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ORAL PRESENTATION ABSTRACTS

Forensic microscopy and the lost art of observation
Christopher S. Palenik
VP and Senior Research Microscopist, Microtrace

“DNA analyzes one molecule, trace evidence handles the rest.” This unofficial slogan of the forensic trace evidence community is a bold statement, but if one stops to consider it, we are surrounded by hundreds of materials and thousands of chemical compounds at any given time. Each of these, whether highly engineered to achieve specific properties, or naturally occurring, has a story to tell. From a single mineral grain on a sandy beach, to a multilayered pigment particle, virtually any material has the potential to play a significant role in a criminal trial, civil litigation, or an industrial quality investigation. Yet, the ability to exploit this information requires the foresight to find potential evidence, the technical skills to analyze it, and the scientific creativity to exploit the significance of this information. The magnified field of view afforded by a microscope provides a means to observe and analyze materials at a scale that is otherwise invisible and inaccessible to a lay investigator. In itself, this is not a novel concept, since microscopy has been used in this capacity as a problem solving tool for well over a century. Yet, in a world of protocols and standardized methods, the free-form observation platform of microscopy is often discouraged, dismissed, or explicitly limited. Despite this common attitude, case after case illustrates, often in dramatic fashion, the value and elegance of the microscopical approach to the solution a wide range of real-world problems. When used today, in concert with other microanalytical methods, this approach affords higher resolution, greater detection limits, and a wider scope of application than ever before possible. Through examples covering a range of pragmatic, unusual, thought provoking, and sometimes humorous applications of microscopy, this keynote address will illustrate the scientific elegance and practical benefits that a non-scripted, but thoughtful microscopical examination can offer to a wide-variety of problems, be they academic, industrial or forensic.

Chemistry in the Crime Lab
Elaine Dougherty
Forensic Scientist, Michigan State Police Crime Lab, Bridgeport

The employees of the Michigan State Police Forensic Science Division represent a diverse group of people, from police officers to chemists. This presentation will introduce you to the way chemistry is used in every unit in the laboratory, whether the analysts knows it or not!
Forensic Chemistry R&D at Michigan State

Ruth Smith  
*Associate Professor, Michigan State University Forensic Science Program*

This presentation will provide an overview of the role of analytical chemistry in forensic science. Specifically, the presentation will focus on two areas of forensic chemistry, fire debris analysis and controlled substance identification, and discuss research projects in these areas that are currently underway in the Forensic Chemistry Laboratory at Michigan State University.

An intentional, rather than accidental fire, is often determined based on the presence of an ignitable liquid, such as gasoline, in the debris collected at the crime scene. Debris samples submitted to the forensic laboratory are typically extracted and analyzed by gas chromatography-mass spectrometry (GC-MS) with the resulting chromatogram compared to a database containing chromatograms of known ignitable liquids. These databases often include chromatograms of the liquids evaporated to a few different levels to take into account chemical changes that occur as a result of evaporation. However, evaporating liquids can be time-consuming and there are a number of variables to consider. Current research in our laboratory is developing a kinetic-based model to model evaporation of ignitable liquids. The model can then be used to mathematically generate chromatograms corresponding to any evaporation level of a liquid. The initial development of the model will be discussed, along with specific applications for fire debris analysis.

The second part of the presentation will focus on identification of controlled substances. Typically, controlled substance samples submitted to a forensic laboratory are analyzed by infrared (IR) spectroscopy or GC-MS. However, definitive identification of synthetic designer drugs using these techniques is often challenging due to the high structural similarity among compounds in the same class and the rapid emergence of new analogs for which no reference standard may be immediately available. Our research in this area uses high-resolution mass spectrometry to understand the fragmentation behavior of these compounds and exploits the mass defect as a tool for characterization purposes. Initial results focusing on synthetic phenethylamines and the development of mass defect filters for their characterization will be presented and discussed.
Steric trapping reveals a cooperativity network in the intramembrane protease GlpG

Heedeok Hong

Assistant Professor, Department of Chemistry & Department of Biochemistry and Molecular Biology, Michigan State University

Membrane proteins are assembled through balanced interactions among protein, lipids and water. Studying their folding while maintaining the native lipid environment is necessary but challenging. Here we present methods for analyzing key elements in membrane protein folding including thermodynamic stability, compactness of the unfolded state and folding cooperativity under native conditions. The methods are based on steric trapping which couples unfolding of a doubly-biotinylated protein to binding of monovalent streptavidin (mSA). We further advanced this technology for general application by developing versatile biotin probes possessing spectroscopic reporters that are sensitized by mSA binding or protein unfolding. By applying these methods to an intramembrane protease GlpG of *Escherichia coli*, we elucidated a widely unraveled unfolded state, subglobal unfolding of the region encompassing the active site, and a network of cooperative and localized interactions to maintain the stability. These findings provide crucial insights into the folding energy landscape of membrane proteins.
A stable, disposable, homogeneous nanostructured substrate for surface enhanced Raman spectroscopy (SERS) detection of various analyte molecules

Honey Madupalli*, Mary Tecklenburg

Department of Science of Advanced Materials, Central Michigan University

Raman spectroscopy of molecules absorbed on metal surfaces with nano-sized features show enhanced intensity, known as surface enhanced Raman spectroscopy (SERS). Improvements in SERS have resulted from research into the effect of metal nanoparticle size, morphology, spacing and as colloids, core-shell particles, and fabricated surfaces. As instruments have become smaller and more robust, portable instruments for Raman spectroscopy outside of the laboratory environment are growing. However, the stability of the metal surface needed for SERS can be a limiting factor as exposure to light, moisture, and air can easily affect the activity of the surface.

In our approach, we have utilized the unique inverse micellar behavior of amphiphilic branched polyethyleimine with a hydrophilic core and a hydrophobic shell. The polar domains effectively stabilize the silver nanoparticles within a non-polar shell. Such a polymer encapsulated nanoparticle solution was made into films to be used as a SERS surface for testing. Our research is also focused on attaining a suitably homogeneous nanoparticle distribution in our modified polymer substrate. The average size, stability and separation of the silver nanoparticles was controlled by tuning the influence of the density of the hydrophobic shell and the amount of reducing agent used. A consistent SERS signal was observed with a relative standard deviation of less than 10% which shows that our long-term stable nanoparticle imbedded films have a homogeneous distribution of the nanoparticles over the entire polymer film.

The laser excitation at 532 nm (near the plasmon resonance peak) produced significantly enhanced SERS for benzotriazole (a drug precursor), a molecule that was extensively examined on our silver nanoparticle imbedded polymer template. SERS for many other analyte molecules – acetaminophen, 4-mercapto benzoic acid, acetyl salicylic acid, diclofenac sodium, melamine, uric acid, etc., are also being studied.
Storage Stable Concentrated Emulsions of Hydrofluoroethers and Perfluoroethers

David L. Malotky+, Robert R. Bills+

The Dow Chemical Co., Midland, MI, U.S.A.

Hydrofluoroethers (HFE) and perfluoroethers (PFE) have unique properties because of their very low surface energy, and omniphobic nature, but these very properties make them difficult to incorporate into aqueous systems. We have addressed this problem with a combination of formulation and process to generate concentrated (up to >90% wt.), storage stable emulsion concentrates with Volume Mean particle size < 5 microns. This process is most effective when performed using Dow’s proprietary mechanical dispersion technology based on rotor start mixing equipment. These aqueous emulsion concentrates are easily diluted by cold mixing and can be easily incorporated into a partial cosmetic formulation to create a finished product.

This series of materials can also provide insight into the emulsification process by Taylor breakup theory because of the wide range of interfacial tensions observed across the class of materials with the same surfactant system.

Using Computational Chemistry Tools to Assist In Process Development

Gregory Cushing

Hemlock Semiconductor Corporation

Computational chemistry tools have been used from predicting chemical reactions to predicting physical properties. Experimentation continues exploring opportunities to navigate computational methods towards higher accuracy. With recent developments in computational chemistry packages, predictions can be made a priori. These software packages have been used to assist in reducing research timelines and improve the accuracy for development of a process. A computational chemistry package such as Gaussian 09 is an electronic molecular structure software capable of predicting thermodynamic values (H, S, Cp), spectroscopic information (NMR, IR, Raman, UV-Vis, CD), Arrhenius reactions rates, and solvent effects. Additional chemical modeling capabilities available such as COSMO, are beginning to be explored to allow for development of physical properties where little to no experimental information is available. Such properties predicted by COSMO are boiling points, solubility, Henry’s Law constants, VLE/LLE, and vapor pressures of pure solvents and mixtures. Several examples of these modeling tools are explored.
**Explosive Cocrystals with High-Nitrogen Energetic Materials**

Rosalyn Kent

University of Michigan

Cocrystallization, the formation of a crystal containing multiple neutral compounds in a defined stoichiometry within a single crystal lattice, has the potential to afford many of the targeted properties desired in energetic materials. In particular, the cocrystallization of energetic materials offers a means to direct crystal packing, enhance intermolecular forces, reduce sensitivity, and alter the oxygen balance of an energetic. While many of these properties can be engineered into new materials through covalent synthesis, cocrystallization is unique in being able to leverage existing high-explosives for the synthesis of new cocrystals. With all these potential advantages, the challenges of actually obtaining energetic cocrystals with useful properties must be addressed.

Absent from the studies discussed above is the construction of cocrystals with high nitrogen explosives. The attractive features of high nitrogen explosives include: 1) high positive heats of formation, 2) high crystal density, 3) insensitivity to impulsive initiation, 4) benign decomposition products making them “greener” and 5) generation of minimal smoke. For these reasons we believe materials based on the tetrazine core represent an exciting new frontier in energetic crystal engineering.

BTATz (3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine) and NGT (3,6’-Bis-nitroguanyl-1,2,4,5-tetrazine), are high nitrogen energetic materials with well-established and scalable syntheses. To date, very little is known about the local interactions and extended packing arrangements specific to BTATz and NGT, due to each compound’s notable insolubility. In this presentation, synthons and extended motifs conserved across BTATz and NGT co-crystals will be discussed.
Surface versus Bulk Chemistry of Water Filtration Membranes

Tamlin Matthews¹, Robert Cieslinski¹, Christopher Alvey¹, Mou Paul², & Abhishek Roy²

¹Core R&D – Analytical Sciences, Surface and Interface Characterization
²Dow Water and Process Solutions R&D

Dow Chemical Company

The polyamide layer of reverse osmosis (RO) thin-film composite membranes is ~100 nm thick. Separation of this thin layer from the supporting layers is a complex process and can only be done chemically, which results in a fragile polyamide layer and makes characterization challenging. X-ray photoelectron spectroscopy (XPS, near-surface) and Rutherford backscattering spectrometry (RBS, bulk) have been applied to characterize the polyamide layer, without the need to separate polyamide from the supporting layers. The combination of these methods allows the comparison of bulk vs. near-surface carboxylic acid content, which is a driver in RO performance. Additionally, elemental composition, thickness, and roughness of the RO membranes can be compared in systems with systematically changed monomers. This talk will focus on how the application of XPS and RBS can be used together for surface vs bulk chemical composition.
Reactive Chemical Hazards of Azide Compounds: A Case Study and Lessons Learned

Min Sheng, John Hull, Todd Tambling, Grant Von Wald, Marabeth Holsinger

Dow Chemical Co., Midland, MI, 48667, USA

While a vacuum pump was being serviced by a researcher an unintended detonation occurred. The pump had been used in a sulfonyl azide synthesis (R-SO₂-N₃). The detonation occurred when he was applying effort to the hose barb from the outlet of the pump to connect it with a rubber hose. Differential Scanning Calorimetry (DSC) and headspace Gas Chromatography/Mass Spectrometry (GC/MS) were employed for the root cause investigation. The DSC showed a large exothermic decomposition (-1388J/g) for the residual sample from the pump fitting. Headspace GC/MS identified the presence of hydrazoic acid in the pump oil. The investigation concluded that either the azide precursor (sodium azide) or hydrolysis of the product (sulfonyl azide) was responsible for generating hydrazoic acid, which escaped from the dry ice trap and appeared in the downstream equipment, and probably reacted with metal parts (brass) to form a highly shock sensitive material (copper azide).

This paper reviews the reactive chemical hazards for azide compounds involved in this case study. Sodium azide is not particularly sensitive to mechanical impact, but its propensity to form hydrazoic acid in water is well-known, even at neutral pH. Likewise, the test data on sulfonyl azide product showed that it is not particularly sensitive to mechanical impact, but it can generate hydrazoic acid upon hydrolysis with water. Metal azides which are formed by the reaction between hydrazoic acid and metal surfaces of equipment parts are highly hazardous due to their extreme impact and friction sensitivity.

Based on lessons learned, this paper also describes further steps for synthesizing organic azides using aqueous sodium azide. These steps include, but are not limited to: (1) Utilizing a dedicated hood and equipments to limit potential HN₃ vapor streams from contacting any reactive metal surfaces. (2) Using a dual caustic trap system designed to scrub the outlet gases swept from the azide reaction step, instead of dry ice trap. (3) Using a 5% aqueous solution of ceric ammonium nitrate as a decontaminating agent for metal surfaces inside the fume hood at the completion of the campaign. (4) Eliminating all brass or copper fittings from equipment used in the synthesis, due to the potential formation of the unstable explosive copper azide that can form from exposure of brass or copper parts to HN₃.
Thermal Properties of Hyperbranched Polyesters

Abhijit Sarkar, Adina Dumitrascu, Tracy Zhang, Bob Howell and Patrick B. Smith

Michigan State University, Midland, MI

Hyperbranched poly(ester)s (HBPE)s of targeted structure and molecular weight can be readily prepared from a variety of multi-functional acids and alcohols. These functional polymers can be synthesized in variety of architectures, possessing either hydroxyl or carboxyl reactive end-groups suitable for the attachment of a diverse group of active entities. These materials find application for controlled delivery of actives, rheology modifiers for coatings and many others. The thermal properties of these polymers and their degradation characteristics were examined using Da variety of thermal and spectroscopic techniques. In particular, the glass transition temperature ($T_g$) of HBPEs from trimethylolpropane and adipic, terephthalic and isophthalic acids with a variety of molecular architectures were determined in order to identify the major structural features that contribute to the $T_g$. These structural features included composition, molecular weight, endgroup functionality and degree of branching. The thermal degradation of these HBPEs will also be described.

Thermal Stability of Castor Oil Based Flame Retardants

Eric Ostrander and Bob A. Howell

Center for Applications in Polymer Science
Department of Chemistry and Biochemistry
Central Michigan University
Mt. Pleasant, MI 48859-0001

Castor oil is a non-edible natural seed oil produced in large quantities annually. It contains both unsaturation and hydroxyl functionality that may be utilized for conversion to a variety of bioderived polymer additives. Compounds containing phosphorus, bromine or both are readily available from the oil. The thermal degradation of these kinds of castor oil derivatives has been examined using thermal and spectroscopic techniques.
How the ACS Bylaw for Director-at-Large Elections Was Changed

Wendell L. Dilling
Department of Chemistry and Biochemistry, Central Michigan University, Mt. Pleasant, Michigan

Prior to 2016 ACS Directors-at-Large were elected by plurality; the winners were those who received the most votes. This procedure resulted in a Director-at-Large being elected by a minority of the voters in five of the past seven years. Because of similar results in elections for ACS President-Elect and District Directors, ACS bylaws were changed over the past 40-50 years so that election to these positions required the winning candidates to receive votes from a majority of the voters. This poster shows highlights of the process by which the bylaw pertaining to the election of Directors-at-Large was changed. ACS bylaws now require that all ACS elections involving more than two candidates be conducted by preferential voting, which guarantees that all winning candidates receive votes from a majority of the voters.
This work describes a method to synthesize SiCl$_4$ from alkyl orthosilicates and gaseous HCl. Reacting tetramethyl orthosilicate with HCl gas at 0 °C in the presence of a catalytic amount of hexamethyl phosphoramide (10 mol %) and four equivalents of acetonitrile afforded an 86 % yield of SiCl$_4$ after six hours. Exchange between HCl and alkoxy groups on silicon during the reaction generates methanol. The methanol then reacts with acetonitrile (in the presence of HCl) to form an imidate, thus removing it from the reaction mixture. Other Lewis acid and base catalysts were also observed to accelerate the reaction. A kinetics experiment using $^{29}$Si NMR to monitor reaction intermediates in situ was conducted to determine the rates of chloride/alkoxide exchange on silicon.

REFERENCE

#3

**Development and Validation of an Optimized Gas Chromatography (GC) Testing Method for Quantitation of Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), and Dodecamethylcyclohexasiloxane (D6) in a Variety of Commercially Available Silicon Personal Care Products**

Michelle Rivard  
Dow Corning Corporation

**Abstract:**

A simple gas chromatography with flame ionization detection (GC-FID) method for analysis of D4, D5, and D6 cyclic siloxanes in emulsions containing silicones is described. Three different sample preparation procedures (Tetrahydrofuran (THF) dilution, Acetone Extraction, and a modified Hexane/Methanol break with derivation) prior to analysis by GC were examined across a variety of silicone emulsions and commercially available hair care products. The objective was to develop a low complexity analysis method that would use common analytical equipment and reagents. The sample preparation involves breaking the emulsion with hexane, methanol and deionized water, and then analyzing the hexane phase after derivation with hexamethyldisilazane (HMDZ) as a silylation reagent. From previous research in this area, it is known that generation of cyclic siloxanes can occur in the inlet of a GC depending on the composition of the emulsion being analyzed. Silylation is performed to reduce this potential. This research investigated the accuracy and robustness of an improved GC test method for quantification of cyclic siloxanes in commercially available silicone emulsions and hair care products.

#4

**Celebrating 25 Years of Exceptional and Significant Contributions of the Mid-Michigan Technician Group**

Michelle Rivard, Jeff Seifferly, Jason Suhr & David Baker  
Mid-Michigan Technician Group

For the past twenty five years, the Mid-Michigan Technician Group has been focused on promoting personal and career related growth throughout the Technician community. Current and past members have participated in numerous public outreach events such as Kid’s in Chemistry, Sci Fest, ACS Day at the Fair, and many many more. This poster presentation will cover various activities MMTG has sponsored or volunteered it’s time to, in both the science community and those interested in one day working in a science related field. Also included are the awards MMTG has received from their contribution to the community and the promotion of technicians.
Looking back at 20 years of Outstanding Technician

Michelle Rivard, Jeff Seifferly, Jason Suhr & David Baker

Mid-Michigan Technician Group

Over the past twenty years numerous members of the Mid-Michigan Technician Group have been honored with either local and/or national awards showcasing their dedication and vast contributions to the field of science. Some of these awards include the Distinguished Service Award from the Midland Section ACS, Outstanding Technologist Achievement Award from the Dow Central R&D Scientists Organization, National Chemical Technician Award from the American Chemical Society, and many more. This poster will showcase some of these outstanding technicians and the awards they have earned over their many years of hard work and dedicated service.

MMTG & Delta College’s Outstanding Chemical Technology Students a Prolific Partnership

Michelle Rivard, Jeff Seifferly, Jason Suhr & David Baker

MMTG & Delta College, University Center, MI 48710

Over its 25 year history the MMTG has had a strong relationship with the Chemical Technology program at Delta College. Many graduates from the Chemical Technology program have had very successful careers with local industry employers. Others have also received the Outstanding Chemical Technology Student Award as a recognition of their expertise and academic excellence. This will be a presentation of the activities and successes these students have had as a chemical technicians over the years. It will include a reflection of their memorable experiences and notable antidotes from colleagues in the laboratory and in academic work at Delta College.
**A practical gas chromatography flame ionization detection method for the determination of cyclosiloxanes in silicone emulsions**

Joel Kerbleski

Dow Corning Corporation

A gas chromatography with flame ionization detection (GC-FID) method for analysis of D4, D5, and D6 cyclic siloxanes in silicone emulsions is described. Sample preparation involves breaking the emulsion with methanol and hexanes, and then analyzing the hexanes phase after derivatization with hexamethyldisilazane (HMDS). Silylation is performed to reduce the potential for formation of cyclic siloxanes during the course of the GC analysis. The accuracy of the method was verified by performing analyses on samples spiked with known levels of D4, D5 and D6 and by comparison to a referee method using atmospheric pressure chemical ionization liquid chromatography with mass spectrometry detection (APCI-LC-MS). Absolute differences of the results obtained between the two techniques were 0.03 weight percent or less, and relative differences were 15% or less. The reproducibility and ruggedness of the method was demonstrated by performing a global round robin test at four different geographic sites on four different types of silicone emulsions. The %RSDs obtained were less than 10% for all analytes and all emulsions examined.

**Characterization of sub-micron dispersions of high M_w polyolefins derived from a HIPE at high temperatures and pressures**

D. Dermody, R. Lundgard, D. Malotky, M. Kalinowski, T. Young, J. Mecca;

Formulation Science, The Dow Chemical Company, Midland, MI.

Dow Chemical has developed a high temperature/high pressure HIPE (high internal phase emulsion) based approach to produce uniform sub-micron aqueous dispersions of traditionally difficult to disperse materials including: polyolefins, epoxies, polyurethanes, polyesters, and alkyds. These aqueous dispersions can be used in a variety of application areas including coatings, home and personal care, adhesives, and composite materials where to impart improved material and performance attributes. In this talk we will give an overview of the HIPE conditions needed to produce these dispersions, the types of particles that can be produced (resins, resin blends, addressable size regimes, particle morphologies, particle surface chemistries), example application areas and impact of the dispersion on application performance as well as technical challenges and future opportunities for the dispersion technology.
An APCI LC-MS-MS Method for the Determination of Octamethylcyclotetrasiloxane (D₄), Decamethylcyclopentasiloxane (D₅), and Dodecamethylcyclohexasiloxane (D₆) in Silicone Emulsions.

Tanya Habitz
Dow Corning Corporation

Introduction

Due to the non-polar nature of D₄, D₅ and D₆ PDMS macrocyclics, these species cannot be detected by conventional electrospray ionization even at relatively high concentrations (100 ppm). D₄, D₅ and D₆ can be quantified by GC-FID or GC-MS, but for silicone emulsions that often contain SiOH-ended linears, \((\text{HO})\text{Me}_2\text{Si}(\text{OSiMe}_2)_x\text{OSiMe}_2(\text{OH})\), inaccurate GC-FID and GC-MS results occur due to cyclization of the SiOH ended linears in the hot GC inlet, resulting in artificially high cyclic siloxane quantification results. For silicone emulsion samples, an alternative robust analytical method for low ppm quantification of D₄, D₅ and D₆ was needed. Development of a direct LC-MS-MS method is described herein that utilizes atmospheric pressure chemical ionization (APCI) coupled to a triple quadrupole mass spectrometer.

Methods

A newly developed APCI LC-MS-MS method was optimized for dimethyl cyclosiloxane UPLC peak shapes, minimum analysis time (4.0 minutes) as well as low ppm detection limits for each analyte. The APCI LC-MS-MS method is direct with minimal sample preparation that involves simply dissolving the entire emulsion sample (50X-2,500X) into THF solvent. The diluted samples are then injected into an Agilent 1290 UPLC system whereby the individual cyclic siloxanes are separated utilizing a C₁₈ UPLC column, then quantified by MRM peak area measurements utilizing an Agilent 6490 instrument. Utilization of the APCI LC-MS-MS method resulted in the ability to measure low concentration analytes in complex silicone emulsion matrices that would normally not be achievable by conventional single quadrupole LC-MS measurements.

Preliminary Data

Each cyclic PDMS calibration standard was analyzed in quadruplicate using the optimized APCI LC-MS-MS method. The PDMS cyclic species calibration curves were found to be linear with \(R^2\) values in excess of 0.98 and yielded the best quantitative results using a \(1/x\) curve weighting. Five silicone emulsion samples and two commercial hair care formulations were also analyzed in quadruplicate using the APCI LC-MS-MS method. These were diluted in THF to various degrees to allow each analyte to fall within the bracketed calibration range for each calibrated cyclic PDMS standard.

The APCI LC-MS-MS data obtained for the seven silicone emulsion samples yielded relative standard deviations that ranged between 3-13% for D₄, 3-12% for D₅ and 2-7% for D₆. The APCI LC-MS-MS method used to obtain results for all the PDMS cyclic standards as well as silicone emulsion samples was found to be a viable alternative to the more commonly used GC-FID and GC-MS approaches.
A side by side method results comparison for the silicone emulsion samples by GC-FID versus APCI LC-MS-MS analytical techniques was completed on the same day. For silicone emulsion samples free of silanol-terminated PDMS structures, comparable results were observed between conventional GC-FID and APCI LC-MS-MS approaches. For example, the percent difference observed between the silicone emulsion samples for GC-FID versus APCI LC-MS-MS for the cyclic PDMS tetramer through hexamer was found to be 1-12% for D₄, 4-11% for D₅ and 11-15% for D₆.

**Novel Aspect**

First demonstrated ability to successfully ionize, detect and quantify non-polar PDMS macrocyclics by APCI LC-MS-MS.

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**Removal of Zinc from Water Utilizing Pressure Stable, Imprinted Polymers**

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Waste water remediation is a pivotal process relied upon by untold millions across the globe. Often overlooked but problematic in high concentrations zinc is an ever-present heavy metal necessary for normal bodily function. Elevated concentrations that could induce toxicity can be found in tailings and industrial waste water. Within the Mueller research group, removal of zinc from water was achieved through the use of zinc-imprinted, pressure-stable polymers. Polymer stability, with regards to pressure, was enhanced through the introduction of a monomer containing a tert-butyl functional group. Polymer performance was investigated to quantify zinc uptake under pressure. Effluent from these studies was subjected to analysis via flame atomic absorption spectroscopy in order to monitor zinc removal. Zinc remediation was investigated in combination with calcium to further understand the competitive affects of ionic species. Water flow and ion retention time were of key interest in order to understand optimal operating conditions. Currently work is being done to develop imprinted polymeric membranes.
Proton Exchange Fuel Cell Membranes that Mimic Biological Proton Transport

Aaron Argall
Central Michigan University

Atmospheric carbon dioxide levels have a strong correlation to increased health care expenditures, human health problems, and permanent global climate changes. As carbon dioxide emissions from the combustion of fossil fuels increases, an alternative fuel source that does not give off carbon dioxide as a byproduct can aid in its reduction. A fuel cell is an energy conversion device that can generate electrical energy from various reactants while emitting only water. Proton exchange membrane fuel cells that use hydrogen as fuel have gained more attention due to their high thermal stability, efficient energy conversion and low pollution output. Nafion is a common perfluoropolymer that is used in fuel cells membranes that have high proton conductivity, thermal stability, and mechanical properties. Current proton exchange membranes require water and strong acid for proton transport, which limits their durability and is usually associated with a higher cost. This study aims to develop a durable and cost effective membrane that transports protons via a dry proton hopping mechanism, similar to how ion channels in the brain move potassium and sodium. The advantage of using a dry proton hopping mechanism is that the membrane itself will not be saturated and exposed to corrosive acid. Additionally, the fuel cell can be run at high temperatures, resulting in a higher energy efficiency. The results of this research project will in the long run lead to a dry, mechanically-strong proton exchange membrane with effective proton transport. Thermal, mechanical, and NMR data will be presented for the complete block copolymer before functionalization giving a baseline for upcoming experiments.
The Use of Alternative Interventions in Organic Chemistry to Increase Student Learning to Higher Bloom’s Taxonomy Levels.

James S. Lamblin

Central Michigan University

This project involved an Organic chemistry two-semester series that taught students in an active learning environment instead of the traditional lecture based environment. The students learned not only the material for Organic chemistry but also team development and increased group skills that employers look for in the workforce. This increase in group skills was effective in raising grades for some of the students. The students in the class were also exposed to several teaching interventions, both traditional and alternative, to help them study and learn more efficiently at a higher learning level instead of trying to memorize it by heart. This presentation will show data, both qualitative and quantitative, that shows improved metacognition and study habits of the students. More quantitative data will be collected in the future to see if these interventions continue to be effective.
An Overview of Green Chemistry

Marissa Dobulis
SVSU Chemistry Club

Humans have always been striving to improve crop protection, commercial products, and medicines. However, until the 1950s the long-term negative effects of these advancements started to present themselves and warranted concern and attention. Many governments began to regulate the generation and disposal of industrial wastes and emissions. In 1970, the United States formed the Environmental Protection Agency (EPA) which was meant to protect human and environmental health through setting and enforcing environmental regulations.

Green Chemistry takes the EPA’s mandate one step further by asking chemists and engineers to design chemicals, chemical processes, and commercial products in a way that avoids the creation of toxins and waste. Through the practice of green chemistry waste can be reduced, the demand on diminishing resources can be reduced, and processes can be employed that use smaller amounts of energy.

In the Fall of 2015, the Saginaw Valley State University Chemistry Club started making green chemistry a priority in their demonstrations and activities. One example was their chemistry demonstration, during the Midland ACS Fall Scientific Meeting, which used chlorine kits to compare a chlorinated cleaning product to a similar “green” product which uses no chlorine. Another example was their trip to Niagara Falls in April 2016 to look at a “green” form of energy at the hydroelectric power plant in New York. This year, we plan to demonstrate green chemistry for the community, have guest lecturers, and tour a LEED-certified building. It is the goal of the chemistry club to educate the community about green chemistry through this poster, and in the future by facilitating even more green chemistry events.
Reproducibility and stability of SERS signal of analytes on a PEI polymer matrix embedded with gold nanoparticles

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The current study is focused on developing stable gold nanoparticles (AuNPs) embedded in a polymer matrix, capable of detecting drug molecules and toxic chemicals in the environment at low concentration via Surface Enhanced Raman Spectroscopy (SERS). The SERS technique involves the enhancement of the Raman scattering of a molecule adsorbed on nanoparticles of gold or silver. In order to fabricate the SERS substrate, gold nanoparticles were synthesized in an aqueous solution of a surfactant, cetyltrimethyl ammonium bromide (CTAB), via a seed mediated process and then the particles were centrifuged to remove excess CTAB before embedding in polyethyleneimine (PEI) and casting polymer films. The reproducibility of the gold nanoparticle size, shape, and particle distribution was confirmed by TEM measurements. We optimized the ratio of AuNPs to polymer to give the strongest and most stable SERS signal. Long term studies of SERS reproducibility on our polymer templates are on-going. Moreover, the SERS enhancement for our AuNP-polymer substrates were evaluated using thiosalicylic acid (TSA) and other molecules.
Stability of Selected Bio based Plasticizers

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Polymeric materials are consumed at the order of three million metric tons per year and account for the high standard of living in the developed world. For most applications these materials must be plasticized. Traditionally, phthalate esters, owing both to cost and effectiveness, have been popular plasticizers. However, these materials may migrate from the host polymer, particularly for waste items discarded in a landfill, and enter the environment. They may bioaccumulate enter the human diet and contribute to various negative health conditions. As a consequence, new bio based plasticizers are being developed. Some of these are now being commercialized. Prominently, one of these, pentaerythritol valerate (Pevalen) is gaining notice. The stability of this material has been evaluated using thermogravimetric and spectroscopic techniques.
Itaconic Acid: A Biosource for Nontoxic Flame Retardants

Victoria Hill
Central Michigan University

Itaconic acid is a four-carbon diacid containing a methylene group at the 2-position and is readily available from biosources. Michael addition of phosphites to the methylene group provides a route to a variety of phosphorus compounds. These compounds may be applied directly for flame-retarding of cellulosic fibers, principally cotton. Alternatively, they may be converted to oligomers with appropriate diols [isosorbide, 2,5-bis(hydroxymethyl)furan, substitutedhydroquinones, etc.]. These oligomers should function as effective, non-migrating replacements for potentially toxic organohalogen flame retardants in a variety of polymeric materials.

De Novo Chemical Synthesis of 3-Azido-3-Deoxy-myoinositol via Ferrier Rearrangement

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Inositol is a non-classical carbohydrate that exists in both prokaryotes and eukaryotes with functions in signaling and anchoring molecules to cell surfaces. Due to the challenges of studying glycoconjugates using traditional biochemical techniques, azido inositol analogues may have value as bioorthogonal chemical reporters for studying inositol-containing biomolecules in various systems. However, the synthesis of these compounds is challenging due to inositol’s internal plane of symmetry and the need to differentiate six secondary hydroxyl groups. In this study, we report progress on a de novo chemical synthesis of 3-azido-3-deoxy-myoinositol starting from a simple precursor, methyl 2-azido-2-deoxy-α-D-glucopyranoside.
Functionalizing Cellulose with Added Amine Groups to Adsorb Phosphates

Darla Martinez, John Radke, Matthew Powers, Jesse Place, and Dr. Jennifer Chaytor

Department of Chemistry, Saginaw Valley State University

With a rise in runoff, there has also been an increase in nutrients and phosphates. As a result of this increase a domino effect occurs in many water ecosystems. It starts with large amounts of phosphates, then due to the mass amounts of these phosphates plant growth increases. Plants, like most living organisms, need oxygen to thrive. When these new plants come about in large numbers they require more oxygen. Excessive plant growth uses up the available oxygen, eventually leading to plant death. This domino effect is called eutrophication. In an effort to reduce the effect of eutrophication, research has been conducted to functionalize cellulose by adding on different amine groups in hopes of adsorbing phosphates out of the water.

Cellulose was put through a tosylation process to produce a tosyl cellulose intermediate. Once tosyl cellulose was created, then the functionalization process of adding on the amines began. The amine-functionalized cellulose products were difficult to characterize, although many tests were ran using the IR and NMR instruments. Obtaining solid products proved difficult in some cases as many of the compounds had a gel-like appearance, making them difficult to isolate via filtration. Due to these issues, many of the reactions had to be repeated in order to isolate usable products that could later be tested.

Once the desired products were isolated, they were subjected to phosphate testing. From this testing we were able to see that cellulose modified with the primary amine methylamine was able to decrease phosphate levels by 89% compared to a negative control. The results of these studies will be presented.
Synthesis of Dianthin G, a Peptide that Promotes the Formation of Osteoblasts

Kathlyn Underwood, Nick Toupin, Patrick Fryfogle, Dr. Jennifer Chaytor

Department of Chemistry, Saginaw Valley State University

Osteoporosis is a common disease that occurs in the bones of both men and women. The disease is more prominent in adults over the age of 60 as it affects 1 in 4 men and 1 in 2 women in this age bracket. While many people have osteoporosis, there are still millions of people who are at risk of developing the disease or have low bone mass levels that may lead to an increased susceptibility of fractures, especially in the hip, wrist, and spine areas. Recently, there has been a discovery of a plant known as Dianthin superbus that has been tested for osteoblastic proliferative activity. The peptide from D. superbus has been shown to activate the production of osteoblasts to increase bone mass. Dianthin G is a cyclic hexapeptide that is extracted from Dianthin superbus and was initially taken from a northern province in China, known as Shandong, and is used in traditional Chinese medicine. This study has examined the chemical synthesis of Dianthin G and its structural analogs. The proliferative activity of these compounds on rat osteoblast cells will later be tested to see if they have the ability to prevent the formation and endurance of osteoporosis. The chemical synthesis and purification of these cyclic peptides will be discussed in this presentation.

Effects of alkyl chain length at the anomeric position of β-D-galactose on gel formation and small molecule solubility

Nicholas Toupin and Dr. Jennifer Chaytor

Department of Chemistry, Saginaw Valley State University

Organogellators are compounds used for a wide range of applications ranging from drug delivery and dissemination to templated material synthesis. This project attempts to explore how variations in the structure of the gelating molecule can affect the overall properties of the gel. Specifically, modifying the length of the nonpolar group of the gelator will be carried out in order to observe the effects that this has on gel formation and the solubility of biologically and medically relevant molecules. To achieve this, firstly the two step synthesis of each β-D-galactose derivative will be carried out. Then these compounds will be characterized through the analysis of spectroscopic data to ensure the correct desired structure. From here each product will be tested with various pure solvents ranging from extremely polar to nonpolar to test for gel formation. Finally, the molecules that were able to form gels will be tested for their ability to solubilize various molecules. This presentation will discuss the chemical synthesis of the galactose derivatives.
Monitoring freshwater microbial contamination with qPCR rapid testing and source tracking methods

Emily Greeson, Aubrie Tacey, Bruce Hart, and Tami L. Sivy, Ph.D.

Saginaw Valley State University

Current testing methods to measure microbial contamination have relied on an 18-24 hour incubation period in order to determine levels of fecal indicator bacteria, usually *E. coli*. These bacteria have shown a strong correlation with contact-associated illnesses, but the long analysis time could result in human contact with harmful pathogens. Our lab has continued to work with the EPA and Michigan DEQ to further adapt the rapid bacterial testing method known as EPA Method C: *Escherichia coli in Water by TaqMan Quantitative Polymerase Chain Reaction (qPCR)*. During the summer of 2016, our testing of the Saginaw Bay Watershed expanded, with 5 sites in Huron County, 5 sites in Iosco County, and 5 sites in Bay County. The water samples were evaluated as either composites or triplicates in order to obtain at least 30 data sets for each site. Meanwhile, our objectives have expanded to use a qPCR method to identify the source(s) of microbial contamination in order for remediation to be undertaken. To this end, we have used qPCR primers and probes that differentiate between *Bacteroides* originating from human or bovine, with tests being run with samples from Isabella County in 2015 and the Pine River in 2016. The results thus far are very promising, with clear quantifications for the presence of *Bacteroides* from human and/or bovine. The method will continue to be refined and future research will be expanded to pursue avian-specific detection and absolute quantification.
3D Printing of Poly (Lactic Acid)-Based Composites

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The effects of filament type, diameter, and orientation on the physical properties were determined for a series of poly(lactic acid)-based 3D printed composites. Poly(lactic acid) (PLA) was chosen because of its sustainability and ease of processing. Composites were prepared using BCN3D or Flash Forge Dreamer ‘entry level’ 3D printers with 0 degree angle and 45/-45 degree angle filament configurations relative to the axial direction of the test samples. The BCN3D and Flash Forge utilize, respectively, 2.85mm diameter and 1.75mm diameter filaments. The commercially available filament types studied were: PLA with 20 wt. % bamboo), natural PLA, white pigmented PLA, PLA with 20 wt. % graphene), PLA with 20 wt. % polyhydroxyalkanoate (PHA), and white Pigmented PLA with 20 wt. % PHA. Differential Scanning Calorimetry (DSC) was used to determine the $T_g$, melting, and recrystallization characteristics of each filament type. The composite with the highest unnotched Izod impact toughness of 349 J/m was prepared from the PLA with 20 wt. % graphene using the Flash Forge with a 45/-45 filament angle configuration. From tensile testing the highest average modulus obtained was 2.87 GPa for the composite printed with natural PLA at a 0/90 angle configuration using the Flash Forge. The highest average tensile strain of break obtained was 2.83 % for the PLA 20 wt. % graphene filament printed at 45/-45 configuration on the Flash Forge. Generally, it was determined that the 1.75 mm diameter filaments yielded composites with better integrity and physical properties than the 2.85 mm diameter filaments.
Elastomer Development for High Flow TPOs

Mary Ann Jones, Russell Barry, Jim Hemphill
The Dow Chemical Company

The automotive market has a sustained interest in the use of plastics for reducing vehicle weight. Thermoplastic polyolefins (TPOs) have made large strides in processing and performance and are often the product of choice for many applications. Product developments continue to target enhanced toughness-stiffness balance, aesthetics, and processability. This presentation will focus on the role of polyolefin elastomers in the TPO formulation to achieve toughness-stiffness, while simultaneously improving mold-flow, and enabling thin-walling and lightweighting in interior and exterior automotive parts.

Gallic Acid Esters with Flame Retarding Properties

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Gallic acid is a renewable biomaterial produced by a variety of plants. Structurally, it is benzoic acid containing three hydroxyl groups which offer the potential for conversion to a variety of phosphorous esters that may function as nontoxic flame retardants for polymeric materials. Treatment of the acid with thionyl chloride followed by analine generates the corresponding amide. The hydroxyl groups may then be converted to phosphorous esters. For example, treatment of the amide with diethyl phosphite in the presence of carbon tetrachloride (Atherton-Todd reaction) may be used to generate the corresponding tris-phosphate. Other phosphorus esters may be generated in a similar fashion.
Alkynols as a Source of Flame Retardants

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Alkynols offer an attractive platform for the generation of dual-functional flame retardant for polymeric materials. They contain functionality, a triple bond and a hydroxyl group, that may be readily converted to a variety of compounds with flame retarding properties. In a simple example 1-pentyn-5-ol may first be treated with bromine and then with diphenyl chlorophosphate. The product containing both bromine (for gas-phase activity) and phosphorus (for solid phase activity) should display good flame retardant properties.

Phosphorus Compounds from Acrylate Derivatives of Gallic Acid

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Gallic acid is a natural product available from a variety of plant sources. It contains three hydroxyl groups which may be utilized for the generation of useful adducts. Treatment of the acid with thionyl chloride followed by aniline generates the corresponding amide. The hydroxyl groups may then be converted to acryloyl chloride. Michael addition of phosphite to the unsaturated acrylate esters may be used to produce a variety of phosphorus compounds. These compounds may be expected to display good flame retardant properties as additive in polymeric materials.
Vegetable Oil Derived Flame Retardants

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Flame retardants Derived from nontoxic biosources, particularly nonhalogen compounds, are increasingly important as the health risks associated with the use of traditional organohalogen flame retardants becomes more apparent. Organohalogen compounds, especially brominated aromatics, are readily available at modest cost and are effective gas phase active flame retardants. However, these compounds are stable in the environment, tend to bioaccumulate and may pose risks to human health. As a consequence, they are facing increasing regulatory pressure around the world. Phosphorus compounds generated from renewable biosources are attractive alternatives to these materials. Oleic acid is available from saponification of triglycerides from a variety of crop seeds, most notably canola, sunflower or soybean oil. Esterification of this acid with 2-dopyl-1,4-benzenediol generates a diester containing unsaturation which can be subjected to thiol-ene reaction using 2-hydroxyethanethiol to afford a diol from which a variety of phosphorus esters may be generated. These compounds have the potential to function as nontoxic flame retardants for polymeric materials.
Comparison between Levels of Nutrients and Bacteria in Urban and Rural Areas of Bad Axe Creek

Marissa Dobulis, Emily Greeson, Katie Kwiatkowski, Trenton Benedict, Olivia Bishop, Kathlyn Underwood, Lee Koski, Tami Sivy, and David S. Karpovich

Saginaw Bay Environmental Science Institute at SVSU

Bad Axe Creek is a tributary of the Pinnebog River, which flows into the Saginaw Bay. In a recent study, nutrient and bacteria data were collected in order to see if geography plays a role in the levels. Elevated phosphorus is of concern because of its role in eutrophication, and fecal coliform bacteria are of concern because of the potential human health issues they pose. During the summer and fall of 2016, samples were collected by the Saginaw Bay Environmental Science Institute biweekly at seven sites. E. coli was analyzed by Colilert-18 in triplicate to determine overall bacteria loading, while quantitative polymerase chain reaction (qPCR) was utilized on composite samples to identify sources of contamination using Bacteroides target sequences. Total levels of E. coli were frequently high at some sites, independent of temperature of weather conditions, suggesting a continuous source. At these sites, Bacteroides source tracking indicated rural sites have more bovine contamination, while urban areas have more human contamination. Phosphorus was tested using 4500-P Method E for both soluble reactive phosphorus and total phosphorus. Additional nutrient data was collected to note any trends that correspond with either phosphorus or bacteria. Dissolved oxygen levels remained constant and low over time. Both soluble reactive phosphorus and total phosphorus levels were regularly above the desired concentration for Saginaw Bay of 15 μg/L at both rural and urban sites, suggesting phosphorus levels are independent of geography. In the future, we will expand our study to include more rain events and nutrient and bacteria loading calculations.
Establishing Better Safety in the Lab

Mohammad A. Almughalaq, Zachary M. French, and Dr. Adam Warhausen
Saginaw Valley State University

For years, SVSU’s Chemistry Labs, specifically the most basic Chem 111 courses, have used the same Lab Safety video, which was produced by the American Chemical Society in the early 1990s. As the years go on though, despite safety being a timeless necessity in the labs and the types of equipment used remaining largely unchanged over the years, incoming freshman pay less and less attention every year. Establishing safety protocols with students is crucial to maintaining a safe lab environment, for the students, professors, and all faculty involved in working in and around the labs.

It is our mission to get the students attention again and help them learn by filming, directing, and producing a new lab safety video. The video we produce will be more relevant to the students as it will involve the familiar faces of SVSU Faculty, and use the exact same equipment they will be using in the same environment. It is also our goal to avoid the dryness of the ACS “Starting with Safety” video that the students find difficult to learn from.

development of synthetic models for iron containing biomolecules with an emphasis on understanding their redox behavior

Bradley Ross, Arti Patel, Andrea Nikolai, and Dr. Adam Warhausen
Saginaw Valley State University

Interactions between nitric oxide and biologically available materials have been widely studied in the field of chemistry. Fortunately, there is much more to learn and to study about organic molecules that are capable of producing nitric oxide within living organisms. The nitic oxide donating molecules utilized in this research are hydroxamic acids. This project aims to study the interactions of these hydroxamic acids with models of iron-containing biomolecules. The emphasis of this work focuses on understanding their redox behavior using electrochemical and spectroelectrochemical methods.


**Electrochemical Investigation of several ruthenium and rhodium complexes utilizing cyclic voltammetry**

Danielle Duranczyk, Rebecca Calangelo, and Dr. Adam Warhausen

Saginaw Valley State University

The complexes tris(triphenylphosphine)rhodium(I) chloride, benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium, and [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium are well-known and extensively studied complexes. They are known for the wide range of reactions that they can be involved in. An area of interest that lacks in current literature is the redox properties of these complexes and their analogues. Our focus is to expand the knowledge of these complexes, more specifically, with respect to their first oxidation potential. Our group set out to investigate the electrochemical, and spectroelectrochemical properties of these complexes as well as their analogues. The redox properties of these complexes have been examined utilizing cyclic voltammetry (CV) techniques. The extensive CV experimentation includes the utilization of screen printed platinum and glassy carbon disk electrodes, as well as varying temperatures.

**Toxicology profile, pharmacology and the revolution of Synthetic Cannabinoids along generic legislations**

Pengchao Hao

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Synthetic cannabinoids have appeared in the market since 2004 and continue to be a growing global drug problem. Due to the relatively easy synthesis methods, synthetic cannabinoids (SCs) have been structurally modified extensively and over 200 compounds were created by clandestine laboratories in recent years. The generic legislations were a smart way of controlling new SCs drugs, however, SCs have gone through revolutions against generic legislations and several generations of SCs have appeared on the market, which not only possess pressure on the regulation of drugs, but also a huge risk on the global public health. This poster structurally analyzed the database of SCs and deduced several trends for the SCs revolution, and the pharmacology vs chemical structure of SCs indicate how potency of SCs have been influenced by the new structure modifications.
Partitioning of Fecal Coliform Bacteria at Bay City State Recreational Area

Cassandra M. McManus, James L. McEvoy, and David S. Karpovich

Saginaw Bay Environmental Science Institute at SVSU

Beach closings in Michigan occur every summer due to high *Escherichia coli* counts in the water. A major cause of these beach closings is believed to be rain events that wash *E. coli*-laden animal feces into the water. However, a positive correlation has been noted between wind events without rain and increased *E. coli* concentrations in water. Analyses were undertaken to determine the prevalence of *E. coli* and other coliforms in sediments and water at Bay City State Recreational Area and to correlate these findings with wind and rain events. Using *E. coli*/Coliforms 3M Petrifilms™, we detected *E. coli* at concentrations as high as 20 colony forming units (CFUs) per cubic centimeter of surface sand sampled above the waterline. Total coliforms were as high as 1380 CFUs/cc. Sediments acquired under the water were found to generally contain *E. coli* and other coliforms at concentrations as high as or higher than those found in sand obtained above the waterline. Following rain and/or wind events, underwater sediment samples harbored more *E. coli* and coliforms than after a stretch of low wind days with no rain. Water samples contained relatively low levels of *E. coli* and coliforms compared to the sediment samples. Bird feces found on the beach often contained high numbers of *E. coli* (> 82,000 CFUs/cc sand) and coliforms (> 136,000 CFUs/cc sand). Further studies are underway to determine 1) the nutrient and organic matter composition of the sediment to better understand how it can support the coliforms, 2) the contribution of bird feces to the coliform numbers found in the beach sediments, and 3) whether the coliforms are colonizing and multiplying in the sediments or merely transient microbes being replenished from sources such as bird feces.
Eleven Days on an Island Doing Analytical Chemistry

Nathen Provo, Rebekah Adams, Nicole Dennis, Dale LeCaptain

Department of Chemistry & Biochemistry and

Institute for Great Lakes Research

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The Central Michigan University Analytical Chemistry course is the analysis and interpretation of quantitative chemical information from volumetric, electrochemical, spectroscopic and chromatographic techniques and is required for chemistry/biochemistry majors and minors. The summer version of this course has environmental analytical as the theme and can be taken ON-LINE for lecture with laboratory experience at the CMU Biological Station on Beaver Island, Michigan. This qualitative presentation will lay out the instructor and student perspectives of teaching/taking a condensed format summer class in such a unique setting (on an island in the middle of Lake Michigan).
Optimization of a Cellular Phone-Based Image Acquisition Method for Nitrate/Nitrite Paper-Based Fluidic Devices

Zachary Velasco, Katie Kwiatkowski, and Dr. Kyle A. Cissell

Department of Chemistry, Saginaw Valley State University

Rapid, on-site testing of nutrient levels is beneficial for the assessment of the health of an aquatic ecosystem. The most common nutrients tested are nitrogen and phosphorus, with nitrite and nitrate being two of the most common chemical forms measured for nitrogen. To facilitate rapid, simple testing for nitrite and nitrate, paper-based fluidic devices were developed by our research group which form a magenta color in the presence of nitrate or nitrite when mixed with Griess reagents (sulfanilamide and N-(1-naphthylethylenediamine dihydrochloride)) in phosphoric acid. For the nitrate test, zinc metal was added as a reducing agent to reduce nitrate to nitrite, which is the detectable form of nitrogen in the assay presented here. This research focuses on two optimization approaches to improve the performance of the device: image acquisition and device optimization. The most important parameters in optimizing cellular phone image acquisitions for semi-quantitative analysis using ImageJ analysis software were found to be consistent lighting and consistent distance between the camera and device. By placing LED lighting inside a white box with a stage for the cellular phone camera, these parameters were met. Additionally, a measurement box was added to the device for consistent ImageJ analysis between devices. In addition, device channel length and width were varied, along with different mixing approaches. Consistent placement of reagents was achieved with the addition of markers along the outer portion of each device. It was found that our optimized devices can detect 1 ppm of nitrogen in the chemical forms of nitrate and nitrite. Data generated from the optimizations will be presented along with a second generation prototype of the SVSU nitrite/nitrate test card that includes a QR code for tracking.
Routes for Continuous Measurement of Dissolved Silica in Mixed Acid Solutions

MADAY, ETHAN M.*; MCINTEE-CHMIELEWSKI, NATHANIEL C.; CUSHING, GREGORY W.

Hemlock Semiconductor Corporation

A key factor in maintaining high purity industrial etching operations is the ability to monitor the composition and impurity loading of the processing baths. These act to limit the useable life of the fluids, with inaccurate analytical results potentially leading to increased chemical consumption, decreased final substrate purity, or both. In the case of a silicon etching process, a substantial reaction is taking place over the lifetime of the bath with the byproduct chemical, fluorosilicic acid, accumulating beyond nontrivial levels. This buildup is one of the major contributors to decreased chemical performance and elevated processing expenses if it is not monitored properly.

Two methods were researched and tested to ensure accurate measurements could be made quickly and consistently to solve this issue. The first involves stepwise titration to provide two strong derivative peaks. This is then coupled with fluoride measurements through an ion selective membrane to provide a manual method for compositional verification. The second method utilizes ion chromatography for determination of the anionic species, followed by silicomolybdate generation and detection through UV/Vis in a post-column process to back out the fluorosilicic acid content. Both methods have proven effective in determining the compositions of mixed acid solutions, with the silicomolybdate method providing the added benefits of ease of implementation and limited manual interaction. Together, these methods allow for fast, in-line measurements and validations to minimize chemical expenditures and potential product defects.
**Encapsulation of Flame Retardant for Polymeric Nanofoams**

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Significant progress has been made towards the development of polymeric nano-cellular foams\(^1\) for several applications including thermal insulation.\(^2\) Polymethylmethacrylate (PMMA) can produce nanofoams with cells below 300 nm but has high flammability. The cellular structure of nanofoams is often compromised by the addition of conventional flame retardants (FRs), which can act as a plasticizer or interfere with cell nucleation. A water soluble molecule, aluminum 2-(diethoxyphosphoryl) acetate, was discovered as an effective FR for PMMA copolymers based on Limiting Oxygen Index (LOI).\(^3\) It remains a challenging task to make FR nanoparticles and prevent them from agglomeration during the processing steps, which can hinder nanofoam formation. Encapsulation of FR nanoparticles is a potentially viable approach to the integration of nanosize FR into PMMA nanofoams.

We have successfully developed two novel methods to encapsulate a water soluble FR into a hydrophobic PMMA copolymer matrix. FR nanoparticles were uniformly distributed in the polymer through the mixing and foaming processes\(^4\). Addition of FR nanoparticles did not interfere with the foam properties and had negligible effects on the pore size and porosity of nanofoams. Additionally, this solid FR does not plasticize the polymer matrix and potentially offers tremendous advantages over many phosphorus flame retardants that are soluble in the polymer matrix.

**References:**


In situ Spectroscopic Monitoring the Degradation of Glucose Conjugated “Sweet” Aspirin

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Aspirin is derived from salicylic acid and is a non-steroidal anti-inflammatory drug (NSAID) used as an analgesic, antipyretic, and anti-inflammatory medication. Prolonged use and high dosages can have negative side effects such as stomach ulcers. Because aspirin has low solubility in water, it is given in high dosages to produce a therapeutic effect on the body, which is composed mostly of water. In our laboratory, a conjugate has been successfully synthesized using salicylic acid and glucose via a glycosidic bond. In this way the solubility of sugarlated salicylic acid increases more than 100 times, which potentially allows for lower dosages thus minimizes side effects. In this study, $^1$H NMR and UV-Vis spectroscopy were used to monitor the in situ degradation of this glucose conjugated salicylic acid at body temperature, 37°C. The results clearly showed that the "sweet" salicylic acid could be degraded at 37°C, the rate constant of this reaction was also determined in this research. Future studies of this glucose-conjugated salicylic acid would include monitoring its degradation under conditions mimicking the body more closely such as the pH of the blood and stomach acid, and in the presence of the naturally occurring glucosidase enzyme.
Comprehensive Structural Characterization of Cholesterol Using a Novel HTMQ NMR Experiment

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A novel NMR experiment (HTMQ) that utilizes Hadamard transform (HT) and multiple-quantum (MQ) coherence selection tools has been designed to efficiently characterize the structures of complicated molecules. Cholesterol is an interesting molecule that’s found in all cells of the body, which helps the body to make hormones, vitamin D, and substances that help us digest foods. The methine (CH, double-quantum), methylene (CH₂, triple-quantum) and methyl (CH₃, quadruple-quantum) groups in the cholesterol structures have different quantum order, which can be selectively detected via a desired multiple-quantum coherence pathway using the new experiment. The results from this research clearly demonstrates that the newly developed NMR technique can be applied to characterize the structure of cholesterol, which allows unambiguous assignments of all signals for both ¹H and ¹³C NMR spectra.
Investigation on the Degradation of Galactose Conjugated Salicylic Acid

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This research aims to work on improving common non-steroid anti-inflammatory drugs (NSAID’s); the project is focused on salicylic acid, a precursor of Aspirin. In this proposed research, the solubility of salicylic acid will be improved using naturally-occurring, biocompatible substances – sugars. Salicylic acid has been successfully conjugated with galactose to form a novel type of “sweet” salicylic acid through organic syntheses. Previous research in our lab has shown that glucosyl and galactosyl “sweet” drugs (i.e. salicylic acid) are 100 times more soluble than salicylic acid alone. Degradation studies have now been conducted on each of the three forms of “sweet” salicylic acid to see how the glycosidic bond holds up under the temperature of the human body, 37°C. This will hopefully provide information on controlled release of these novel “sweet” drugs in situ. Several analytical techniques have been employed through the research during synthesis, characterization and degradation analysis, including HPLC, NMR, and UV-Vis spectroscopy. This work will open a new avenue for future research to continually improve the bio-efficacy of the other NSAIDs and anticancer drugs that often suffer from poor water solubility, by increasing their compatibility and absorptivity in the body with controlled drug delivery in a novel format, “sweet” drug.
UV-Vis & NMR Studies on Degradation of Mannose Conjugated “Sweet” Aspirin

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Aspirin, or salicylic acid, is a universally used drug with analgesic, antipyretic, and anti-inflammatory effects, which is classified among other common painkillers like ibuprofen and naproxen as Non-Steroidal-Anti-Inflammatory-Drugs (NSAIDs). NSAIDs are commonly prescribed for chronic inflammation such as rheumatoid arthritis, but long-term use can lead to ulcers and gastrointestinal bleeding. In their current state, NSAIDs have to be prescribed in large dosages to reach therapeutic levels in the body due to their low water solubility. By conjugating NSAIDs with hydrophilic sugar molecules, one can dramatically increase their solubility with the potential to eliminate the large dosages that cause gastrointestinal damage. With salicylic acid, the conjugation has been successfully done with Mannose, Galactose, and Glucose in Dr. Chai’s lab. The focus of this research is on the degradation of these conjugated “sweet” drugs. So far, the degradation of mannosyl salicylic acid has been studied at body temperature (37°C) using NMR and UV-Vis. More studies on the degradation will be examined in the future under different physiological (blood and stomach) pH conditions, as well as with glycosidase which is an enzyme that targets glycosidic bonds.

The mystery of Cercospora Control

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In general there are two ways to stop microbes from infecting or deteriorating materials—disinfection and antimicrobial surfaces. The first is usually realized by disinfectants, which are a considerable environmental pollution problem and also support the development of resistant microbial strains. Antimicrobial and/or antifungal surfaces are usually designed by impregnation of materials with biocides that are released into the surroundings whereupon microbes are killed.

Because control with Fungicides, both systemic and contact fungicide options, have not been totally effective to control Cercospora leafspot in sugarbeets, we have been evaluating the effectiveness of a covalently bound antimicrobial/antifungal organosilane against Cercospora leafspot fungus. This poster covers the R&D effort to apply, sample and test field applied bound antimicrobial on a sugar beet field.