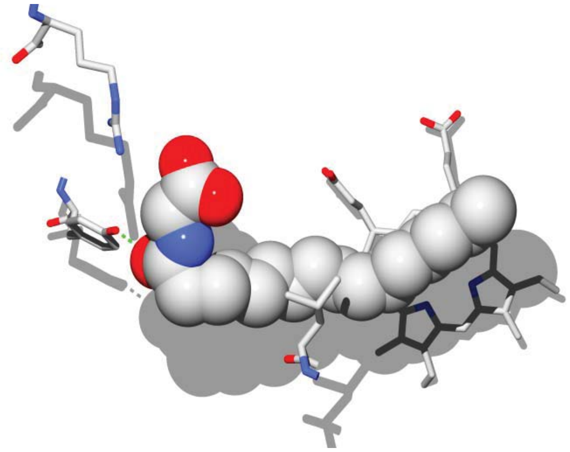


Figure 2. Amino acid side chains of a bacterial P450 which allow it to interact with an acylamino acid substrate (larger spheres).

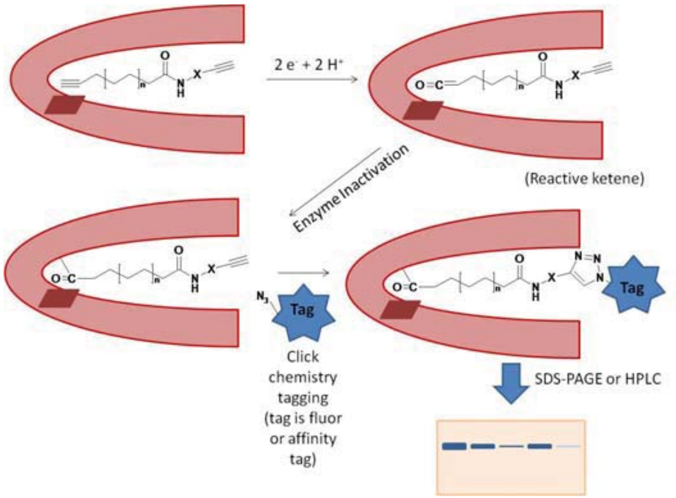


Figure 3. Some of our substrates and inhibitors are probes that can be used for advanced proteomics experiments like Activity Based Protein Profiling.

Haines' Recent Funding

American Cancer Society ($15K, former university)

Welch Foundation ($150K, former university)

SHSU Faculty Research Grant ($5K)

Dr. Rick Norman

Bioinorganic and Transition Metal Chemistry

Dr. Dustin Gross

Organic, Supramolecular, and Macromolecular Chemistry

Dr. Ilona Petrikovics

Chemical Defense, Nanotechnology, and Enzymes in Drug Antagonism

Dr. David E. Thompson

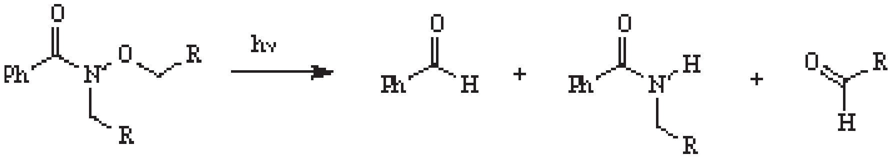
Surface Enhanced Raman and Nonlinear Spectroscopies, Environmental Nanosensing

Dr. Rick C. White

Photochemistry of Amides and Hydroxylamine Derivatives

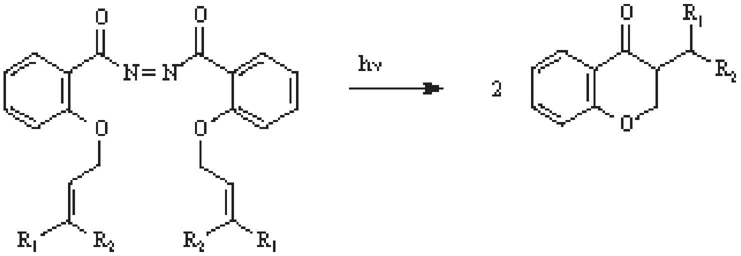
We are currently involved in the photochemistry of organonitrogen compounds. This research looks at the cleavage of the N-O bond as a route to photoactivated DNA cleavage reagents. First, we are examining the factors that influence the N-O bond cleavage in hydroxamic acid derivatives. We have found that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

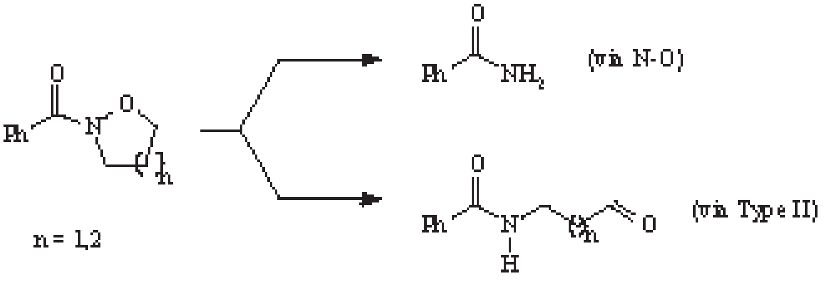
In the cyclic series of compounds, it appears that the size of the ring influences the relative amounts of Type II reactions versus N-O bond cleavage.

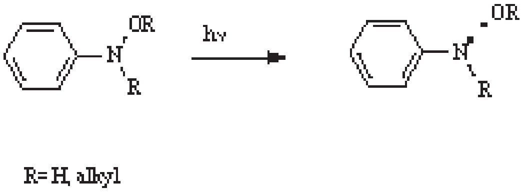


We also are looking at the photochemistry of hydroxylamines such as phenylhydroxylamine derivatives that serve as potential sources of alkoxyl or hydroxyl radicals that can photonick plasmid DNA.

Finally we are looking at the long wavelength induced photolysis of dibenzoyldiazenes 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.







<u>White's Recent Funding</u>:

Petroleum Research Fund, $20,000

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

Deutscher Akademischer Auschtausdienst, 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.

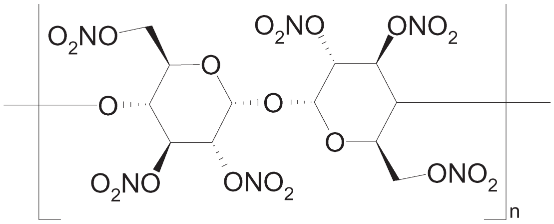
Topics in this area include the following.

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.

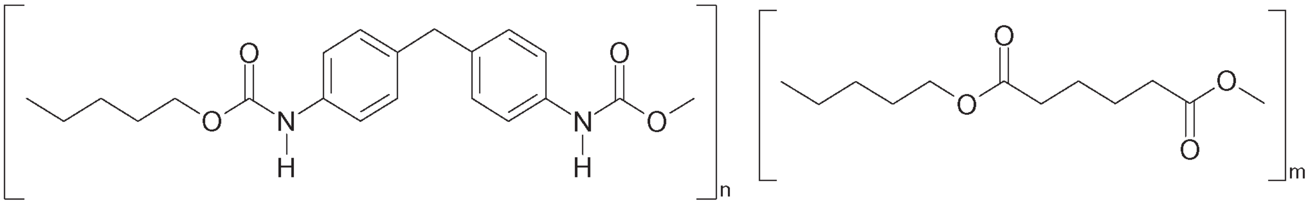
Nitrocellulose – a nitrated natural material – has a complicated degradation chemistry. Discovered in 1832 by Henri Braconnot, the process for nitrating cotton fibers to make gun cotton was optimized by F. J. Otto in 1946. Since then, nitrocellulose (NC) has been used in a variety of applications from 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

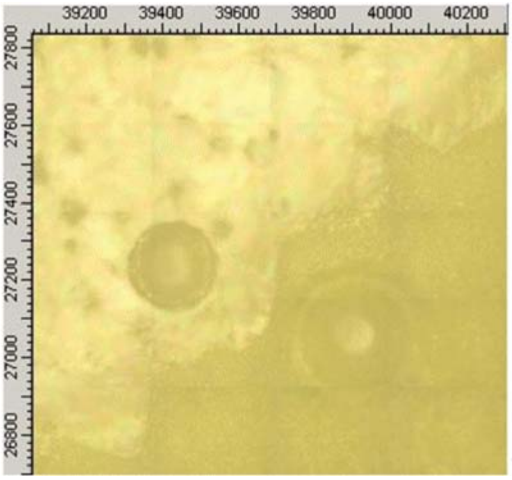
The stability of high explosives depends upon the molecular properties of the explosive, binder, stabilizer, and plasticizer. Micro-infrared (IR) spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, ion mobility spectrometry (IMS), and gas / liquid chromatography – mass spectrometry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

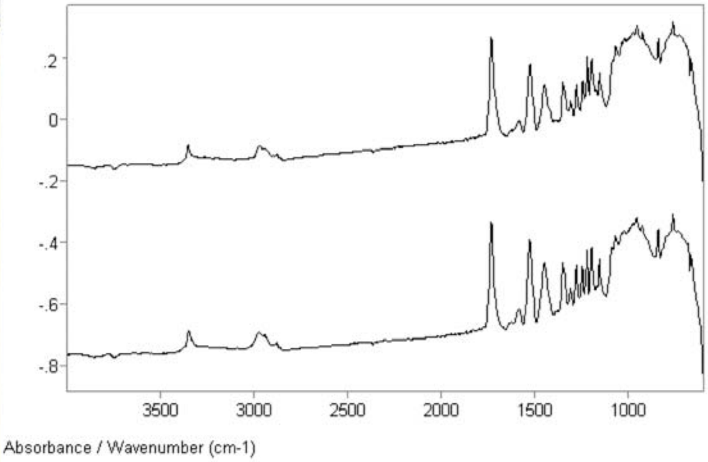
These various techniques are combined to determine the spectroscopic signatures that indicate compatibility issues and aging mechanisms.



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.



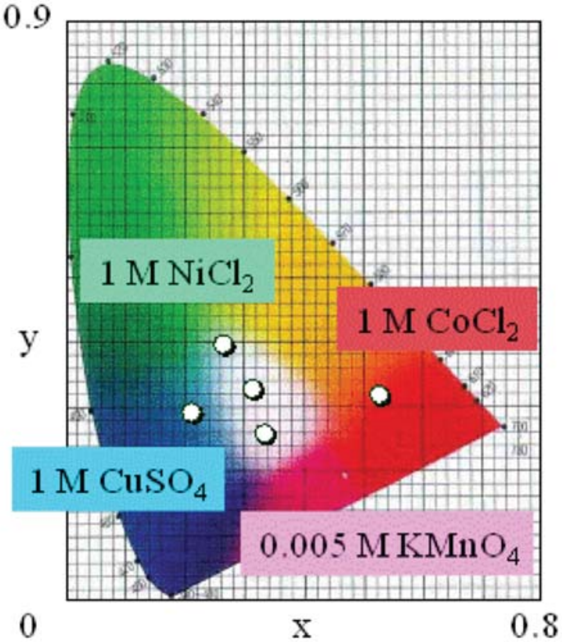


Color Changes

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., Wrobleski 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.